<table>
<thead>
<tr>
<th>Contents</th>
<th>Page number</th>
<th>Pagination in paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Abbreviations</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>List of Figures</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>List of Tables</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Abstract</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Declaration</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Copyright Statement</td>
<td></td>
<td>17</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>Preface</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>1. Introduction and Overview</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1.0. Objectives</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1.1. Format of Thesis</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1.2. Status of Manuscripts and Author Contributions</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1.3. Background</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1.4. A Brief Overview of Electronic Energy Deposition in Materials...</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td>1.5. Outline of the Following Sections</td>
<td></td>
<td>23</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>2. Energy Loss Properties of Ions in Materials</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>2.0. Objectives</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>2.1. Motivation</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>2.1.1. Inelastic Cross Sections, Stopping Power and other Energy Loss Properties</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>2.1.2. Stopping Power Models and Programs</td>
<td></td>
<td>27</td>
</tr>
<tr>
<td>2.1.3. Charge Considerations</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>2.1.4. Aims for this Work</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>2.2. Model Development</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>2.2.1. Inelastic Cross Section Formalism</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>2.2.2. DOSD Construction</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>2.2.3. Other Chosen Parameters</td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>2.3. Inelastic Cross Sections and Energy Loss Properties by Non-Relativistic Heavy Ions in Zirconium Dioxide</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>1. Introduction</td>
<td></td>
<td>119</td>
</tr>
<tr>
<td>2. Methodology</td>
<td></td>
<td>119</td>
</tr>
<tr>
<td>3. Results and Discussion</td>
<td></td>
<td>122</td>
</tr>
<tr>
<td>4. Conclusions</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td>2.4. Comparison of the Electronic Collision Cross Sections and Energy Loss Properties of Ions in Silicon Carbide and Various Solid Oxides</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>1. Introduction</td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>2. Methodology</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>2.1. DOSD Formulation</td>
<td></td>
<td>43</td>
</tr>
<tr>
<td>2.2. Formalism to Calculate Inelastic Cross Section</td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>3. Results and Discussion</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>4. Conclusions</td>
<td></td>
<td>56</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>Supplementary Material</td>
<td></td>
<td>60</td>
</tr>
</tbody>
</table>
3. Charge Exchange Equilibrium Charge State Fractions in Materials

3.0. Objectives

3.1. Motivation and Aims

3.2. Previous Work and Possible Options
  3.2.1. Thin Films
  3.2.2. Uranium Dioxide Thin Films
  3.2.3. Experimental Options

3.3. Set-up in this Experiment

References

3.4. Charge Cycling of Light Ions in Titanium, Zirconium and Copper from an Experimental and Theoretical Perspective

1. Introduction
2. Experimental Methodology
3. Models for Ion Charge
4. Results and Discussion
5. Conclusions
Acknowledgements
References

4. Hydrogen Radiolysis from Water-Nanoparticle Systems

4.0. Objectives
4.1. Motivation
4.2. Methodology for Hydrogen Production Measurement
References

4.3. Radiolytic Hydrogen Generation at Silicon Carbide-Water Interfaces

1. Introduction
2. Experimental
  2.1. Sample Preparation and Analysis
  2.2. H₂ Production and Gamma Irradiation
  2.3. Irradiations with γ-rays and He Ions for Surface Analysis
3. Results and Discussion
  3.1. Characterization of SiC Surfaces
  3.2. Production of H₂ with γ-ray Radiolysis
  3.3. Changes to the SiC Surface
4. Conclusions
Acknowledgements
References

5. Remarks on the Body of Work and Future Directions

5.1. Inelastic Cross Sections and Energy Loss Properties
  5.1.1. Summary
  5.1.2. Limitations

5.2. Equilibrium Charge State Distribution of Ions Through Materials
  5.2.1. Summary
  5.2.2. Limitations

5.3. Hydrogen Production in Materials
  5.3.1. Summary
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.2. Limitations</td>
<td>123</td>
</tr>
<tr>
<td>5.4. Future Directions</td>
<td>124</td>
</tr>
<tr>
<td>5.4.1. Energy Loss and Inelastic Cross Sections</td>
<td>124</td>
</tr>
<tr>
<td>5.4.2. Charge Exchange Cross Sections</td>
<td>125</td>
</tr>
<tr>
<td>5.4.3. Hydrogen Production on Silicon Carbide Particles</td>
<td>126</td>
</tr>
<tr>
<td>References</td>
<td>128</td>
</tr>
<tr>
<td>Appendix 1</td>
<td>130</td>
</tr>
<tr>
<td>Appendix 2</td>
<td>136</td>
</tr>
<tr>
<td>Appendix 3</td>
<td>148</td>
</tr>
<tr>
<td>Appendix 4</td>
<td>150</td>
</tr>
<tr>
<td>Appendix 5</td>
<td>152</td>
</tr>
<tr>
<td>Appendix 6</td>
<td>154</td>
</tr>
</tbody>
</table>

Word count: 63,200
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_q$</td>
<td>Normalised ion counts for a given charge state</td>
</tr>
<tr>
<td>$F_q$</td>
<td>Charge state fraction of an ion with exiting charge $q$</td>
</tr>
<tr>
<td>$I_{\text{eff}}$</td>
<td>Mean excitation energy, units of eV</td>
</tr>
<tr>
<td>$I_q$</td>
<td>Current at a given ion charge state</td>
</tr>
<tr>
<td>$N_q$</td>
<td>Normalisation count from silicon detector</td>
</tr>
<tr>
<td>$Z_{\text{eff}}$</td>
<td>Effective number of electrons able to be excited in a material at a given energy</td>
</tr>
<tr>
<td>$Z_t$</td>
<td>Atomic number of the target material</td>
</tr>
<tr>
<td>$a_0$</td>
<td>Bohr radius, equal to $5.29 \times 10^{-11}$ m</td>
</tr>
<tr>
<td>$f_j$</td>
<td>Weight factor for $j^{\text{th}}$ electron target resonance according to Sigmund</td>
</tr>
<tr>
<td>$\bar{n}$</td>
<td>Number of electrons attached to an atom in Ziegler's model</td>
</tr>
<tr>
<td>$v_0, v_B$</td>
<td>Bohr velocity equal to $2.19 \times 10^6$ m s$^{-1}$</td>
</tr>
<tr>
<td>$v_F$</td>
<td>Fermi velocity of a material</td>
</tr>
<tr>
<td>$w_j$</td>
<td>Resonance frequency for $j^{\text{th}}$ electron target resonance</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>'Binding energy', loss of energy to the system in an ion collision (eV)</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space equal to $8.85 \times 10^{-12}$ F</td>
</tr>
<tr>
<td>$\Delta L_{\text{Barkas-Anderson}}$</td>
<td>Higher order corrections to classical portrayal of the stopping number</td>
</tr>
<tr>
<td>$\Delta L_{\text{Bloch}}$</td>
<td>Higher order corrections to classical portrayal of the stopping number</td>
</tr>
<tr>
<td>$\Delta a$</td>
<td>Difference in optical absorbance, this is a dimensionless ratio of 2 absorbance values</td>
</tr>
<tr>
<td>$\Delta \varepsilon$</td>
<td>Molar extinction coefficient with units L mol$^{-1}$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\cdot\text{OH}$</td>
<td>Hydroxyl radical</td>
</tr>
<tr>
<td>3C, 4H, 6H</td>
<td>Forms of packing describing SiC crystallographic structure</td>
</tr>
<tr>
<td>$^{60}\text{Co}$</td>
<td>Cobalt isotope with atomic mass number 60</td>
</tr>
<tr>
<td>$^{\text{Li}^2+}/^{\text{Li}^3+}$</td>
<td>Isotope of lithium (mass number 7) with charge state +2 or +3</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>Aluminium oxide, alumina</td>
</tr>
<tr>
<td>AMS</td>
<td>Accelerator Mass Spectrometer</td>
</tr>
<tr>
<td>$b$</td>
<td>Measure of cross sectional area, units of Barns, $1b = 10^{-28}$ m$^2$</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller theory of adsorption of gas molecules on solid surfaces</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>Bromide ion (with a charge of -1)</td>
</tr>
<tr>
<td>$c_1$</td>
<td>Variable from Schwieitz and Grande see Section 2.1.3</td>
</tr>
<tr>
<td>$c_2$</td>
<td>Variable from Schwieitz and Grande see Section 2.1.3</td>
</tr>
<tr>
<td>DCF</td>
<td>Dalton Cumbrian Facility</td>
</tr>
<tr>
<td>DOSD</td>
<td>Dipole Oscillator Strength Distribution, units eV$^{-1}$</td>
</tr>
<tr>
<td>E</td>
<td>Incident ion energy, unit of eV</td>
</tr>
<tr>
<td>ELF</td>
<td>Energy Loss Function</td>
</tr>
<tr>
<td>eV, keV, MeV</td>
<td>Unit of energy, electronvolt, $1\text{ eV} = 1.602 \times 10^{-19}$ J, kilo-electronvolt $(10^3$ eV), mega-electronvolt $(10^6$ eV)</td>
</tr>
<tr>
<td>Fe$^{\text{III}}$/Fe$^{\text{II}}$</td>
<td>Oxidation state of species</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>G (species)</td>
<td>The yield of species in a reaction, units of molecules/ 100 eV</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatograph</td>
</tr>
<tr>
<td>Gen III+</td>
<td>A generation three or more nuclear reactor design</td>
</tr>
<tr>
<td>Gy, kGy</td>
<td>Gray, kiloGray, SI unit of absorbed dose 1 Gy = 1 J kg$^{-1}$</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck’s constant, equal to $6.63 \times 10^{-34}$ m$^2$ kg s$^{-1}$</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Reduced Planck’s constant, $\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34}$ J s</td>
</tr>
<tr>
<td>H$_2$</td>
<td>Molecular hydrogen</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Water</td>
</tr>
<tr>
<td>HIS</td>
<td>Helium Ion Source</td>
</tr>
<tr>
<td>$L$</td>
<td>Stopping number, dimensionless part of the stopping power</td>
</tr>
<tr>
<td>LET</td>
<td>Linear Energy Transfer</td>
</tr>
<tr>
<td>m, mm, cm, Å</td>
<td>Units of length, metres, micrometres ($10^{-6}$ m), centimetres ($10^{-2}$ m), Angstrom ($10^{-10}$ m)</td>
</tr>
<tr>
<td>$M$, mM</td>
<td>Units of concentration, milliMolar ($10^{-3}$ M), where $1\text{ mM} = \text{ mol m}^{-3}$</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo computation method</td>
</tr>
<tr>
<td>MFP</td>
<td>Mean free path of an ion through a material, units of length</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesium oxide, magnesia</td>
</tr>
</tbody>
</table>
mL: Units of volume, millilitres, where 1 L = 10⁻³ m³
mol: Unit of measurement for amount of substance
MV: Units of electrical potential, MegaVolts (10⁶ V), 1 V = kg m²/A s³
N, Nᵢ: Number density of molecules in a given material
NDA: Nuclear Decommissioning Authority
R: Range of an ion, with units of length
RTP: Room temperature and pressure, this corresponds to 298 K and 1 atmosphere of pressure
S: Stopping power, SI Unit of J m⁻¹
SCS: Stopping cross section
SEM: Scanning Electron Microscope
SiC: Silicon carbide
SiO₂: Silicon dioxide, silica
SNICS: Source of Negative Ions by Caesium Sputtering
SRIM: The Stopping and Range of Ions in Matter software developed by Ziegler
t₁/₂: Half-life, units of seconds
TCD: Thermal conductivity detector
TEM: Transmission electron microscope
TOF: Time of flight measurements
TPD: Temperature programmed desorption
TRIM: Program within SRIM used to predict the transport of ions in matter
TRISO: Tristructural-isotropic fuel, a proposed fuel type for new nuclear reactors
UV: Ultraviolet
XPS: X-ray photoelectron spectroscopy
XRD: X-ray diffraction
Z: The fully stripped charge of an ion, atomic number of projectile
ZrO₂: Zirconium dioxide, zirconia
S(M, Z, E): Stopping of an ion with mass M and charge Z at energy E
V, Vᵣ, v: Incident ion velocity, units of m s⁻¹
Y: Y function
c: Speed of light equal to 2.99 × 10⁸ m s⁻¹
e: Elementary charge, 1 e = 1.602 × 10⁻¹⁹ C
f(γ): DOSD of an incident of photon energy γ, units of eV⁻¹
k: Extinction coefficient of a material (dimensionless)
l: Path length of light through sample during UV spectroscopy, typically 1 cm
m: Mass of the electron, 9.1 × 10⁻³¹ kg
n: Refractive index of a material (dimensionless)
q, qₑₑ, qₑₑₑ: Charge of ion inside a material
x: Scaling velocity according to Schwietz and Grande, see Section 2.1.3
β: The speed of an object relative to the speed of light: β = v/c
γ: Energy loss of an ion on collision with target electron (eV)
ε: Reduced energy, units of eV, Section 5 only
ε₁, ε₂: The dielectric response function, real and imaginary parts respectively
λ: The screening function as described by Ziegler, Section 2.1.2
ρ: The density of a material, units of g cm⁻³
σ(E): Inelastic cross section for an ion at energy E
τ(E, γ): Probability of an ion with energy E undergoing an energy loss γ
Section 2.

Figure 2.1. The evolution of lithium charge in ZrO$_2$ as a function of incident ion energy. The solid black line refers to Zeigler [25], the red line is the model from Pierce and Blann [24], the blue dashed line is Northcliffe [23] and the pink line is the effective charge from Schiwietz and Grande [28]. The vertical black line at 0.1 MeV/µ is where the formalism developed in this work breaks down.

Figure 2.2. The construction of the silicon carbide DOSD utilised in this study. Pink shows the optical data from Choyke and Palik [33], blue shows the interpolation between the optical data and the black photo absorption cross section data.

Section 2.3.

Fig. 1. The allowed integration region of the γ − γ' energy plane for heavy ion–electron collisions. When evaluating cumulative inelastic cross-sections for energy transfers greater than $\gamma = V^2$ careful consideration of the bounds is necessary. For example, when integrating at 0.6 as shown in the graph (double hashed), one must calculate the area from 1 to 0.6 and subtract this from the whole cross-section.

Fig. 2. Experimentally derived energy loss functions for monoclinic ZrO$_2$ taken from references [21–24]. The ELF of Prieto et al. is the unbroken line, that of McComb is the dashed line, Frandon et al. is the open circles and Tahir et al. is the filled squares.

Fig. 3. Differential dipole oscillator strength distribution for ZrO$_2$. The raw DOSD developed from the energy loss function of Prieto et al. [23] interpolated to the absorption cross-sections of Veigele [20] is given in the broken line, and the revised DOSD modified to reproduce the Fano sum rule for the number of electrons is given in the solid line. The inset compares the raw and modified sections of the DOSD for the optical data.

Fig. 4. Number of electrons per ZrO$_2$ unit influenced by a given energy transfer and the atomic electron binding energies for oxygen and zirconium. The $Z_{\text{eff}}$ calculated using the raw DOSD derived from the ELF of Prieto et al. [23] is shown by the broken line and that calculated using the modified DOSD is shown by the solid line. The atomic electron binding energies for oxygen and zirconium are from reference [26].

Fig. 5. Comparison of stopping powers of ZrO$_2$ for protons and helium ions. Open symbols are experimental data for from [29] for protons (□) and helium ions (○). Filled symbols (●) are experimental data from helium ions from [32]. The solid lines refer to the predictions of this study, with the black line for helium ions from Eq. (25) and the grey line from using Eq. (26) to calculate effective charge. The black dotted lines show the predictions of the SRIM code [18]. The grey dashed line is the prediction for protons from Abril et al. [28]. The grey dashed line shows the predictions of Behar et al. [29] for helium ions.

Fig. 6. Stopping powers of ZrO$_2$ for O ions. Experimental data are taken from the studies of Msimanga et al. (□) and Zhang et al. (○) [31,32]. The solid black line shows the prediction of this study and the dashed line the prediction of a SRIM calculation. Thin solid lines are the predictions of the formalism from this study with specific charge states (as labelled).

Fig. 7. Ion energy dependence of the stopping power of ZrO$_2$ for Mg and Al ions. Experimental data are taken from the studies of Msimanga et al.: Mg (□), Al (○).
List of Figures

[31,32]. The solid lines show the predictions of this study and the dashed line the predictions of SRIM calculations.

Fig. 8. Comparison of the mean free path of a helium ion calculated for an effective charge given by Eq. (26) with that for $^4\text{He}^+$ and $^4\text{He}^{2+}$. The solid lines show the predicted values using the effective charge approximation, the dashed line the predictions for $^4\text{He}^+$ and the dotted line the predictions for $^4\text{He}^{2+}$.

Fig. 9. Differential $Y$ function for various ions with energy 0.5 MeV/u in ZrO$_2$ as a function of energy loss.

Section 2.4.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1.</td>
<td>Dipole oscillator strength distribution formulated for water (top left), silicon carbide (top right), magnesium oxide (middle left), silicon dioxide (middle right), aluminium oxide (bottom left) and zirconium dioxide (bottom right). The inset graphs show the evolutions of effective charge as a function of photon energy.</td>
</tr>
<tr>
<td>Fig. 2.</td>
<td>Normalised graph of the evolution of the electrons affected by an energy transfer to the medium in question.</td>
</tr>
<tr>
<td>Fig. 3.</td>
<td>Mean free path of protons in different materials. The black solid line represents water; dark yellow shows Al$_2$O$_3$ and cyan is MgO. The blue line is the prediction for SiO$_2$; red is SiC; the dashed black line is ZrO$_2$.</td>
</tr>
<tr>
<td>Fig. 4.</td>
<td>Mean free path for oxygen ions in silicon carbide. The solid line denotes the mean charge state as described in Equation (8). The black dashed lines are levels of stripping of the ion with the bottom line corresponding to a fully stripped ion and the top a $1+$ charge state.</td>
</tr>
<tr>
<td>Fig. 5.</td>
<td>The differential $Y$ function of 0.5 MeV/u oxygen ions in the oxides and materials of interest in this study (see the key). The most probable energy loss can be seen for this incident ion energy and is clearly material dependent reflecting the different DOSD structures.</td>
</tr>
<tr>
<td>Fig. 6.</td>
<td>The stopping power of protons in various materials. The formalism presented here is shown using lines for Al$_2$O$_3$ (dark yellow), MgO (teal), SiO$_2$ (blue), SiC (red), ZrO$_2$ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Bauer [55] (+) and [50] (●), Turner [51] (●) and (○), Reuter [54] (▲), for SiO$_2$ in blue from Bauer [55] (+), for water in black from Wenzel on ice [49] (○), Bauer [48] (●), Shimizu [52] (○) and [53] (+), Siiskonen [56] (○) and for ZrO$_2$ in grey from Behar [57] (●).</td>
</tr>
<tr>
<td>Fig. 7.</td>
<td>The stopping power of alpha in various materials. The formalism presented here is shown using lines for Al$_2$O$_3$ (dark yellow), MgO (teal), SiO$_2$ (blue), SiC (red), ZrO$_2$ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Mai [58] (○), Santry [59] (●), Thomas [60] (○) and Pascual-Izarra [61] (+) and (●). SiC data is in red from Zhang [62] (●) and [63] (○). Silica data in blue is from Thompson [64] (●) Pascual-Izarra [65] (○) Santry [59] (●) Meyer [66] (○) and Lennard [67] (+). Water is shown black Akhaven-Rezayat (●) Matteson [68] (○) Plamer (●) Haque (○) and Thwaites (+). Finally Zirconia data is shown in grey from Behar [57] (●) and Zhang [69] (○).</td>
</tr>
<tr>
<td>Fig. 8.</td>
<td>The stopping power of oxygen ions in various materials. The formalism presented here is shown using lines for Al$_2$O$_3$ (dark yellow),</td>
</tr>
</tbody>
</table>
List of Figures

MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Mizohata [72] (●) and (□) and Pascual-Izarra [61] (●). Silicon carbide data is shown from Janson [71] (●) and from Zhang [73] (□). Silica data is shown from Zhang [74] (●) and zirconia data is shown from Zhang [75] (●) and Msimanga [76] (□). No experimental data was found for water.

Figure 9. The stopping power of protons in various materials. The formalism presented here is shown using lines for Al₂O₃ (dark yellow), MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Bauer [55] (●) and [50] (▲), Turner [51] (●) and (○), Reuter [54] (▲), for SiO₂ in blue from Bauer [55] (●), for water in black from Wenzel on ice [49] (□), Bauer [48] (●), Shimizu [52] (○) and [53] (+), Siiskonen [56] (●) and for ZrO₂ in grey from Behar [57] (●) and ( eks).

Figure 10. The stopping power of alpha in various materials. The formalism presented here is shown using lines for Al₂O₃ (dark yellow), MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Mai [58] (□), Santry [59] (●), Thomas [60] (○) and Pascual-Izarra [61] (●) and (○), SiC data is in red from Zhang [62] (●) and [63] (□). Silica data in blue is from Thompson [64] (●) Pascual-Izarra [65] (○) Santry [59] (●) Meyer [66] (○) and Lennard [67] (+). Water is shown black Akhaven-Rezayat (●) Matteson [68] (□) Plamer (●) Haque (○) and Thwaites (+). Finally Zirconia data is shown in grey from Behar [57] (●) and Zhang [69] (□).

Figure 11. The stopping power of oxygen ions in various materials. The formalism presented here is shown using lines for Al₂O₃ (dark yellow), MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from (●), Mai [58] (□), Santry [59] (●), Thomas [60] (○) and Pascual-Izarra [61] (●) and (○), SiC data is in red from Zhang [62] (●) and [63] (□). Silica data in blue is from Thompson [64] (●) Pascual-Izarra [65] (○) Santry [59] (●) Meyer [66] (○) and Lennard [67] (+). Water is shown black Akhaven-Rezayat (●) Matteson [68] (□) Plamer (●) Haque (○) and Thwaites (+). Finally Zirconia data is shown in grey from Behar [57] (●) and Zhang [69] (□).

Figure 12. Comparison of DOSDs constructed or used in this study....

Section 3.

Figure 3.1. Schematic of electron loss and non-radiative capture for a C⁵⁺ ion. The left hand side shows a C⁵⁺ ion, the middle diagram depicts electron loss to the material, and the right hand shows non-radiative electron capture.

Figure 3.2. Equilibrium charge state fractions of 15 MeV iodine ions in oxygen taken from [3]. Lines are drawn to guide the eye only.

Figure 3.3. Mounting chamber for the magnetron sputter at the University of Bristol. Samples mounted upside down to allow uranium ions from below to sputter onto the surface.

Figure 3.4. Schematics of the supports used for this study. Steel supports were ≈2 mm in diameter which is sufficient to stop ions passing through.
List of Figures

Figure 3.5. Schematic of Ishihara and Shima experimental set-up [24]. This is typical of charge exchange studies. ................................................................. 70

Figure 3.6. Diagram of functioning of the Helium ion source at the NSF Nuclear Structure Laboratory at the University of Notre Dame from [37]. 71

Figure 3.7. The Source of Negative Ions from Caesium Sputtering apparatus at the NSF Nuclear Structure Laboratory at the University of Notre Dame from [37]. ........................................................................... 72

Figure 3.8. Marion and Young data tables [41] for lithium and carbon ions. This empirical formalism deems charge state fractions to be target independent................................................................. 73

Figure 3.9. Diagram of the experimental apparatus used at the NSF Nuclear Structure Laboratory at the University of Notre Dame. Some inside components of the tandem accelerator are shown................................. 74

Figure 3.10. Diagram of the charging system inside the Notre Dame tandem accelerator [37]........................................................................................................... 74

Figure 3.11. a) Picture of the ladder used to mount samples. This shows the Faraday cup at the top and two broken foils. b) The scattering chamber, ladder mount is in the centre with silicon detector in the bottom left hand side, beam runs right to left horizontally across the page.................................................................................................................. 75

Figure 3.12. a) Schematic of the Brown-Buchner spectrograph [36]. b) Photo of the spectrograph during this experiment......................................................... 75

Figure 3.13. Image of the Faraday Cup used in the spectrograph for collection of charge.................................................................................................................. 76

Figure 3.14. Preliminary experimental data on titanium film, showing lithium ion data (January 2014). The anomalous results for 4 MeV and possibly 3 and 5 MeV are seen clearly........................................................................... 78

Figure 3.15. Geography of the AMS, incident beam c) is hitting the Faraday cup without suppression giving a false reading................................. 78

Section 3.4.

Figure 1. Schematic representation of the experimental layout. Beam direction indicated by the arrows. HIS: helium ion source. SNICS: source of negative ions by caesium sputtering (used to produce Li ions)................................................................................................................................. 84

Figure 2. Effect of incident ion energy on the equilibrium charge state fractions of lithium ions exiting titanium thin films of thickness 0.1 and 0.25 µm. Incident ions initially of charge +2 or +3 were used, the same key is used for both. Open data points correspond to experiments performed with the thinner film and filled data points correspond to experiments performed with the thicker film. Square data points represent the fractions of exiting ions in the +2 charge state and circles those in the +3 charge state. The solid lines are the charge state fractions predicted by the approach of Marion and Young [11]........................................ 89

Figure 3. Effect of incident ion energy on the equilibrium charge state fractions of lithium ions exiting a zirconium thin film of thickness 0.1 µm. Incident ions initially of charge +2 or +3 were used. Open data points correspond to incident ions with charge state +3 and filled data points correspond to incident ions in whith charge state +2. Square data points represent the fractions of exiting ions in the +2 charge state and circles those in the +3 charge state. The solid lines are the charge state
List of Figures

fractions predicted by the approach of Marion and Young [11]..............
Figure 4. Effect of incident ion energy on the equilibrium charge state fractions of lithium ions exiting a copper thin film of thickness 0.1 µm. Incident ions initially of charge +2 or +3 were used. The same key is used for both. Filled data points are data from this experiment. Open data points are from reference [24]. Square data points represent the fractions of exiting ions in the +2 charge state and circles those in the +3 charge state. The solid lines are the charge state fractions predicted by the approach of Marion and Young [11].................................

Figure 5. Material dependence on the effect of incident ion energy on the +3 charge state fraction of lithium ions exiting thin film of thickness 0.1 µm. Experiments with titanium films (■), zirconium (●), copper (▲), gold (○) and carbon (△). Filled points are from the experiments reported here, open points are from Schmitt [6] and half-filled points are from Itoh [24]. The solid line is the charge state fraction predicted by the approach of Marion and Young [11]...........................................

Figure 6. Comparison of experimentally determined mean ion charge for lithium with the predictions of empirical models for effective ion charge. Experiments are shown for titanium films (■), zirconium (●), and copper (▲). The formalism of Northcliffe, Equation (4) is shown as the solid line, those of the formalism of Pierce and Blann, Equation (5) by the dashed line, and that of the formalism of Ziegler, Equation (6), by the dotted line...................................................

Figure 7. Effect of ion energy on the charge state fractions of helium ions in titanium (■), zirconium film (●), and copper (▲). The +1 charge state fractions are the lower set of open data points and the +2 charge state fractions are the upper filled set. The solid lines are the charge state fractions predicted by the approach of Marion and Young [11]........................................................................

Figure 8. Comparison of experimentally determined mean ion charge for helium with the predictions of the three empirical models for effective ion charge. Experiments are shown for titanium films (■), zirconium (●), and copper (▲). The formalism of Northcliffe, Equation (4) is shown as the solid line, the formalism of Pierce and Blann, Equation (5) by the dashed line, and the formalism of Ziegler, Equation (8), by the dotted line...................................................

Section 4.

Figure 4.1. Graph illustrating the effects of radiation in water. In the presence of other impurities this scheme becomes exponentially more complicated. These primary yields react further at longer timescales......
Figure 4.2. The 3 main polytypes of SiC. There are many more polytypes, this is from reference [30]..........................................................
Figure 4.3. Equipment used in this project, samples are of around 1 g and outgassing is performed under heating (50 °C). The lower left hand cylinder is the sink, the right is the sample holder........................................
Figure 4.4. BET graph of silicon carbide. Red is α-phase and black is β-phase. The absorption and desorption curves are marked in the key......
Figure 4.5. Flame sealed argon atmosphere vessel with SiC/Water slurry.............................................
## List of Figures

<table>
<thead>
<tr>
<th>Figure number</th>
<th>Page in paper</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6</td>
<td>106</td>
<td>Windmill rotator, made by Thomas Donoclift, 2012. Samples are attached to the circular disk with cable ties and the disk rotates at 3 rotations/minute.</td>
</tr>
<tr>
<td>4.7</td>
<td>107</td>
<td>Cobalt-60 irradiator at the DCF. Samples are inserted into the chamber and the $^{60}$Co source rises up to irradiate the sample.</td>
</tr>
<tr>
<td>4.8</td>
<td>107</td>
<td>Decay scheme of cobalt-60. Information on the decay scheme was taken from [35].</td>
</tr>
<tr>
<td>4.9</td>
<td>109</td>
<td>Set-up of the GC. When in the ‘OFF’ position, carrier gas bypasses the sample (connection 2 and 10). In the ‘ON’ configuration the carrier gas flows through the sample.</td>
</tr>
<tr>
<td>4.10</td>
<td>109</td>
<td>a) The GC apparatus with the crush tube apparatus attached. b) Crush tube sample apparatus.</td>
</tr>
<tr>
<td>4.11</td>
<td>110</td>
<td>Schematic of the crush tube system: Argon (Ar) flows round the system.</td>
</tr>
<tr>
<td>4.12</td>
<td>111</td>
<td>Gas chromatograph response from different amounts of hydrogen. The residual chi-squared value from this fit is 4.65.</td>
</tr>
<tr>
<td>4.13</td>
<td>111</td>
<td>Typical response on the PeakSimple program.</td>
</tr>
<tr>
<td>4.14</td>
<td>112</td>
<td>FTIR sample holder. Sample cell: with the yellow thermocouple and white water-cooling pipes to regulate the temperature.</td>
</tr>
<tr>
<td>4.15</td>
<td>113</td>
<td>Schematic of energy level where electron is ejected during XPS.</td>
</tr>
<tr>
<td>4.16</td>
<td>114</td>
<td>SEM images of typical SiC powder. SiC $\alpha$-phase is shown on left, $\beta$-phase is on the right.</td>
</tr>
</tbody>
</table>

### Section 4.3.

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>$N_2$ adsorption (▲) and desorption (●) isotherms for $\alpha$-phase (black) and $\beta$-phase (red) SiC nanoparticles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>Temperature programmed desorption curves for water on $\alpha$-phase (black) and $\beta$-phase (red) SiC surfaces. Desorption energies calculated using Redhead's method [20]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>DRIFT spectra of $\alpha$-phase SiC powder (upper) and $\beta$-phase SiC powder (lower) from room temperature to 400 °C. Spectra are offset for clarity. The spectra for water ice are show for comparison [22].</td>
</tr>
<tr>
<td>4</td>
<td>46</td>
<td>Yield of $H_2$ with $\alpha$-phase SiC and 70 % water mass as a function of dose. Yields on the upper plot are calculated with respect to the entire slurry sample (SiC + water), and yields on the lower plot right are calculated only with respect to the mass of water in the sample.</td>
</tr>
<tr>
<td>5</td>
<td>46</td>
<td>Yields of $H_2$ from $\alpha$-phase and $\beta$-phase of SiC in water slurries as a function of the percentage of water mass. Yields on the upper plot are calculated with respect to the entire slurry sample (SiC + water), and yields on the lower plot right are calculated only with respect to the mass of water in the sample. The dashed line represents the yield expected from the law of mixtures.</td>
</tr>
<tr>
<td>6</td>
<td>47</td>
<td>Normalized Raman spectra of pristine (top), $\gamma$-ray irradiated (middle), and He ion irradiated (lower) for $\alpha$-phase SiC samples (upper plot) and $\beta$-phase SiC (lower plot). Spectra are offset for clarity. The lower plot for $\beta$-phase SiC includes spectra for two different regions following He irradiation.</td>
</tr>
</tbody>
</table>
List of Figures

Fig. 7. High resolution XPS scan with peak fitting of the C 1s photoelectrons from a pristine (top), γ-ray irradiated (middle), and He ion irradiated for α-phase SiC (upper plot) and β-phase SiC (lower plot). Spectra are offset for comparison........ 47

Fig. 8. High resolution XPS scan with peak fitting of the O 1s photoelectrons from a pristine (top), γ-ray irradiated (middle), and He ion irradiated for α-phase SiC (upper plot) and β-phase SiC (lower plot). Spectra are offset for comparison........ 48

Fig. 9. High resolution XPS scan with peak fitting of the Si 2p photoelectrons from a pristine (top), γ-ray irradiated (middle), and He ion irradiated for α-phase SiC (upper plot) and β-phase SiC (lower plot). Spectra are offset for comparison........ 48

Section 5.

Figure 5.1. The nuclear and electronic contribution to stopping power as calculated for a proton in ZrO₂. The effect of nuclear collisions only occurs below the energy at which our code breaks down......................... 120

Figure 5.2. Charge cycling cross sections for helium in water vapour. Type of charge exchange is noted in the inset legend. Data in red is from Rudd [11], data in blue is from Greenwood [12] and data in black is from Seredyuk [13]................................................................. 122

Appendix 1.

Figure 1. The electronic inelastic collision process of a heavy ion with mass M with an electron in the medium................................. 130

Figure 2. Energy-energy bounds which are valid in the case of an ion impacting on a bound electron.............................................. 132

Appendix 4.

Figure 1. Basic set-up of the patterning chamber at Imperial. Whilst not ideal this could be useful to produce neutral beams.......................... 149

Figure 2. The changes that would need to be made to the apparatus at Imperial.................................................................................. 150

Appendix 5.

Figure 1. Pertaining to Section 3.3. An example of the output from the silicon detector used in the normalisation of the beam during charge exchange experiments at Notre Dame.................................................. 152

Figure 2. Pertaining to Section 4.2. An example of the XRD changes seen pre and post irradiation of SiC powders with He ions. Little change is seen with this irradiation............................................. 153
List of Tables

Section 1.
Table 1.1. Status of the manuscripts put forward in this thesis including a summary of the Author’s contribution................................................................. 20

Section 2.3.
Table 1. Comparison of values for mean excitation energy and number of electrons for zirconia from a range of sources............................................................. 123
Table 2. Mean free path and range of protons and helium ions in ZrO₂. The effective charge formalism used for helium ions here is that developed by Ziegler. The E notation is equivalent to ‘10 to the power of’............................................................ 125
Table 3. Mean energy loss per inelastic collision of various protons in ZrO₂ for different energies........................................................................................................ 126

Section 2.4.
Table 1. Table showing the material properties of importance in this study. Mean excitation energies with a superscript b have been calculated from values of elemental excitation energies and added according to Bragg additivity........................................................................... 50
Table 2. The first three columns correspond to the mean energy loss per inelastic collision (in eV) for oxygen ions at various different incident specific energies. The final column describes the most probable energy loss (in eV) for oxygen ions at 0.5 MeV/u................................................................. 52

Section 3.
Table 3.1. Material properties of the films used in this study............................................ 76
Table 3.2. Results from TRIM calculation for lithium +3 ions in materials, data averaged over at least 10,000 ions................................................................. 77

Section 3.4.
Table 1. Material properties of the titanium, zirconium and copper thin films used for this project. Errors are given as quoted by LeBow company........................................................................................................ 85
Table 2. Bulk density and electrical properties for the materials considered in Figure 4. Free electron density calculated using the Drude method assuming a valency of: Ti=4, Zr=4, Cu=1, Au=1, C=0. Parentheses give data from the CRC handbook for copper and gold [28] and from G. H. Kinchin [29] for carbon. First Ionisation Potential data from Kramida et al. [30]........................................................................................................ 92
Table 3. Experimentally determined mean charge states of lithium ions passing through the thin films of titanium, zirconium and copper......................... 94

Section 4.
Table 4.1. Table of the BET determined particle sizes of our powders.................. 104
Table 4.2. Table of the thermal conductivities of gases used in GC measurements. Data from [39]-thermal conductivity will change with temperature but the relative differences should remain the same............ 108

Section 4.3.
Table 1. Atomic composition for α-phase and β-phase SiC samples....................... 49
Table 2. Peak atomic concentrations........................................................................... 49
Abstract

The University of Manchester
Jennifer Schofield
PhD
Effects of Ionising Radiation on nuclear materials
March 2016

The prediction of energy loss properties and track structure effects of ionising radiation in materials is of importance to many areas of science, healthcare and technology, especially the nuclear industry. This study examines three different aspects of the electronic effects of ionising radiation on solid materials: the calculation of inelastic cross sections, the measurement of charge state fractions of ions through materials, and the radiolytic hydrogen produced from slurries under gamma irradiation.

Predicting how ionising radiation will interact with matter often utilises collision cross sections for the interaction process. The electronic energy loss cross sections of ions in materials are predicted using a novel formalism requiring only the dipole oscillator strength distribution (DOSD) of the material of interest. DOSDs are constructed for silicon carbide and various oxides of interest to the nuclear industry. Electronic collision cross sections as well as average energy loss properties for incident protons, helium and other ions are calculated using the developed formalism. The formalism is shown to predict macroscopic energy loss properties well, especially at higher energies, suggesting the formalism is an acceptable simple yet elegant method for calculating electronic cross sections for use in Monte Carlo simulations of radiation track structures.

The charge of an ion in a material affects the rate of energy loss during the passage through that material. The charge state fractions of lithium and helium ions in several metallic materials pertinent to the nuclear industry are measured and compared in order to improve the understanding of ion charge states in a radiation track structure. The new charge state fraction measurements show a clear dependence on material properties which appears to correlate with the ionisation potential of the material; however, a full understanding of the dependence is lacking.

Radiolytic hydrogen production is of importance when considering the safety of spent nuclear material in cooling ponds and after disposal. One proposed clad coating for accident tolerant fuel currently under investigation is silicon carbide however its radiation chemistry is relatively unknown. The hydrogen produced from gamma-irradiated silicon carbide water slurries is investigated. The measured yield of H₂ produced is greater than would be expected from a mixture rule. This excess production of H₂ is believed to be due to transfer of energy from the solid ceramic to the aqueous phase by either low energy electrons or exciton dissociation at the water-carbide interface.

These three areas of investigation are complementary aspects of the interaction of ionising radiation with solid material and add to the knowledge base necessary for an acceptable risk-based justification for sustainable energy production by nuclear fission power plants.
Declaration

I declare that that no portion of the work referred to in this thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.
Copyright Statement

i. The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see http://documents.manchester.ac.uk/DoculInfo.aspx?DocID=487), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see http://www.manchester.ac.uk/library/aboutus/regulations) and in The University’s policy on Presentation of Theses.
Acknowledgements

I would like to take this opportunity to thank everyone who contributed in any way to the research in this thesis. First I would like to thank my supervisor Simon Pimblott for his support throughout the years, his flexibility in allowing me to conduct my research as I would like, and his practical advice. I would also like to thank my co-supervisor Jon Billowes for his enthusiasm concerning this subject. I would also like to acknowledge the support of the EPSRC and the Nuclear FiRST DTC.

To all those who have provided invaluable technical support during my research, thank you: Sarah, Dan and in particular Jay at The University of Notre Dame; you all helped me along with all my experiments in America. I would also like to thank Ross and Sophie from the University of Bristol for making collaboration so easy and enjoyable. I owe Tom Donoclift at the DCF a debt for his experimental know-how so freely given. I am also grateful to the NDA and Rick for allowing me to spend a happy 6 months on placement learning about the wider nuclear industry.

My fellow co-workers, both on the 7th floor of Chemistry, and at the DCF deserve my thanks. You have all been infectious in your enthusiasm for your research areas and a good laugh, and you kept my respective desks clear whilst I’ve spent time away, for which I thank you! My thanks also go to Marisa, Rhiannon and Laura for providing a friendly ear and advice whenever required.

The fencers of the University of Manchester have been some of my closest friends, allowing me respite in clashing swords when the pressures of science become too great. To all the fencers: Hannah, Meg, James, Mike and others, mates, I owe you all thanks. To all my friends from afar who have been patient in my many cancellations I am grateful. I must also thank Luke and my family for their unwavering support.

And finally, most importantly, I must thank Mum and Bex, there are no words to describe my gratitude for the many long chapters you read and the many supportive phone calls.

“A positive attitude may not solve all our problems, but it will annoy enough people to make it worth the effort.” (Herm Albright)
The Author studied ‘Physics with a Year’s Study in Europe’ at the University of Manchester, in 2011 obtaining a 1st class MPhys (Hons); the third year was spent in Grenoble studying at the Université de Joseph Fourier. The topics which the Author most enjoyed during this degree were Nuclear and Particle Physics. Following undergraduate studies, the Author entered the Nuclear FiRST Doctoral Training Centre at the University of Manchester in 2011 and undertook a mini-project on stress corrosion cracking before starting this PhD research.

During the current research period the Author has collaborated with researchers at the University of Bristol and the University of Notre Dame on various projects. The Author took two short research placements at the University of Notre Dame in 2014 characterising silicon carbide powders and investigating the charge state fractions of ions through materials. A third (not research-related) placement was at the NDA. This secondment involved working in their Strategy and Technology team and exposed the Author to real industrial applications of the research occurring at University level. The Author also interacted with Government, writing a letter for DECC on provision for nuclear liabilities, and helping to organise the UK-Japan Nuclear Dialogue.

The Author has acted as President for the University of Manchester Fencing Club during the research period and has competed widely, including representing England, in this sport.
1. Introduction and Overview

1.0. Objectives

The aim of this project is to extend the fundamental knowledge base concerning the interaction of ionising radiation, especially light ions, with materials and material systems of importance in the safe and secure generation of nuclear power.

1.1. Format of Thesis

This thesis is presented in the alternative format style, chosen in order to make the best use of time, and to highlight the high impact publishable research obtained. Some topics are unavoidably repeated, although attempts have been made to minimise this where possible.

1.2. Status of Manuscripts and Author Contributions

<table>
<thead>
<tr>
<th>Manuscript</th>
<th>Authors</th>
<th>Author Contribution</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inelastic Cross Sections and Energy Loss Properties by Non-Relativistic Heavy Ions in Zirconium Dioxide</td>
<td>J. Schofield, S. M. Pimblott</td>
<td>First author, data acquisition and analysis</td>
<td>Published in Nuclear Instruments and Methods B</td>
</tr>
<tr>
<td>Comparison of the Electronic Collision Cross Sections and Energy Loss Properties of Ions in Silicon Carbide and Various Solid Oxides</td>
<td>J. Schofield, S. M. Pimblott</td>
<td>First author, data acquisition and analysis</td>
<td>Intending to submit to Radiation Physics and Chemistry</td>
</tr>
<tr>
<td>Charge Cycling of Light Ions in Titanium, Zirconium and Copper from an Experimental and Theoretical Perspective</td>
<td>J. Schofield, J. A. LaVerne, D. Robertson, P. Collon, S. M. Pimblott</td>
<td>First author, data acquisition and analysis</td>
<td>Intending to submit to Journal of Physical Chemistry</td>
</tr>
<tr>
<td>Radiolytic Hydrogen Generation at Silicon Carbide - Water Interfaces</td>
<td>J. Schofield, S. C. Reiff, S. M. Pimblott, J. A. LaVerne</td>
<td>First author, data acquisition for H₂ production and analysis</td>
<td>Published in Journal of Nuclear Materials</td>
</tr>
</tbody>
</table>

Table 1.1. Status of the manuscripts put forward in this thesis including a summary of the Author’s contribution.

1.3. Background

The discovery by Marie Curie that uranium ‘rays’ caused the air around them to conduct electricity began the study of radiation science. This radiation she suggested, correctly, was an intrinsic property of the uranium itself [1]. However this intrinsic radiation is also capable of interacting with material surrounding it, causing many changes. In fact, any radiation of sufficient energy, regardless of its source, can interact and impart energy to the material it is incident on. Radiation interacts with a material depending on its type and energy;
however, in general the interaction can be broken into two forms: interactions with the nucleus of the target and interactions with the electrons.

Interactions of radiation with the nucleus of the target material could include transmutation or displacement of the atoms. Transmutation of material occurs when incident radiation (usually neutrons or light ions) changes the nature of an atom in the target. This could be radiation inducing a fission process (as happens inside uranium itself) or, more simply, a change to the isotope of an element. Alternatively, incident ion radiation can impact the nucleus and cause displacement of atoms. This can affect the material properties, for example density and brittleness, which can impact on the functioning of equipment in radiation fields [2].

The second type of interaction between radiation and a material is electronic interaction. Most types of radiation will interact with the electrons of a target. Photons will interact via the photoelectric effect, the Compton effect and pair production. Electrons and heavy ions also interact with the target’s electrons over most of the energy range of incident radiation. These cause ionisation or excitation of the electrons in a material which can have effects on the chemistry of a system [3]. The electronic interaction of ionising radiation with material is the focus of this thesis. Ionising radiation is radiation of a high enough radiation to cause excitation or ionisation of the target electrons. This can take the form of beta (electron/positron) radiation, high energy gamma radiation or energetic incident ions.

1.4. A Brief Overview of Electronic Energy Deposition in Materials

There are two possible effects of ionising radiation on the material being irradiated; these are electronic excitation and ionisation. Some short term effects of this electronic interaction are most apparent in the field of radiation chemistry with excess hydrogen production of oxide powders under irradiation [4]. Other longer term effects of this type of radiation are seen in materials science with the possibility of enhanced corrosion caused by excess hydrolysis products [5].

This project comprises three complementary but related studies of the interaction of radiation with matter: prediction of electronic collision cross sections, measurements of charge exchange, and measurements of radiolytic hydrogen production.

The first of these, inelastic cross sections, are of interest to multiple areas of physics in order to simulate the interaction of radiation with matter. This has uses not only in the nuclear industry but also in many other fields such as radiation chemistry, medical therapy, and astrophysics. The collision cross sections calculated can be used to predict average energy loss properties (as will be done in this work) but can also be incorporated into detailed track structure simulations capable of providing precise information on the amount,
position and time of energy deposition events. Predictions of inelastic cross sections exist but there are many areas for improvement [6]. The focus of this work will be to develop a formalism for cross section prediction for ions which is elegant, simple to implement and to evaluate.

One of the challenges with calculating energy loss properties, such as the stopping power, is how to describe the charge of the ion as it passes through a material. This cannot be ignored for ions as it will drastically change any results from simulations and is currently a challenge of interest to the radiation science community [7]. The equilibrium charge state fractions of ions in materials give the probability that an ion is in a given charge state at a given velocity. This work presents charge state fraction measurements of light ions in nuclear materials which have not been studied previously.

Simulated ion track chemistry calculations are able to predict more complex effects of ionising radiation, for example the kinetic yields of species formed from ionising radiation. A specific example of this is radiolytic hydrogen production of oxides in contact with water [4]. The focus of this work is to investigate this hydrogen production in a non-oxide material, silicon carbide, which has been proposed as a nuclear fuel coating. These new results will both underpin safety information concerning uses of silicon carbide in radiation environments and also explore the topic of ionising radiation interaction from a different angle to the theoretical formalism and fundamental charge exchange work. In particular this interaction is proposed to be due to energy deposited in the solid transferring into the surrounding liquid phase. Current calculations of this type are capable of predicting single phase yields well however mixed systems require more information and understanding.

This project focuses on materials of interest to the nuclear industry due to the ubiquitous nature of ionising radiation in this setting. There are many types of functioning nuclear reactors in the world, with a wide variety of materials, therefore, in contact with radiation. The materials considered in this work are from all parts of the nuclear fuel cycle. When considering power generation, uranium dioxide is a common nuclear fuel with an intrinsic radiation field, whilst zirconium is used as the clad for many nuclear fuel rods (with the surface of this frequently composed of zirconium dioxide). From the field of spent fuel management, silicon carbide, copper and magnesium oxide are all proposed encapsulants for nuclear waste. Other materials discussed in this work are of interest more widely such as aluminium oxide and titanium.

The three projects undertaken all examine the interaction of ionising radiation with materials from different angles. The calculation of cross sections and charge state descriptions are targeted at improving Monte Carlo models that can be formed to simulate interfacial radiation chemistry capable of predicting chemical yields from a variety of
incident radiation sources (i.e. both electron and heavy ion radiation). It is for this reason that the materials of interest to this work are all solid state materials. This is unusual in radiation chemistry which normally focusses on liquid and gaseous phases. A study of these three subjects gives an overview of energy deposition in materials from ionising radiation at three different scales, from fundamental first principles to applied practical effects.

1.5. Outline of the Following Sections
The following sections present the work undertaken during this research programme. They have been arranged to first cover a theoretical formalism for electronic collision cross sections. This is followed by two complementary experimental pieces of work; fundamental charge cycling measurements are taken for lithium and helium ions in a variety of materials; the final experimental chapter describes the measurement of hydrogen produced from irradiated silicon carbide-water powder slurries, and shows the benefit of improvements to underlying theory in order to understand the results of modern experimental studies.

Chapters include an introductory section covering the specific subject matter in-depth and outlining the aims for the work. This is followed by papers which present obtained results. Following the three main sections a section covering the main conclusions and further work from this study is presented.
References

2. Energy Loss Properties of Ions in Materials

2.0. Objectives
To develop a model to predict electronic cross sections and energy loss properties of ions in materials using experimentally available optical data and to investigate its limitations through comparisons with stopping power data, focusing on oxide materials and silicon carbide.

2.1. Motivation

2.1.1. Inelastic Cross Sections, Stopping Power and other Energy Loss Properties
For over a hundred years, scientists have studied the interaction of charged particles with matter. Understanding has increased significantly since the famous alpha experiments of Rutherford [1]. This research has found applications in the fields of radiation therapy, accelerator physics and nuclear fission power production, amongst others.

Incident radiation of all types traversing matter will interact with the material it passes through, with individual processes dependent on radiation type and energy. A description of all interaction processes can be found in reference [2]. This study focuses on charged particle and electronic interactions especially those leading to ionisation. Ionising radiation includes high energy electromagnetic radiation (typically gamma radiation), electrons and positrons, and all ions. Ionisation is the dominating interaction process for ions passing through a material at non-relativistic energies. Ion interactions differ from incident electrons as the mass of the incoming energetic particle is much larger than that of the ‘stationary’ target electron. A second major consideration must be the charge state of the ion which has a large effect on the amount of energy lost to a material, as the interaction is essentially Coulombic.

When describing quantitatively the effect of interactions of radiation with matter, a key parameter to define is the cross section of an interaction. In their most general sense cross sections indicate the probability of a given interaction to occur for a fluence of particles, and take units of barns (b) where $1 \, \text{b} = 10^{-28} \, \text{m}^2$. Cross sections are used to describe many different events during the interaction of radiation with matter, and are a function of the target, projectile type and its velocity.

Two types of cross sections are referred to particularly often in the field of radiation interactions: electronic and nuclear cross sections. These correspond to inelastic and
elastic collisions respectively; an elastic collision is one where an incident projectile's internal energy is not changed on collision with the target (either increased or transferred); an inelastic event is a change in this internal state [3]. In the field of radiation science the distinction is made in a single collision between an inelastic and elastic component. The loss of internal projectile energy into either the potential/kinetic energy of the electrons is deemed inelastic and the transfer of centre of mass energy an elastic collision (transfer of energy with the nuclei of the target material) [4]. This work focusses on the prediction of inelastic or electronic cross sections (loss of energy to the electrons of the target). The two terminologies, inelastic and electronic, will be used interchangeably.

It is important in many branches of science to determine the average energy loss properties of radiation in a material. These properties are usually the range and stopping power of a particle in a material. The range of an ion in a material can be described in several ways (see [5]) however in all senses it is a measure of the distance travelled by the incident particle as its energy is reduced to thermal. The continuous-slow-down-approximation (CSDA) range can be used where there is little range variance (called straggling) and can be described

$$R = \int_0^E \frac{dE'}{NS(E')},$$

where $N$ is the number density of the target, $E$ the incident ion energy and $E'$ the energy at which the range is being measured; $S(E')$ is the stopping power at that energy. Stopping power of an incident ion with energy $E$ is defined as:

$$S(E) = -\frac{dE}{dx},$$

and is the mean kinetic energy loss per unit path length in a material. In fact, stopping power should more accurately be called a stopping force given its definition. Literature uses both terms however this study will tend to use stopping power. A second term for the energy loss of an ion as a function of distance is linear energy transfer (LET). Although similar, the two terms differ slightly in their definitions. The LET is the energy lost by the ion taking into account secondary electron interactions, these electrons are also called delta-electrons ($\delta$-electrons), up to a defined energy [2]. The stopping power refers to energy absorbed in a medium; therefore an ‘unrestricted’ LET (which takes into account all possible secondary electron energies) will be equal to the stopping power. The difference is generally small and this work looks at energy lost to the medium, therefore stopping power, however both terms are of use. Stopping power has become the most common method of exploring energy loss and is generally the most developed method when describing these properties.

The study of heavy ion radiation and energy loss properties is important to many fields of science and technology. Cosmic ray studies use heavy ion energy loss properties, as do ion accelerators and mass spectrometers [6]. This information is also of great importance to
medical radiation therapy [7]. Another growing field with interest in these effects is microelectronics for the development and fabrication of devices [8]. Finally, this field must be of primary importance to radiation damage and radiation chemistry studies, where the energy loss properties of ions in materials can vastly change the material’s properties and response [9].

The following sections detail background on stopping power formalisms (which can also be used to find other energy loss properties), a description of the different charge models for incident ions and then an outline of the model considerations necessary for this work.

2.1.2. Stopping Power Models and Programs

There are many models which have been developed to predict energy loss properties. These particularly focus on stopping power although some are capable of predicting other properties. It is impractical to detail them all; therefore the following is a description of the main types of approach, with examples and further references where appropriate. Stopping power calculation is a field with many similar terms and these can become confused unless care is taken. The stopping power of an ion is described as in Equation (2.22) however this is often portrayed as a density normalised value, the mass stopping force $-\frac{dE}{\rho dx}$, where $\rho$ is the target density; or as a stopping cross section (SCS) $-\frac{dE}{Nd\chi}$ where $N$ is the number density of molecules in the target medium. Stopping power of an incident ion with speed $v$ and charge $Z$ into a target of atomic number $Z_t$ can be expressed (in SI units of J m$^{-1}$) as

$$S(E) = \frac{NZ_t^2Z_t e^4}{\alpha e_0^2 m v^2} L$$  \hspace{1cm} (2.3)

where $\epsilon_0$ is the permittivity of free space, $m$ the mass of the electron and $e$ the electron charge. The function $L$ is a dimensionless ‘stopping number’, and its utilisation is helpful as corrections and changes for different models can be expressed as amendments to this function.

The first attempts to describe stopping power in the early 20th Century were classical treatments of incident particles by Bohr [10]. This formalism described the stopping number as

$$L = \ln\left(\frac{1.1229 m v^3}{Z v_0 \hbar \nu}\right) - \ln(1 - \beta^2) - \frac{\beta^2}{2}$$  \hspace{1cm} (2.4)

where $\nu$ is the resonance frequency of target electrons. The variable $\beta = v/c$ with $c$ being the speed of light in a vacuum, $\hbar$ is the reduced Plank’s constant and $v_0$ is the Bohr velocity. This classical theory is accurate at higher energies, however, it becomes less accurate as incident ion energy decreases. This approach is widely used since it gives a reasonable description of the interaction of target electrons with projectiles [11, 12].
In the 1920s, Bethe suggested a different approach to the purely classical treatment. This theory treats the Coulomb interaction between the projectile and target electrons by quantal scattering theory in the first Born approximation [13]. As with classical Bohr theory there is a simple $Z^2$ relationship of stopping power to the incoming ion charge. Bethe theory gives perhaps the most well-known form of the stopping power equation:

$$L = \ln \left( \frac{2m v^2}{\hbar w} \right) - \ln (1 - \beta^2) - \beta^2$$  \hspace{1cm} (2.5)

The $\hbar w$ variable can be re-termed $I$ the mean excitation energy of the target material.

At low energies both theories require correction due to the motion of target electrons in the medium. This correction takes the form of the Bloch correction. This can be described as:

$$\Delta L_{\text{Bloch}} = \psi(1) - \text{Re} \psi \left( 1 + i \frac{Z v_0}{v} \right)$$  \hspace{1cm} (2.6)

with $\psi(x) = \frac{d \ln \Gamma(x)}{dx}$ and $\Gamma$ the gamma function. The Bloch correction is added to first order quantal perturbation theory and is proportional to $Z^2$ at low speeds, becoming negligible at higher speeds.

Another effect requiring a correction to theory due to a difference in stopping between a particle and antiparticle was discovered by Barkas et al. [14] and confirmed by measurements of Anderson et al. [15]. This higher order correction to the $Z^2$ quantum theory is proportional to $Z^3$ and is also more prominent at low energies. It was described by Ashley et al. [16] as the addition to Bethe theory

$$\Delta L_{\text{Barkas–Anderson}} = Z e^4 w_I m v^3.$$  \hspace{1cm} (2.7)

Further changes to the Bethe formula are described in ICRU report 73 [5] and take into account relativistic and ultra-relativistic effects not of interest here.

When studying compounds, Bragg additivity is often used to relate the stopping of elements with those of the material. This assumes that binding energy between elements has no effect on stopping power. The stopping power of a molecule can be expressed in this case therefore as

$$-\frac{dE}{dx} = \sum_i N_i S_i$$  \hspace{1cm} (2.8)

where $N_i$ is the number density and $S_i$ the stopping power of the $i$'th target element in the compound. An in-depth review of this subject can be found in reference [17].

As an ion passes through a material the fluctuation of energy loss is called energy loss straggling. This straggling occurs as interactions with matter are stochastic in nature; when a mean characteristic like stopping power (or range) is defined there is a distribution around this predicted value. This project aims to develop inelastic cross sections that can be incorporated into a Monte Carlo code, furnishing a direct value for the mean parameters and for this straggling effect.
Whilst many different developments for predictions of stopping power exist, the following are some of the most developed and well known models.

Binary theory, developed by Sigmund and Schinner [18], is similar to that of classical Bohr theory, however, it avoids Bethe and Bloch’s perturbation theory, as well as the necessity for discerning between close and distant collisions as is the case with classical theory. This simplification is achieved by considering binary scattering of the projectile and the target electrons [3]. The projectile electrons are treated as a screening of the interaction [5]. This theory is deployed in the PASS computer program which was used in the ICRU data tables for the ‘Stopping of ions heavier than helium’ [5]. The code is one of the most developed, widest range models. Oscillator strengths are used as an input, however not in their raw form: they are ‘bundled’ into shells and sub-shells to form \((f_j, w_j)\) pairs which are used in the calculation of stopping data. This model includes corrections for relativistic effects and shell effects with the program inherently inclusive of the Barkas-Anderson effect [5].

Unitary convolution approximation provides an impact parameter dependent version of quantal perturbation theory. The impact parameter in a collision denotes the perpendicular distance between the incoming projectile trajectory and the target nucleus (initially at rest) [5]. Close and distant interactions are treated differently in this approach with distant interactions determined using a ‘traditional’ perturbation approach and close interactions determined by a Coulomb interaction with respect to an impact parameter [5]. This covers energies in the transition from the classical to the perturbation regime. The theory does not currently account for Barkas-Anderson corrections. This theory developed by Grande and Schiwietz [19] is used in the CasP program. Input data avoids the need for effective charge considerations (see Section 2.1.3) but uses the mean ionisation value of the target material.

The non-linear electron gas model, proposed by Lifshitz and Arista [20] uses the concept of a Fermi gas target and transport cross sections in order to predict low speed stopping. Shell corrections are accounted for, as are Barkas-Anderson corrections. Results are very good for metals due to their free electrons, however it is only in recent years that heavier ions and insulators have been described well using this model.

Convergent kinetic theory, is well aligned with plasmas and focusses on descriptions of partially ionised ions in a partially ionised target [5]. Maynard et al. [21] describe this as an extension to Bethe theory which at close collisions uses transport cross sections. This model avoids the use of oscillator strengths as input data.
Ziegler et al.'s SRIM software is probably the most widely used computer program to predict stopping powers of ions in matter. This software also includes a Monte Carlo program to predict other macroscopic and microscopic energy loss properties, TRIM. Developed by Ziegler, this treatment uses classical theory and the concepts of ‘cores’ and ‘bonds’ in order to compensate for compounds, with additions for nuclear stopping and scattering [22].

No one model addresses all of the failings of classical stopping power theory. Rather, certain codes are more suited to certain challenges. A more detailed overview of some of the more common stopping power models can be found in the ICRU review [5]. The review is entirely focussed on stopping power. The purpose of this study is to use stopping power data as a way to evaluate electronic inelastic collision cross sections. These will eventually be used in collision-to-collision Monte Carlo simulations of radiation tracks.

2.1.3. Charge Considerations

One of the main challenges to predicting the interactions of heavy ions with matter is the charge of the heavy ion. The charge of the ion inside the target material will affect the energy loss properties of an ion on passage through that material, as can be seen from the $Z^2$ terms in Equations (2.3-2.8).

Ideally, ion and material-dependent charge cycling cross sections should be measured and used, with the average stopping power given by the weighted sum of the stopping powers for the different charge states i.e.:

$$ S(M, Z; E) = \sum_{q=0}^{Z} F_q S(M, q; E) $$

where $S(M, Z, E)$ is the stopping power of a material for an ion of mass $M$, stripped charge $Z$ and kinetic energy $E$ and $q$ is the charge state of the ion inside the material, i.e. up to $Z$.

Historically, one of the most widely used, albeit inappropriate, methods of describing the charge state of an ion is an ‘effective’ charge. The effective ion charge is constructed by compiling stopping powers for many ions over a large energy range and then empirically fitting the data for the ions to that for protons with the same velocity to obtain a multiplication correction (or “fudge” factor) for the ion data. Generally, effective charge models are not target material-specific. In other words in this the stopping power is described as

$$ S(M, Z; E) = q_{eff}^2 S(1,1; \frac{E}{M}) $$

where $q_{eff}$ is the fitted effective charge, which depends upon the velocity of the ion as well as its fully stripped charge, $Z$.

Strictly speaking, assuming the stopping power of an ion can be related to that of a proton with the same velocity, then the effective charge should be equivalent to the root mean
squared charge obtained from the charge state distribution defined by charge exchange experiments, this would be described as

\[ q_{\text{eff}} = \sqrt{\sum_{q=0}^{Z} q^2 F_q} \]  

(2.11)

with \( F_q \) the fraction of ions in a given charge state determined by charge cycling cross-sections. In other words, the measured experimental stopping power of an ion should be given by

\[ S(M, Z; E) = S(1,1) \sum_{q=0}^{Z} F_q q^2. \]  

(2.12)

In practice, collating the data required to describe every ion through every material is a daunting task.

Three empirical effective charge models are considered in this study. They are described in detail in references [23], [24] and [25]. The first is that of Northcliffe, who suggested the effective charge on an ion could be described by the equation

\[ q_{\text{eff}} = Z \left( 1 - 1.85 \exp \left[ -2 \frac{v}{v_0} \right] \right)^{1/2}. \]  

(2.13)

Pierce and Blann extended this approach of relating \( q_{\text{eff}} \) to the Bohr velocity. They obtained a fit by considering 4 ions in 11 different targets including both solids and gases [24], and suggested effective charge could be described by

\[ q_{\text{eff}} = Z \left( 1 - \exp \left[ -0.95 \frac{v}{v_0} \right] \right), \]  

(2.14)

including a proportionality to the fully stripped ion charge, \( Z \).

The final empirical effective charge model considered here was developed by Ziegler, who compiled a larger dataset comprising hundreds of targets for many different ions. The data set was used to obtain the following expression for effective charge:

\[ q_{\text{eff}} = Z \left( 1 - \exp \left[ -0.95 \frac{V_f}{v_0 Z^{2/3}} - 0.07 \right] \right) + Z \left( \exp \left[ -0.95 \frac{V_f}{v_0 Z^{2/3}} - 0.07 \right] \right) \left( \frac{v_0/V_f}{2} \right)^2 \ln \left[ 1 + \frac{2 \Lambda V_f}{a_0 v_0} \right] \]  

(2.15)

with \( V_f \) the Fermi velocity, \( a_0 \) the Bohr radius and \( V_r \) being the relative velocity of the incident ion to that of the electrons in the medium as described in Ziegler [25]. \( \Lambda \) is a screening length, describing the electronic distribution around the projectile ion, which separates ‘close’ and ‘distant’ collisions. The screening length will change as a function of the number, \( \bar{n} \), of electrons remaining on the projectile and can be described

\[ \Lambda = \frac{n^{3/8}a_0^5}{Z^{1/2} \bar{n}^{7/2}}. \]  

(2.16)

The formalism in Equation (2.15) is similar to that of Pierce and Blann, relating \( q_{\text{eff}} \) to the relative velocity of electrons in a medium and the ion charge; however, it goes further by including an additional second term incorporating the effect of incomplete shielding of the ion nucleus by any associated electrons i.e. to account for electrons in the medium which
penetrate the electronic shells of the incident ion and thereby giving less shielding to the ion nucleus. This correction is the second term in Equation (2.15) with the first term being the effective charge for ‘distant’ collisions. This first order perturbation approach is explained in detailed in reference [25] and relies on Brandt and Kitagawa’s ‘BK’ theory [26].

For helium, Ziegler has obtained a more specific empirical fit to the compilation of experimental data in which the effective charge is given by

\[ q_{\text{eff}} = Z \left(1 - e^{-\sum_{i=0}^{5} a_i \ln(E_{\text{He}})}\right)^{1/2} \]  

(2.17)

where \( Z = 2 \), \( E_{\text{He}} \) is the energy of the incident helium ion in MeV. The fitted parameters are: \( a_0 = 0.2865 \), \( a_1 = 0.1266 \), \( a_2 = -0.001429 \), \( a_3 = 0.02402 \), \( a_4 = -0.01135 \) and \( a_5 = 0.001475 \) [25].

It is clear from Equation (2.11) that the effective charge does not actually portray the mean charge state of an ion in a material. Furthermore, because of the nature of the fitting, it incorporates other corrections required to change the proton stopping power to reflect the stopping of the ion in question. Sigmund recently stated that the empirical methods used to account for the cycling of an ion’s charge lack rigorous theory and that a better method should be found to predict mean charge states [27].

In addition to effective charges, fitted expressions for the mean equilibrium charge have been obtained by various authors including Schiwietz and Grande [28]. These fits should be superior to effective charge as they are fitted to (mean) equilibrium charge state data, rather than relating back to stopping power. The data-set comprises mostly of captured ions in carbon as there have been most experiments on carbon: Grande and Schiwietz describe the mean equilibrium charge state of projectiles in materials as [28],

\[ q_{\text{mean}} = Z \frac{(0.29x + x^4)}{\frac{8}{3} + 4x + 4x + x^4} \]  

(2.18)

with the scaling variable

\[ x = c_1 \left(\frac{\bar{v}}{1.54 c_2}\right)^{1+1.83/Z} \]  

(2.19)

where

\[ c_1 = 1 - 0.26 \exp\left(-\frac{Z_t}{11} - \frac{Z_t - Z}{9}\right) \]  

(2.20)

\[ c_2 = 1 + 0.030 \bar{v} \ln(Z_t) \]  

(2.21)

and

\[ \bar{v} = Z^{-0.543} \frac{v}{v_0} \]  

(2.22)

here \( Z_t \) is the “nuclear” charge of the target material. As, by definition,

\[ q_{\text{mean}} = \sum_{q=0}^{Z} F_q \]  

(2.23)

use of the square of this parameter in expressions for stopping power is not a wholly satisfactory representation of the effects of charge exchange of an ion in a material, especially as the empirical expressions are only applicable over a limited energy range.
Figure 2.1 shows the evolution of the 4 considered predictions of charge as a function of energy for lithium ions in ZrO$_2$. There is clearly a large difference at lower energies. The papers in Section 2.3 and 2.4 discuss the effect this has on the developed formalism.

![Figure 2.1](image.png)

**Figure 2.1.** The evolution of lithium charge in ZrO$_2$ as a function of incident ion energy. The solid black line refers to Zeigler [25], the red line is the model from Pierce and Blann [24], the blue dashed line is Northcliffe [23] and the pink line is the effective charge from Schiwietz and Grande [28]. The vertical black line at 0.1 MeV/u is where the formalism developed in this work breaks down.

### 2.1.4. Aims for this Work

Predicting the energy loss properties of ceramics, such as metal oxides, poses more of a challenge when making predictions for elementary materials due to their more complex electronic state distribution [17]. Bragg additivity cannot be implemented without error and separating the oscillator strengths into shells is not facile. Due to these challenges oxides present a good test of any formalism developed for predicting energy loss properties. The aims of this project are:

1. to develop a model to predict electronic collision cross sections using a novel method;
2. to explore the effect that the charge state description will have on energy loss properties; and
3. to find the limitations of this model by studying oxides and silicon carbide.

To accomplish these goals will also necessitate the construction of dipole oscillator strength distributions for various materials considered.
2.2. Model Development

2.2.1. Inelastic Cross Section Formalism

The model developed in this work describes the inelastic collision cross section of non-relativistic heavy ions in a material. It is an extension of previous work by Ashley who presented work on the energy loss properties from incident electrons and positrons [29].

The model’s main attribute, and difference from traditional quantum perturbation theory, is the direct use of a dipole oscillator strength distribution to predict energy loss in target materials. Many other methods [18, 30] require lengthy analysis of optical data when constructing oscillator strength distributions. This work has a further advantage over traditional Bethe theory as shell corrections are inherent in the calculation, (i.e. the Bloch correction).

The Appendix 1 outlines the in-depth calculations necessary to form inelastic cross sections and energy loss properties using this method. A description of both the main calculation steps and the classical kinematic bounds of the system are also found in the paper in Section 2.3.

2.2.2. DOSD Construction

Incident electromagnetic radiation will interact with the electrons bound to molecules in the material. This incident radiation (whilst not enough to break any bonds) if at the correct frequency, will incite oscillation in the bound electrons. In other words, the radiation will be absorbed at this energy [31]. The strength of this forced oscillation as a function of energy is the dipole oscillator strength distribution (DOSD). Knowledge of this DOSD is necessary for the implementation of many stopping power models, including the one developed here.

In order to form a DOSD it is necessary to obtain optical data for the material required in the phase required. This can be in the form \( n, k \) (refractive index and absorption coefficient) or the dielectric response function, which can be described \( \varepsilon = \varepsilon_1 + i \varepsilon_2 \), with the real and complex parts being related to the refractive index and absorption coefficient

\[
\varepsilon_1 = n^2 + k^2 \tag{2.24}
\]

and

\[
\varepsilon_2 = 2nk. \tag{2.25}
\]

The necessary optical data can be derived in several ways, depending on the required energy range. In the construction of DOSD as wide an energy range as possible is required and therefore multiple methods will be used in concert for their formation. Some common methods to calculate optical properties include: reflectance and transmittance, Electron Energy Loss Spectrometry (EELS) and Ellipsometry, along with traditional spectroscopy methods (e.g. vacuum ultraviolet spectroscopy) [32]. Kramers-Kronig analysis is often
performed on the optical data. This allows the complex dielectric function to be determined from the real part (and vice-versa) and is therefore a valuable tool when forming the dielectric function and energy loss functions [33].

The energy loss function is directly related to the frequency dependent refractive index and extinction coefficient of the medium, \( n \) and \( k \) respectively, through the complex dielectric response function, and the energy loss function

\[
\text{Im} \left[ \frac{-1}{\varepsilon(0, E)} \right] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}.
\] (2.26)

The differential DOSD of a material, \( f(E) \), at energy \( E \) is related to the energy loss function by the equation:

\[
f(E)/E = \frac{2m}{\hbar^2 eN} \text{Im} \left[ \frac{-1}{\varepsilon(0, E)} \right]
\] (2.27)

with \( m \) the electron mass, \( e \) its charge, Planck’s constant \( \hbar \) and \( N \) the number density of molecules of the medium.

In practice many sources in literature give energy loss functions directly from the obtained optical constants for a material. Where this is the case the energy loss function can be used directly to form the DOSD as long as the experimenter is satisfied with the analyses performed to construct these energy loss functions.

For energies above 100 eV, \( n \) is close to one and \( k \) is small, so \( \varepsilon_1 \) tends to \( n^2 \) and \( \varepsilon_2 \) to \( 2k \). Consequently, the energy loss function, \( \text{Im}(-1/\varepsilon(0, E)) \), is determined solely by \( k \) and we are able to assume that the core electrons are localised and summing atomic absorption cross sections is an acceptable substitute for optical data for compounds. In the following studies, atomic absorption cross sections for energies above 100 eV are taken from the compilation of Veigele [34]. When converting Veigele atomic absorption cross section data to the DOSD the equation required is [35]:

\[
f(E) \ [\text{eV}^{-1}] = \sum_i \sigma_i \ [\text{b/atom}] \times 9.17 \times 10^{-9} \ [\text{b^{-1}eV^{-1}}]
\] (2.28)

where \( \sigma_i \) is the photoabsorption cross section from the \( i \)th element in the compound, the constant serving to convert to the correct DOSD units. When experimental measurements of the energy loss function do not reach up to 100 eV (which is usual), the available data are interpolated using a \( \log(f) \) vs \( E \) plot between the two energy ranges, see Figure 2.2 for an example of this interpolation for the construction of the SiC DOSD in this work.
Figure 2.2. The construction of the silicon carbide DOSD utilised in this study. Pink shows the optical data from Choyke and Palik [33], blue shows the interpolation between the optical data and the black photoabsorption cross section data.

Once constructed, the DOSD is evaluated according to the $f$ sum rules (although they go by many names) [36]. The first of these rules is that the ‘effective number of electrons which may receive energy from an energy transfer from an incident electron’ [2] is calculated by integrating the DOSD:

$$Z_{\text{eff}} = \int_{E_0}^{E_{\text{max}}} f(E) dE.$$  \hspace{1cm} (2.29)

To confirm the acceptability of any modification of the DOSD, the mean excitation energy, $I_{\text{eff}}$, is also given by the second moment sum rule,

$$Z_{\text{eff}} \ln(I_{\text{eff}}) = \int_{E_0}^{E_{\text{max}}} f(E) \ln(E) dE.$$ \hspace{1cm} (2.30)

If these sum rules do not obey the known properties of the material then a choice can be made to either re-examine the optical properties which have been used to form the DOSD, or, to normalise the DOSD to the correct effective number at high energies, $Z$. In this study this is done by modifying the optical data, as there is usually a larger uncertainty in this data than the photoabsorption cross sections. In addition analyses of optical data by the publishing source can modify the height of optical structure in order to conform to sum rules. No change is made to the energy of features, only to the absolute height of the differential DOSD. The modified DOSD will form the main input for this model and is usually quite simple to form.

2.2.3. Other Chosen Parameters

The model used to describe the ion charge can be changed at will in this model. As described in the following papers, this is something which has been studied during this
project. The models used are the ones described in the previous Section 2.1.3. In these energy loss predictions protons, due to convention, are considered to have a charge of one despite some evidence to the contrary and corrections for a non-unitary charge in some of the charge models [24, 28]. Mass stopping power (i.e. density normalised) is given in units of MeV cm²/mg in this work.

In this model the ion is only considered below relativistic speeds. At higher speeds, the ion can also lose energy by electromagnetic radiation in addition to the Coulombic processes. This leads to additional terms which require to be considered. For example the Fermi density effect, the reduction in stopping power due to polarisation of the medium which becomes non-negligible at relativistic speeds. Additionally the ion can undergo nuclear reactions which would need to be factorised into the model. This becomes more complex as this would change the species. This model treats energy loss as an average quantity, factoring in nuclear reactions would not be trivial. It is common for models to avoid the relativistic range [20].

The computational model was programmed in Fortran 77, the programme of which can be found in Appendix 2. All computation was performed using Danzek the high performance cluster at the University of Manchester. All analysis was made using Microcal-OriginPro®.
References

[34] J. Veigele, Photon cross sections from 0.1 keV to 1 MeV for elements Z = 1 to Z = 94, Atomic Data and Nuclear Data Tables, (1970).
2.3. Inelastic Cross Sections and Energy Loss Properties by Non-Relativistic Heavy Ions in Zirconium Dioxide

Authors: J. Schofield, S. M. Pimblott

Status: Published in Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms

Thesis Page Number: 40

Author contributions: First author of the paper. Formed the DOSD of ZrO₂, calculated all energy loss properties presented, and analysed results making comparison to experimental data. Wrote first draft of the manuscript.

Relevance: This paper presents a novel formalism to predict electronic collision cross sections of (heavy) ions in materials from solely optical data. The paper details the formation of the methodology and also presents predictions for a material of relevance to the nuclear industry. The energy loss properties are shown to agree with experimental data well at high energies. The limitations of the formalism are presented.
Inelastic cross-sections and energy loss properties by non-relativistic heavy ions in zirconium dioxide

Jennifer Schofield a,*, Simon M. Pimblott a,b

a School of Chemistry, The University of Manchester, Oxford Road, M13 9PL, UK
b The University of Manchester Dalton Cumbrian Facility, Westlakes Science and Technology Park, Moor Row, Cumbria CA24 3HA, UK

1. Introduction

There have been numerous studies of the energy loss properties of charged particle radiation in matter since Bethe’s pioneering work [1]. Over the last 20 years, extensive effort has been spent attempting to incorporate material and phase information, in particular Ashley has proposed an approach based on the use of the dipole oscillator strength distribution (DOSD) for a material [2]. This formalism has subsequently been deployed by a number of research groups [3–7] primarily to look at the energy loss of electrons, positrons and protons in water [3,4]; however there are limited applications to other materials including DNA and hydrocarbons [7,8]. The simulation and microscopic understanding of the structure of ion tracks in a material relies upon the availability of suitable cross-sections for the various collision processes, especially electronic ionisation and excitation and charge exchange between the irradiation particle and the medium.

This study describes the development formalism for the facile prediction of the inelastic cross-section for electronic ionisation and excitation of ions in a wide variety of materials which avoids the use of a model for the general oscillator strength (GOS) for each material. The formalism is based on the approximation developed by Ashley and the use of experimental DOSD from optical data thereby allowing significant flexibility and applicability. The formalism is applied to zirconium dioxide (ZrO2) in order to assess its effectiveness. Elucidating radiation damage and the energy loss characteristics of ions in ZrO2 is an important challenge in understanding the performance of light water reactor fuel cladding for both in-reactor operation and interim storage, as zirconium is the principal component of LWR fuel cladding.

In this paper, the methodology used for calculating both the inelastic cross-sections and energy loss properties of heavy ions is described, detailing the application of the ‘Ashley’ approximation to heavy ions and describing considerations of the effective charge of the incident ion on the stopping power. The DOSD of ZrO2 is formulated from the available experimental data and the energy dependent inelastic cross-section, Y function and mean free path for electronic ionisation and excitation are evaluated as well as various energy loss properties, specifically the stopping power, and csda (continuous slowing down approximation) range. Mean energy loss characteristics for incident ions in ZrO2 are compared, where possible, to experimental data.

2. Methodology

The electronic collision cross-section as well as stopping power and energy loss properties of an ion in a material can be related to
the dielectric response function $\epsilon(p, \gamma)$ for the medium in question. This complex function gives information on how a medium responds to a momentum, $p$, or energy, $\gamma$, transfer to it. When a fully stripped ion with incident energy $E = MV^2/2$ enters a material the probability of the ion undergoing an energy loss per unit distance is given by [3]

$$\tau(E, \gamma) = \frac{Z^2}{\pi \epsilon} \int \left| -1/[\epsilon(p, \gamma)] \right| dp / \rho$$  \hspace{1cm} (1)

where the reduced atomic units $e = m_e = h = 1$ are used (and are used throughout this work) with $e$ the electronic charge, $m_e$ the electron mass, $h$ Planck’s constant and $M$ the reduced mass of the ion. The $Z^2$ term in Eq. (1) distinguishes the expression for heavy ions from that for singly charged electrons and positrons, as noted in reference [9].

The probability of an energy loss event can be related to the inelastic collision cross-section by

$$\sigma(E) = \frac{1}{N} \int \tau(E, \gamma) d\gamma$$  \hspace{1cm} (2)

with $N$ being the number density of molecules in the medium. Furthermore,

$$\sigma(E) = (N \Lambda(E))^{-1}$$  \hspace{1cm} (3)

where $\Lambda$ is the mean free path of an ion in the medium. The stopping power, $S(E)$, and $csda$ range, $R(E)$, are given by the two equations

$$S(E) = \int \gamma \tau(E, \gamma) d\gamma$$  \hspace{1cm} (4)

$$R(E) = \int \frac{1}{S(E)} dE.$$  \hspace{1cm} (5)

Crucially, the expressions for the energy loss properties in a medium for an ion given above rely on $\text{Im}[-1/\epsilon(p, \gamma)]$, the imaginary part of the complex dielectric response function. This function is not available from experiment for most materials, however, the energy loss function (ELF) for optical data, where $p = 0$, is much easier to obtain. Ashley has suggested an approximation to allow the evaluation of the energy loss properties, namely, the quadratic expansion of the DOSD into the energy–momentum plane [2]

$$\text{Im}[-1/\epsilon(p, \gamma)] = \int \frac{Z^2}{2} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma') \sqrt{\gamma - \left( \gamma' + \frac{p^2}{2} \right)}} \right] d\gamma'$$  \hspace{1cm} (6)

where $\gamma'$ can be identified as a ‘binding energy’ associated with the molecules in the medium. This approximation allows us to use solely optical data in the previous Eqs. (1)–(5).

When evaluating the expressions (1)–(5) of an ion interacting with the electrons in a medium the kinematic constraints of the situation must be considered to determine the bounds of integration. The ion with mass $M$ and incident energy $E = MV^2/2$ is assumed to collide with an electron at rest. The ion then leaves with energy $MV_1^2/2$ and the electron has energy $\nu_2^2/2$ with the contribution of $\gamma'$ the ‘binding energy’ given to the system. According to energy conservation, we can say that $MV_1^2/2 = MV^2/2 + \nu_2^2/2 + \gamma'$. We can also define the ‘energy loss’ as $\gamma = (V^2 - V_1^2)M/2 > \gamma'$, which gives through simple rearrangement,

$$V_1 = \sqrt{V^2 - 2\gamma}/M.$$  \hspace{1cm} (7)

For all possible energy losses, the value of $\gamma_{\text{min}}$ is 0 while the maximum value of $\gamma_{\text{max}}$ always corresponds to the minimum possible momentum transfer for a given energy transfer. By applying conservation of momentum, the following inequality for the minimum momentum transfer is defined

$$p_{\text{min}} = M(V - V_1) < \rho.$$

When combined with the definition for $V_1$ above and the fact that $\nu_2 = \sqrt{2(\gamma' - \gamma)}$, Eq. (7) becomes

$$\gamma' < \gamma - M \left( \frac{\nu_2^2}{M} - V \sqrt{V^2 - 2\gamma} \right) = \gamma_{\text{max}}.$$  \hspace{1cm} (8)

We can now apply a Taylor expansion to the square root terms in Eq. (8) as $\gamma < MV^2/2$ for an ion colliding with an electron; giving

$$\gamma_{\text{min}} = 0 < \gamma' < \gamma - \nu_2^2/2V^2 = \gamma_{\text{max}}$$  \hspace{1cm} (9)

Taking the right hand side of Eq. (9) allows us to determine the limits on energy transfer as

$$\gamma_{\text{min}} = V^2 - V \sqrt{V^2 - 2\gamma' < \gamma < V^2 + V \sqrt{V^2 - 2\gamma'}} = \gamma_{\text{max}}.$$  \hspace{1cm} (10)

These inequalities, Eqs. (9) and (10), define the bounds of integration to a symmetric curve in the energy-transfer/binding-energy plane with allowable values under the curve; see the hashed area in Fig. 1.

Applying these constraints to Eq. (1) gives the following probability of energy loss,

$$\tau(E, \gamma) = \frac{Z^2}{2 \pi \epsilon} \int_{\gamma_{\text{min}}}^{\gamma_{\text{max}}} \text{Im}[-1/\epsilon(0, \gamma)] - G(\gamma'; \gamma') d\gamma'$$  \hspace{1cm} (11)

where $G(\gamma'; \gamma') = \frac{-1}{\gamma'}. \text{ }$ From this we are able to define the inelastic cross-section and stopping power for electronic collisions as:

$$\sigma(E) = \frac{Z^2}{2 \pi \epsilon} \int_{0}^{\nu_2^2/V^2} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] \ln \left[ \frac{(1 + s - a)(1 + s)}{(1 - s - a)(1 + s)} \right] d\gamma'$$  \hspace{1cm} (12)

$$S(E) = \frac{Z^2}{2 \pi \epsilon} \int_{0}^{\nu_2^2/V^2} \gamma' \text{Im}[1/\epsilon(0, \gamma')] \ln \left[ \frac{1 + s - a}{1 - s - a} \right] d\gamma'$$  \hspace{1cm} (13)

with $a = \gamma'/V^2$ and $s = \sqrt{1 - 2\gamma'/V^2}$. From Fig. 1 it is clear to see that when evaluating total cross-sections $\gamma_{\text{min}} = 0$ and $\gamma_{\text{max}} = V^2/2$.

When modelling ion track structures, the simulations follow the trajectory of an ion collision by collision until the energy of the ion is less than a defined cut-off energy. The nature of a collision is determined from relative cross-sections for each type of collision at the energy of the ion, i.e. ionisation, excitation, vibration or
elastic collisions. In the case of inelastic collisions, the differential inelastic cross-section is used to calculate energy loss via the so-called Y function [10]. This Y function corresponds to the ratio of the cumulative inelastic cross-section σ(E, Ê) to the total inelastic cross-section σ(E, Emax) and is equivalent to the probability of an energy loss smaller than an quantity E [10]. Evaluation of the cumulative inelastic cross-section requires careful attention to the bounds of the integral in the γ − γ̂ plane conditions, as seen in Fig. 1. The bounds are defined by Eqs. (9) and (10) with a maximum value of γ̂ = V̂2/2 when γ = V̂. For an energy loss in the range 0 < E < V̂̂, the cumulative cross-section is given by

\[ \sigma(E, Ê) = \frac{Z^2}{2\pi EN} \int_{Ê}^{E\text{max}} \ln\left[1/\gamma(0, \gamma')\right] \ln\left[\frac{(b - a)(1 + s)}{ab}\right] d\gamma' \] (14)

where b = Ê̂/V̂̂. However, when V̂̂̂ < E < 2V̂ evaluating the integral is more complicated as we have to consider the appropriate “region of integration”. The most straightforward approach is to subtract the “missing” cross-section due to energy losses in the range E to Emax from the total cross-section, that is to determine the following

\[ \sigma(E, Ê) = \sigma(E, E\text{max}) - \frac{Z^2}{2\pi EN} \int_{Ê}^{E\text{max}} \ln\left[1/\gamma(0, \gamma')\right] \ln\left[\frac{(1 + s - ab)}{(b - a)(1 + s)}\right] d\gamma' \] (15)

The probability of an energy loss from E to E + dE is given by the differential Y function, dY/dE. This quantity is analogous to the differential energy loss distribution for a particle at the energy in question. Since the Y function is independent of the charge and of the mass of the ion, depending only on its velocity, all ions at the same specific energy will have the same differential energy loss distribution. Heavy ion energy differential Y functions show peaks at the same energy of the DOSD and ELF, however with differing relative magnitudes. This is due to the underlying relationship between the three quantities.

Examination of Eqs. (11)–(15) reveals that the charge of the ion in the target material influences the energy loss properties of the ion in the material. Furthermore, this dependence on ion charge has significant implications for understanding radiation effects since as the ion passes through the material and slows down, it will capture electrons from the target material, changing its net charge. This captured electron can also be lost back to the medium. The gain and loss of electrons cycles the ion’s charge, affecting the rate of energy loss and the associated properties. Ideally, ion and material dependent charge cycling cross-sections should be (measured and) used in the interpretation of the energy loss and radiation track structure; however, the effects of charge cycling on the energy loss properties of ions are frequently approximated using an empirical approximation for the mean or the effective charge obtained by fitting experimental data.

The mean charge of an ion defined by charge exchange experiments is

\[ \bar{q} = \sum_{q=0}^{n} qF_q \] (16)

with F_q the fraction of ions in a given charge state determined by charge cycling cross-sections and n the number of different charge states for an ion.

Several empirical expressions exist to approximate the mean equilibrium charge state of projectiles in materials, for instance Schiwietz et al. suggest [11],

\[ q_{\text{mean}} = \frac{8(2.9x + x^3)}{(x^3 + 4 + 7.4x + x^3)} \] (17)

with the scaling variable

\[ x = \frac{\bar{q}}{1.54c} \] (18)

where

\[ c_1 = 1 - 0.26 \exp\left(-\frac{Zt}{11} - \frac{(Zt - Z)^2}{9}\right) \] (19)

\[ c_2 = 1 - 0.26 \exp\left(-\frac{Zt}{11} - \frac{(Zt - Z)^2}{9}\right) \] (20)

\[ c_2 = 1 + 0.030 \nu \ln(Zt) \] (21)

and

\[ \bar{\nu} = Z^{-0.543} \nu / \nu_B \]

with Zt being the “nuclear” charge of the target material and νB the Bohr velocity.

As with any empirical model, specifying the mean or effective charge based on fitting to experimental data is only appropriate for the experimental systems originally considered and is only valid over the energy ranges considered. Furthermore, these empirical fits will incorporate discrepancies between theory and experiment that do not arise from charge exchange. Sigmund recently stated that the empirical methods used to account for the cycling of an ions charge lack rigorous theory and that a better method should be found to predict mean charge states [12]. In addition, according to the formalism presented here the stopping power, S_{\text{ion}} of a material for an ion with fully stripped charge Z should be related to the stopping power of a proton with the same velocity, S_{\text{proton}} by

\[ S_{\text{ion}} = S_{\text{proton}} \sum_{q=0}^{n} q^2 F_q < q^2 > S_{\text{proton}} \] (22)

where <q^2> is the mean squared charge. By definition, the mean of a distribution is not equal to the distribution’s root mean square so the use of (the square of) this parameter is not even a mathematically satisfactory substitute for the charge state cross-sections of an ion in a material.

The effective charge of an ion in a material is usually defined as the implied non-integer “charge state [of an ion at a given energy] required to reduce calculated Bethe-Bloch stopping [powers] to agree with experimental stopping values” [13]. Specifically, the effective charge is defined by relating the experimental stopping power of an ion with fully stripped charge Z to the experimental stopping power of a proton with the same velocity,

\[ q^2_{\text{eff}} = S_{\text{ion}} / S_{\text{proton}} \] (23)

where the charge state of the “hydrogen ion” is taken to be to be one at all energies. The parameter q_{\text{eff}} is usually determined by considering the stopping of many ions in many materials and determining an empirical fit. This approach results in a single expression which is presumed to be target independent.

A variety of different expressions for effective charge, q_{\text{eff}}, have been proposed [11,14–18] and are discussed straightforwardly in Ziegler [18]. These expressions are generally based on Bohr’s postulate that heavy ions stripping will depend on the electron orbital velocities relative to the ion’s velocity; electrons with orbital velocities less than the ions velocity can be deemed to be stripped [19]. The first to suggest an exponential relationship to velocity was Northcliffe [17], who proposed an empirical effective charge of

\[ q_{\text{eff}} = Z \left(1 - 1.85 \exp\left(-\frac{2V}{\nu_B}\right)\right)^{1/2} \] (24)
relating the effective charge to the velocity of the incident ion with respect to the Bohr velocity. As more data has become available more accurate parametrisations over a greater number of ions and energies were suggested, for example Pierce and Blann [16] suggested

$$q_{\text{eff}} = Z \left( 1 - \exp \left[ -\frac{0.95V_i}{v_F} \right] \right)$$  \hspace{2cm} (25)

with $V_i$ the relative velocity of the incident ion to the electrons in the medium as described in [16]. Ziegler has made a study of hundreds of datasets including light and heavy ions in many different materials [18] and obtained the following parametrisation,

$$q_{\text{eff}} = Z \left( 1 - \exp \left[ -\frac{0.95V_i}{v_F} - 0.07 \right] \right) + \left( \exp \left[ -\frac{0.95V_i}{v_F} - 0.07 \right] \right) \frac{(v_F/V_i)^2}{2} \ln \left[ 1 + \left( \frac{2.4V_i}{a_0v_F} \right)^2 \right]$$  \hspace{2cm} (26)

with $V_i$ the fermi velocity of the target. This expression includes a treatment of the screening of an ion by unstripped electrons, with the parameter $A_i$, being a screening length to describe the electrons associated with the ion and $a_0$ the Bohr radius [18]. The screening length $A_i$ details how the electronic distribution changes size as the amount of ionisation changes (as a function of energy) [18].

In the particular case of helium, Ziegler has suggested the following parametrisation equation for the effective charge of

$$q_{\text{eff}} = Z \left( 1 - \exp \left[ -\sum_{i=0}^{5} a_i \ln |E_{\text{He}}| \right] \right)^{1/2}$$  \hspace{2cm} (27)

where $Z = 2$, with $a_i$ being a set of empirically fitted parameters and $E_{\text{He}}$ the energy of the incident helium ion [18]. The fitted parameters are: $a_0 = 0.2865$, $a_1 = 0.1266$, $a_2 = -0.001429$, $a_3 = 0.02402$, $a_4 = -0.01135$, $a_5 = 0.001475$. The two equations suggested by Ziegler, Eqs. (25) and (26) will be used in this study to describe effective charge.

In this study, stopping power is used merely as a way to challenge the suitability of the formalism developed with the ultimate goal being to employ the formalism to produce cross-sections for use in track structure simulations. The choice of effective charge over mean equilibrium charge formalisms is not of primary concern; future iterations of this code may explore this dependence further.

3. Results and discussion

Construction of dipole oscillator strength distributions relies on the availability of experimental refractivity and absorption data in the very low energy range (0–100 eV), and frequently there is the need for interpolation between the available data and photon cross-sections at higher energies. The differential DOSD of a material, $f(\gamma)$, at energy $\gamma$ is related to the energy loss function $\text{Im}[-1/\varepsilon(0, \gamma)]$ by the equation:

$$f(\gamma)/\gamma = \frac{2m}{\hbar^2 \varepsilon^2 N} \text{Im}[-1/\varepsilon(0, \gamma)]$$  \hspace{2cm} (28)

with $m$ the electron mass, $e$ its charge, Planck’s constant $\hbar$ and $N$ the number density of molecules of the medium. The energy loss function is related to $n$ and $k$, the frequency dependent refractive index and extinction coefficient of the medium, respectively, through the complex dielectric response function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, and the energy loss function

$$\text{Im}[-1/\varepsilon(0, \gamma)] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}$$  \hspace{2cm} (29)

by

$$\varepsilon_1 = n^2 + k^2$$  \hspace{2cm} (29a)

and

$$\varepsilon_2 = 2nk$$  \hspace{2cm} (29b)

where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary components of the dielectric response function, respectively. For energies above 100 eV, $n$ is close to one and $k$ is small, so $\varepsilon_1$ tends to $n^2$ and $\varepsilon_2$ to $2k$. Consequently, the energy loss function, $\text{Im}[-1/\varepsilon(0, \gamma)]$, is determined solely by $k$ and we are able to assume that the core electrons are localised and summing atomic absorption cross-sections is an acceptable substitute for optical data for compounds. In the following, atomic absorption cross-sections for energy above 100 eV are taken from Veigele [20]. When experimental measurements of the energy loss function do not reach up to 100 eV (which is usual), the available data is interpolated using a log $(f)/\gamma E$ plot between the two energy ranges.

Partial energy loss functions for ZrO$_2$ derived from experimental data by Frandon et al., Prieto et al., McComb, and Tahir et al. are shown in Fig. 2 [21–24]. The energy loss functions of Frandon et al. and of McComb extend to 50 and 60 eV, respectively, while that of Prieto et al. and Tahir et al. covers a wider energy range, extending up to 80 eV.

The four sets of data are very similar, although that of Tahir et al. appears to be shifted by a couple of eV to higher energy than the other data. There are key transitions at 14, 26 and 41 eV (discussed in detail in reference [23]); however, the absolute strengths of the peaks differ. The lowest energy maximum at around 14 eV, which has been described as a ‘bulk plasmon’ contribution, is the dominant peak in the ELF of Prieto et al. and Tahir et al., but is much smaller in the data sets of McComb and of Frandon et al. The 26 eV maximum corresponding to the $O 2p \rightarrow Zr 4d$ transition is larger. The maximum at 41 eV, identified as the $Zr 4p$ resonance peak, is larger in the data set of McComb than those of Prieto et al., Tahir et al. and Frandon et al. [23].

The energy loss function of Prieto et al. [23] is used in this study primarily as it requires less interpolation to the point at which photon absorption cross-section data is available and the locations of the dominant features match the energies of the same features in Frandon et al. and McComb. The DOSD of ZrO$_2$ has been formulated up to 1 MeV. The complete differential DOSD obtained is shown in Fig. 3. Peaks corresponding to the three transitions
identified in the energy loss function remain, but the relative strengths differ as the $\gamma^{-1}$ weighting in Eq. (27) reduces the importance of the peaks at lower energy.

According to the Fano sum rules [25], the ‘effective number of electrons which may receive energy from an energy transfer from an incident electron’ [2] is calculated by integrating the DOSD:

$$Z_{\text{eff}} = \int_{E_0}^{E_{\text{max}}} f(E) dE.$$  \hspace{1cm} (30)

In the case of ZrO$_2$, there are 56 electrons, and the raw DOSD developed here and shown as a broken line in Fig. 3 gives a value of $Z_{\text{eff}} = 50.41$ electrons at 1 MeV, which is not correct. Rather than simply renormalizing the raw DOSD to reproduce the sum rule, the component of the DOSD derived from the energy loss function of Prieto et al. was rescaled (increased) and the interpolation to the well-known atomic absorption cross-sections repeated. The dependence of $Z_{\text{eff}}$ on the magnitude of an energy transfer is shown in Fig. 4 for both the raw and modified DOSD. Obviously, the modified DOSD data gives the correct asymptotic value of 56 electrons. Modification of the DOSD increases the “heights of the steps”, i.e. the number of electrons that can be influenced by a given energy transfer. The step changes can be considered as relating to the energy levels of the electrons in the ZrO$_2$ crystal. At least for the core electrons, these step changes correspond well to the binding energies for the atomic Zr and O components. The binding energies for the various atomic orbitals are highlighted in the figure [26]. Energy transfers below about 40 eV affect only the outer 16 ‘bonding’ electrons of the oxide. For energy transfer up to 100 eV, a further 6 electrons corresponding to the 2 s electrons from oxygen (2 sets of 2 for the 2 oxygen atoms in ZrO$_2$) and 4 s electrons from zirconium are influenced. Further sharp discontinuities are apparent at 200 and 2000 eV and reflect the remaining inner-shell electrons, culminating in the final Zr 1 s core electrons experiencing effects for energy transfers above 20 keV.

To confirm the acceptability of the modification of the DOSD, the mean excitation energy, $I_{\text{eff}}$, given by the second moment sum rule,

$$Z_{\text{eff}} \ln(I_{\text{eff}}) = \int_{E_0}^{E_{\text{max}}} f(E) \ln(E) dE$$  \hspace{1cm} (31)

was also calculated for ZrO$_2$ using the raw and the modified DOSD. Table 1 compares the asymptotic values of $Z_{\text{eff}}$ and $I_{\text{eff}}$ obtained using the raw and modified DOSD with the value obtained by applying Bragg additivity and values available elsewhere in the literature. The raw DOSD leads to a predicted value for $I_{\text{eff}}$ which is significantly larger, almost twice, the value found by using Bragg’s rule, 295 eV [27]. The modified DOSD yields a mean excitation value of 327 eV, which is much closer to the value obtained using Bragg additivity and is in good agreement with the value of 313 eV in reference [28] calculated using the energy loss function of Frandon et al.

The use of data from Prieto et al. rather than the data of Frandon et al., McComb or Tahir et al. does not significantly alter the energy loss function or the derived DOSD. The formalism developed here to calculate cross-sections and energy loss properties avoids the construction of a generalised oscillator strength distribution. It is not necessary to explicitly consider outer electron orbitals, as is necessary in other methods [28]. The flexibility lent to the model by avoiding this step means this approach to calculating electronic collision cross-sections is much swifter and more straightforward than others in the literature and can be applied to even the most complex materials.

The most important test of any model is comparison with the available experimental data. There is relatively little data on the energy loss properties of ions in ZrO$_2$. The largest volume of experimental and theoretical data is for the stopping power of ZrO$_2$ for various ions [29–31]. Figs. 5–7 shows stopping powers calculated with the formulation described here using the DOSD derived above. The figures make a comparison with the available data (either experimental or from other modelling studies). Generally, good agreement is found. In all cases, the Bragg peak (the

![Fig. 3. Differential dipole oscillator strength distribution for ZrO$_2$. The raw DOSD developed from the energy loss function of Prieto et al. [23] interpolated to the absorption cross-sections of Veigele [20] is given in the broken line, and the revised DOSD modified to reproduce the Fano sum rule for the number of electrons is given in the solid line. The inset compares the raw and modified sections of the DOSD for the optical data.](image)

![Fig. 4. Number of electrons per ZrO$_2$ unit influenced by a given energy transfer and the atomic electron binding energies for oxygen and zirconium. The $Z_{\text{eff}}$ calculated using the raw DOSD derived from the ELF of Prieto et al. [23] is shown by the broken line and that calculated using the modified DOSD is shown by the solid line. The atomic electron binding energies for oxygen and zirconium are from reference [26].](image)

<table>
<thead>
<tr>
<th>Source</th>
<th>Mean excitation energy (eV)</th>
<th>No. electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work modified DOSD</td>
<td>327</td>
<td>56</td>
</tr>
<tr>
<td>Present work raw DOSD</td>
<td>578.4</td>
<td>50.41</td>
</tr>
<tr>
<td>Bragg additivity</td>
<td>295</td>
<td>56</td>
</tr>
<tr>
<td>Behar et al. [29]</td>
<td>377</td>
<td>56</td>
</tr>
<tr>
<td>Abril et al. [28]</td>
<td>312.8</td>
<td>56</td>
</tr>
</tbody>
</table>
maximum of the stopping power vs ion energy curve) occurs at around the same energy as found elsewhere, about 0.1 MeV/u for lighter ions and rising to 0.3 MeV/u for heavier ions.

Fig. 5 compares experimental data for the stopping power of ZrO$_2$ for protons and helium ions with predictions from the formalism presented here and other calculations in the literature. For protons at energies higher than the Bragg peak (>0.2 MeV/u), there is a good agreement between all of the calculations and the experimental data; however, where there is no experimental data available, below the Bragg peak, the three calculations differ with the method presented here, predicting a smaller stopping power than the other studies. The discrepancy between the formalism presented here and the SRIM experimental data is within 6% at high energies and falls to 12% at lower energies, close to the Bragg peak.

The experimental data for helium ions are in good agreement for specific energies above 0.2 MeV/u; however, there is a significant discrepancy between the available experimental data in the region of the Bragg peak below specific energies of 0.2 MeV/u. As was found for protons, the calculations are in good agreement at high energy, for ion energies greater than 1 MeV/u where the helium ion will be fully stripped. At lower energies, where the helium ion will not be fully stripped, the predictions of the calculations differ. This difference is most evident in the two calculations of this study: the two different empirical approximations for the effective charge give significantly different predictions for the stopping power. Eq. (26), the helium specific effective charge proposed by Zeigler, gives much better agreement with the experimental data than the Eq. (25). This discrepancy reflects the fact that the former is significantly more tailored than the latter, resulting from fitting 287 data sets for specifically helium ions in solid materials, rather than formulating the equation over all ions. The phase of the material is important due to a density effect, which drastically alters the charge exchange cross-sections in a material [12]. The experimental stopping powers measured by Zhang et al. [32] are in excellent agreement with the predictions of SRIM; however, the measurements at all energies by Behar et al. [29] agree more closely with the predictions of the formalism presented here.

While one failing in the energy loss formalism developed here has already been highlighted, specifically the use of an effective empirical charge rather than target dependent cross-sections, there is a significant secondary failing at low energies below about 0.1 MeV/u. This failing is the breakdown in the approximation used in developing the formalism, specifically the quadratic extension of the DOSD into the energy momentum phase space. It is well known (e.g. from studies of liquid water [3]) that this approximation is not adequate at low incident ion energies where relatively large momentum transfers are possible, as the quadratic expansion does not accurately reproduce the general oscillator strength distribution.

The prediction of the formalism developed here for the dependence of the stopping power of ZrO$_2$ for oxygen ions on their energy is shown in Fig. 6. At high energies, the predictions of our formalism are again in good agreement with those of a SRIM calculation. The only available experimental data are for ion energies close the Bragg peak. While the SRIM calculation agrees with the experimental data, our calculation underestimates the experimental data by 20.7% at 0.4 MeV/u. In addition, the energy dependence predicted by our calculation has a considerably wider Bragg peak than shown by the experimental data and the predictions of SRIM.
The origins of this broadening lie in the empirical expression used for the effective ion charge, Eq. (25). The figure also shows the predicted ion energy dependence of the stopping power of ZrO$_2$ for O ions in each of the eight possible charge states. As expected the Bragg peak for each of the ion states occurs at the same ion energy, 0.14 MeV/u. This energy is significantly lower than the energy at which the experimental Bragg peak occurs (0.3–0.4 MeV/u) as well as the energy range of the broad Bragg peak calculated using an effective ion charge given by Eq. (25) (0.3–1 MeV/u).

Fig. 7 shows the ion energy dependence of the stopping power of ZrO$_2$ for magnesium and aluminium ions. The figure reveals similar trends to those highlighted in Fig. 6 for oxygen ions; however, the discrepancy between the predictions of our calculations and the experimental data (and the predictions of the SRIM code) decrease with ion mass, i.e. in the order O > Mg > Al. It is quite clear that one of the principal sources of this discrepancy is the treatment of the charge of the ion in the material, which is clearly inadequate.

First order perturbation theories often consider stopping power to be proportional to $Z^2$. However for heavy ions at intermediate energies higher order corrections to classical first order perturbation theory must be considered [14]. Higher order corrections to the stopping power, i.e. in $Z^2$ and $Z^n$ known as the Barkas-Anderson and Bloch corrections respectively, are not taken into account in the current formulation. These corrections will have large effects on heavy ions at low velocities. So, whilst the predictions for protons and helium ions are not significantly affected, the calculations presented for magnesium and aluminium ions will underestimate the experimental data. The next iterations of the formalism must address this challenge.

The inelastic mean free path and csda range of protons and helium ions in ZrO$_2$ at a variety of energies in the range 0.1–3.2 MeV are listed in Table 2. The mean free path, which reflects the average distance between electronic energy transfers for an ion with the specified energy, is inversely dependent on the inelastic collision cross-section through Eq. (3). For energies covering the region of the Bragg peak, i.e. ~0.1 MeV/u for protons and ~0.3 MeV/u for helium ions, the mean free path is comparable to or smaller than the distance between the ionic constituents of the ZrO$_2$ crystal lattice, ~2 x 10$^{-8}$ cm from [33], implying that every crystallographic ion in the radiation particles path will be ionised (or undergo electronic excitation).

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Mean free path (cm)</th>
<th>csda range (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>He$^{+2}$</td>
<td>H$^+$</td>
</tr>
<tr>
<td>1.00E+00</td>
<td>2.50E-02</td>
<td>2.81E-08</td>
</tr>
<tr>
<td>1.59E+01</td>
<td>3.96E-02</td>
<td>3.19E-08</td>
</tr>
<tr>
<td>2.51E+01</td>
<td>6.28E-02</td>
<td>4.05E-08</td>
</tr>
<tr>
<td>5.01E+01</td>
<td>1.25E-01</td>
<td>6.33E-08</td>
</tr>
<tr>
<td>7.94E+01</td>
<td>1.99E-01</td>
<td>8.74E-08</td>
</tr>
<tr>
<td>1.00E+02</td>
<td>2.50E-01</td>
<td>1.03E-07</td>
</tr>
<tr>
<td>1.59E+02</td>
<td>3.96E-01</td>
<td>1.46E-07</td>
</tr>
<tr>
<td>2.51E+02</td>
<td>6.28E-01</td>
<td>2.10E-07</td>
</tr>
<tr>
<td>5.01E+02</td>
<td>1.25E+00</td>
<td>3.66E-07</td>
</tr>
<tr>
<td>7.94E+02</td>
<td>1.99E+00</td>
<td>5.34E-07</td>
</tr>
<tr>
<td>1.00E+03</td>
<td>2.50E+00</td>
<td>6.46E-07</td>
</tr>
<tr>
<td>1.59E+03</td>
<td>3.96E+00</td>
<td>9.46E-07</td>
</tr>
<tr>
<td>2.51E+03</td>
<td>6.28E+00</td>
<td>1.39E-06</td>
</tr>
<tr>
<td>5.01E+03</td>
<td>1.25E+01</td>
<td>2.43E-06</td>
</tr>
<tr>
<td>7.94E+03</td>
<td>1.99E+01</td>
<td>3.49E-06</td>
</tr>
<tr>
<td>1.00E+04</td>
<td>2.50E+01</td>
<td>4.15E-06</td>
</tr>
<tr>
<td>1.59E+04</td>
<td>3.96E+01</td>
<td>5.77E-06</td>
</tr>
<tr>
<td>2.51E+04</td>
<td>6.28E+01</td>
<td>7.73E-06</td>
</tr>
<tr>
<td>3.16E+04</td>
<td>7.91E+01</td>
<td>8.81E-06</td>
</tr>
</tbody>
</table>

Fig. 8. Comparison of the mean free path of a helium ion calculated for an effective charge given by Eq. (26) with that for 4He$^+$ and 4He$^{+2}$. The solid lines show the predicted values using the effective charge approximation, the dashed line the predictions for 4He$^+$ and the dotted line the predictions for 4He$^{+2}$.

Fig. 8 examines the effect of ion charge on mean free path, comparing the mean free path of a helium ion calculated for an effective charge given by Eq. (26) with that for single, and doubly charged ions, 4He$^+$ and 4He$^{+2}$ respectively. The higher mean free path values are found for 4He$^+$ meaning that, for a given energy, a singly charged incident ion is less likely to ionise or excite the material than a doubly charged ion. Ions considered to be fully stripped in ZrO$_2$ would result in a more dense interaction track.

The csda ranges listed in Table 2 are obtained by integrating the calculated stopping power according to Eq. (13) to a minimum cut-off energy of 25 keV/u. In the calculations for helium ions reported in Table 2, the effective charge of the ion was incorporated using Eq. (26). As the trajectory of an ion is close to linear until nuclear collisions become an important attenuation pathway, the ranges correspond to the penetration of the proton or helium ion at the specified energy into ZrO$_2$.

The differential Y functions in ZrO$_2$ for 0.5 MeV/u protons and a variety of heavier ions of energy of 0.5 MeV/u are shown in Fig. 9. The distributions are clearly the same and independent of ion charge. The most probable energy loss is approximately 15 eV. Calculations for other energies (not included here) reveal that this value is more-or-less independent of the ion's energy.
Table 3

<table>
<thead>
<tr>
<th>Energy (MeV/u)</th>
<th>Mean energy loss per inelastic collision (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>61.4</td>
</tr>
<tr>
<td>1</td>
<td>71.7</td>
</tr>
<tr>
<td>5</td>
<td>94.1</td>
</tr>
<tr>
<td>10</td>
<td>101.9</td>
</tr>
<tr>
<td>100</td>
<td>117.1</td>
</tr>
</tbody>
</table>

The differential Y function shows maxima at the same energies as the ELF and the DOSD of ZrO$_2$. The relatively higher density of the differential Y function for low energy transfers compared to the DOSD reflecting the range of non-zero momentum transfers possible.

The mean energy loss per inelastic collision for protons at a range of incident ion energies is shown in Table 3. As the differential Y function for a given ion velocity is dependent of the incident ion, the mean energy loss of an ion only depends on the velocity of the ion and not the ion type. (This behaviour is specified by the equation defining the ratio of the cumulative cross-section to the total cross-section, which depends only upon $E/M$, i.e. upon $V_*$. As the maximum possible energy transfer, given by $4E/M$ in the reduced units used here, the mean energy transfer increases gradually with ion velocity.

4. Conclusions

An approach for calculating the inelastic cross-sections of ions in materials based on the differential dipole oscillator strength of the material is presented. As the DOSD is dependent on phase and on crystallographic structure, this formalism naturally incorporates effects on the energy loss processes due to phase and crystallographic structure. The DOSD for monoclinic ZrO$_2$ has been constructed and its validity demonstrated by calculating the zero and first Fano sum rules to give the effective number of medium electrons which may receive energy from an energy transfer, $Z_{eff}$, and the mean excitation energy, $I_{eff}$. The DOSD has been used to predict energy loss properties in order to evaluate this formalism. Specifically the stopping power, mean free path and cSDA range protons and helium ions in ZrO$_2$ as well as the stopping powers of a variety of heavier ions are considered. Comparison of the predictions with available experimental stopping powers and other calculations in the literature shows good agreement especially at ion energies greater than the Bragg peak. Failings of the approach developed are highlighted: the inadequate treatment of the effective charge of the ion; the breakdown of the formalism for evaluation of the probability of the ion undergoing an energy loss per unit distance, $\tau(E, y)$, from the DOSD at low energies (<0.1 MeV/u) and the lack of incorporation of higher order effects. Challenges in these areas will be considered before the use of these inelastic cross-sections in track structure simulations however this paper describes a novel formulation of these cross-sections for heavy ions.

Acknowledgements

The research described was supported by the EPSRC and the Dalton Cumbrian Facility project, a joint initiative of the Nuclear Decommissioning Authority and The University of Manchester. J. Schofield is supported by a studentship from the EPSRC Nuclear FiRST Doctoral Training Centre.

References

2.4. Comparison of the Electronic Collision Cross Sections and Energy Loss Properties of Ions in Silicon Carbide and Various Solid Oxides

Authors: J. Schofield, S. M. Pimblott

Status: Intending to submit to Radiation Physics and Chemistry

Author contributions: First Author on the paper. Constructed several of the DOSDs. Calculated all the energy loss properties presented and performed all the analysis. Wrote first draft of manuscript.

Relevance: This paper details the construction of several DOSDs which add to the available dataset for use in track structure and energy loss predictions. It includes the comparison of the materials considered showing the importance of electronic structure of irradiated material. This confirms results discussed in the first paper (Section 2.3) regarding the limitations of the formalism. Material properties effect on the predicted energy loss properties are explored.
Comparison of the Electronic Collision Cross Sections and Energy Loss Properties of Ions in Silicon Carbide and Various Solid Oxides

Jennifer Schofield#, Simon M. Pimblott##

##Wolfson Laboratory, Chemistry Building, University of Manchester, M13 9PL, UK
##Dalton Cumbrian Facility, Cumbria, CA24 3HA, UK

Abstract

A facile formalism for calculation the electronic collision cross sections in solid materials has been developed that relies solely on the dipole oscillator strength distribution (DOSD) of the materials. The DOSD of silicon carbide and various solid oxides are determined from experimental optical data. Inelastic cross sections for protons, helium and oxygen ions in these materials are determined and compared. Various energy loss properties including the mean free path, stopping power and Y function of ions are evaluated. Predictions of the electronic stopping power is compared to experimental data to test the accuracy of the formalism, good agreement found, particularly at higher energies where Barkas-Anderson corrections as well as charge effects are not as important.

Keywords: Silicon carbide, Oxide, DOSD, Energy loss properties

1. Introduction

The principle goal of this study is to develop and apply a simple formalism for calculating the electronic collision cross section for ions in solid ceramic materials (and water) to be used in Monte Carlo track structure simulation codes. The proposed formalism relies solely on experimentally available optical data and a simple approximation, first proposed by Ashley, which relates the dipole oscillator strength distribution (DOSD) of a material to the imaginary part of the complex dielectric response function for the material.

Understanding the effects of ionising radiation, including its energy loss properties for key materials, is essential for the nuclear industry. It helps facilitate in-reactor performance and to gauge the safe running lifetime of nuclear fuel and plants. In addition to metallic materials, ceramics also play an important role in nuclear systems. Materials such as aluminium oxide are used as thermal absorbers and neutron absorbers [1]; magnesium oxide, silicon carbide and zirconia are important surface coatings as nuclear fuel cladding; and silicon dioxide is a principal component of the glass and cement used to encapsulate high and low level and intermediate level wastes respectively [2].

Typical ionising radiation fields found in nuclear fuel and nuclear waste environments include helium and heavy ion radiation as well as gamma radiation. Protons are produced
as recoil ions in coolant water, they are also the species most often used in accelerated ion experiments.

The energy loss properties of materials have been of interest to science for many years [3]. In general the formalisms developed for their calculation are better suited to metals than ceramic materials like oxides [4]. This deficiency is due to increased complexity of intermolecular bonds and interactions in ionic and molecular solids (i.e. the presence of a band gap in semiconductor materials).

The formalism for (heavy) ions used here is able to approach these materials regardless of their crystal structure or phase, as it uses the dipole oscillator strength distribution (DOSD) formed from optical data to approximate the energy loss function of a material and it is then possible to calculate the inelastic cross sections as well as energy loss properties of ions, electrons and positrons in materials straightforwardly [5, 6]. The DOSD of a material, which describes how the oscillator strength behaves in the optical domain [7] is fundamental to the method, incorporating all effects due to the material, including phase.

In this paper the methodology for the calculation of inelastic cross sections for heavy ions is briefly presented. A full explanation can be found in reference [8]. Construction of the DOSDs for the materials of interest in this paper is described: SiC and the oxides MgO, Al₂O₃ and SiO₂. Two other materials, ZrO₂ and H₂O, are also considered. The construction of their DOSDs are detailed in reference [8] and reference [9] respectively. The mean free paths of protons, helium ions and oxygen ions in the materials are presented (as representations of the inelastic cross sections) as well as the differential electron collision cross section in energy loss of 0.5 MeV/u ions. The electronic stopping power is calculated using a mean charge model suggested by Schiwietz and Grande [10] for oxygen ions and Ziegler [11] for helium ions, and is compared to experimental data where available.

2. Methodology

2.1. DOSD Formulation

The construction of accurate dipole oscillator strength distributions (DOSDs) relies upon the availability of experimental optical data. The approach used to build the DOSD from optical data has been described in detail previously. Complete distributions are currently available for a large number of molecular gases [12, 13], for the gaseous and liquid phases of water [9, 14], for DNA [15] and for various condensed phase hydrocarbons [16] as well as zirconium dioxide [8].

The DOSD of a material, \( f(\gamma) \), at photon energy \( \gamma \) is related to the energy loss function \( \text{Im} \left[ -1/\varepsilon(0, \gamma) \right] \) by the equation:
\[ f(\gamma) / \gamma = \frac{2m}{\hbar^2 e^2 N} \text{Im} \left[ -1/\varepsilon(0, \gamma) \right] \]  

with \( m \) the electron mass, \( e \) its charge, \( \hbar \) is Planck’s constant and \( N \) the number density of molecules of the medium. The energy loss function is related to \( n \) and \( k \), the frequency dependent refractive index and extinction coefficient of the medium, respectively, through the complex dielectric response function, \( \varepsilon = \varepsilon_1 + i \varepsilon_2 \), and to the energy loss function

\[ \text{Im} \left[ -1/\varepsilon(0, \gamma) \right] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} \]  

by

\[ \varepsilon_1 = n^2 + k^2 \]  

and

\[ \varepsilon_2 = 2nk \]  

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary components of the dielectric response function, respectively.

Construction of a dipole oscillator strength distribution relies on the availability of experimental refractivity and absorption data in the very low energy range (0 to 100 eV). The principle challenge in constructing a dipole oscillator strength distribution is usually the lack of optical experimental data in the energy range 50-100 eV, above 100 eV the DOSD represents core electrons so Bragg’s additivity can again be asserted and photoabsorption cross sections utilised [17].

For energies above 100 eV, \( n \) is close to one and \( k \) is small, so \( \varepsilon_1 \) tends to \( n^2 \) and \( \varepsilon_2 \) to \( 2k \). Consequently, the energy loss function is determined solely by \( k \) and it can be assumed that the core electrons are localised. Therefore summing atomic absorption cross sections is an acceptable substitute for optical data for complex molecular and ionic materials. In the following study, atomic absorption cross sections for energy above 100 eV are taken from Veigele [17]. When experimental measurements of the energy loss function do not reach up to 100 eV, the available data is interpolated using a \( \log(f) \) vs \( E \) plot between the two energy ranges.

### 2.2. Formalism to Calculate Inelastic Cross Sections

The formalism used in this study to investigate ions in materials has been discussed previously in reference [8], which builds on previous work for electrons and positrons [6]. The formalism relies on an approximation first made by Ashley for the extension of the optical energy loss function into the energy-momentum transfer plane [18]. Only non-relativistic heavy ions are considered here. All equations are presented using reduced units \( \hbar = m_e = e = 1 \) where \( \hbar \) is the reduced Planck’s constant \( (\hbar / 2\pi) \), \( m_e \) the mass of the electron and \( e \) the electronic charge respectively.
For an incident ion of charge $Z$ and energy $E$ (with a velocity of $v$), the inelastic cross section, mean free path and stopping power of heavy ions in materials can be respectively described as:

$$\sigma(E) = \frac{Z^2}{2\pi Ne^2} \int_0^{v^2/2} \frac{v'^2}{v} Im\left[\frac{1}{\varepsilon(0, y')}\right] \ln\left[\frac{(1+s-a)(1-a)}{(1-s-a)(1+a)}\right] dy'$$ \hspace{1cm} (4)

$$\lambda(E) = (N\sigma(E))^{-1}$$ \hspace{1cm} (5)

$$S(E) = \frac{Z^2}{2\pi Ne^2} \int_0^{v^2/2} v'^2 y' Im\left[\frac{1}{\varepsilon(0, y')}\right] \ln\left[\frac{(1+s-a)}{(1-s-a)}\right] dy'$$ \hspace{1cm} (6)

with $a = y'/v^2$ and $s = \sqrt{1-2y'/v^2}$ [8]. In these equations $\gamma$ refers to the energy transfer from the projectile to the medium and $\gamma'$ is identified as a 'binding energy' associated with the molecules in the medium. The number density of molecules in the medium is denoted $N$ and the energy loss function, $Im\left[\frac{1}{\varepsilon(0, y')}\right]$ can be drawn from the optical properties of the material in question.

The so-called $Y$ function is the ratio of the cumulative inelastic cross section $\sigma(E, E')$ to the total inelastic cross section $\sigma(E) = \sigma(E, E_{\text{max}})$. It is equivalent to the probability of an energy loss smaller than an a quantity $E'$ by an ion with energy $E$ in a material [19]. The probability of an energy loss from $E'$ to $E' + \delta E'$ is given by the differential $Y$ function, $dY/dE'$. This quantity usually known as the differential energy loss distribution can be thought as the differential electronic collision cross section for an ion at the energy in question. Since the $Y$ function and differential $Y$ function are independent of the charge and of the mass of the ion, depending only on its velocity, all ions at the same specific energy will have the same differential energy loss distribution. Heavy ion energy differential $Y$ functions show peaks at the same energy of both the DOSD and energy loss function, however with differing relative magnitudes due to the underlying relationship between the three quantities.

From Equations (4), (5) and (6) it is apparent that the charge of the ion in the target material influences the energy loss properties of the ion in the material. This dependence on ion charge has significant implications for understanding radiation effects since as the ion passes through the material and slows down it will capture and lose electrons from the target material, changing its charge. The gain and loss of electrons will cycle the ion’s charge and affect the electronic collision cross section as well as the associated energy loss properties such as the stopping power. Ideally, ion and material dependent charge cycling cross sections should be measured and used in the interpretation of radiation track structure and energy loss; however, the effects of charge cycling of ions are frequently approximated using an empirical approximation for the mean or the effective charge which is obtained by fitting experimental data.
There are many discussions in the literature about the best method of describing the charge state of an ion on passage through a material [20]. It is not the intention of this paper to evaluate the effect of different models on the formalism developed here. Instead the charge of protons will be considered to be one (as is convention). Helium ions will be described using an expression for the effective charge suggested by Ziegler after fitting over 200 stopping power datasets [11]. In this case, the effective charge is given by

\[ q_{\text{eff}} = Z \left( 1 - \exp \left[ - \sum_{i=0}^{5} a_i (\ln[E_{\text{He}}])^i \right] \right)^{1/2} \]  

(7)

where \( Z = 2 \) is the fully stripped helium charge, \( E_{\text{He}} \) denotes the energy of the incident helium ion and \( a_i \) are a set of empirically fitted parameters. The fitted parameters are: \( a_0 = 0.2865 \), \( a_1 = 0.1266 \), \( a_2 = -0.001429 \), \( a_3 = 0.02402 \), \( a_4 = -0.01135 \) and \( a_5 = 0.001475 \) [11].

In this study the oxygen ion charge will be described using an empirical expression for the mean equilibrium charge state of projectiles in materials, suggested by Schiwietz and Grande by fitting an extensive compilation of mean charge states for ions exiting solids [10]. The mean charge of an ion with velocity \( v \) is given

\[ q_{\text{mean}} = \frac{Z \left( 8.29x + x^4 \right)}{\left( \frac{0.06}{x} + 4 + 7.4x + x^4 \right)} \]  

(8)

with the scaling variable

\[ x = c_1 \left( \frac{\bar{v}}{1.54 c_2} \right)^{1+1.83/Z} \]  

(9)

where

\[ c_1 = 1 - 0.26 \exp \left( -\frac{x}{11} - \frac{(x-x_0)^2}{9} \right) \]  

(10)

\[ c_2 = 1 + 0.030 \bar{v} \ln(Z_T) \]  

(11)

and

\[ \bar{v} = Z^{-0.543} v/v_B \]  

(12)

with \( Z_T \) being the “nuclear” charge of the target material and \( v_B \) the Bohr velocity.

Any empirical model, specifying the mean or effective charge based on fitting to experimental data is only appropriate for the experimental systems originally considered (especially for the effective charge) and is only valid over the ion energy ranges covered. Furthermore, these empirical fits will incorporate discrepancies between theory and experiment that do not arise from charge exchange. Sigmund recently stated that the empirical methods used to account for the cycling of an ions charge lack rigorous theory and that a better method should be found to predict mean charge states [20].

### 3. Results and Discussion

Using optical data found in literature combined with photo absorption cross sections above 100 eV, dipole oscillator strength distributions (DOSDs) are formulated for single crystal
Magnesia, amorphous alumina, $\alpha$-crystalline silica and $\alpha$ phase-6H silicon carbide. Liquid water and zirconia DOSDs have been previously formed, their construction can be found in the following references [14, 21, 22]. Sum rules are used to verify the appropriateness of the formulated distribution. According to the Fano sum rules [23], the ‘effective number of electrons which may receive energy from an energy transfer from an incident electron’ [2] is calculated by integrating the DOSD:

$$Z_{\text{eff}} = \int_{E_0}^{E_{\text{max}}} f(E) dE.$$  \hspace{1cm} (30)

The mean excitation energy, $I_{\text{eff}}$ is given by the second moment sum rule,

$$Z_{\text{eff}} \ln(I_{\text{eff}}) = \int_{E_0}^{E_{\text{max}}} f(E) \ln(E) dE.$$  \hspace{1cm} (31)

These properties can be compared with known values to assess the modifications necessary to any formulated DOSD. Figure 1 presents all the DOSDs formed or used in this study, with the first sum rule as a function of energy inset in each graph. The Table 1 shows the first sum rule pre and post modification, the material densities used in this study and a comparison of the mean excitation energies calculated here compared to literature values.

Silicon carbide (SiC) is a temperature resistant material, suggested for use in both semiconductors and in the nuclear industry. Of the many existing polytypes [24], alpha phase 6H-silicon carbide is the most common and therefore is chosen for this study. There is also the most optical data available for this phase of SiC. Several experimental sources for silicon carbide optical data exist [25-28]. The optical data used to form the DOSD was from the data table by Choyke and Palik spanning from 0-30 eV [28]. The choice of this dataset over other possible datasets was made as it has one of the largest energy ranges, larger than Pégourié (0-12 eV) [26] and Logothetides (1.5-9 eV) [27]. In addition the sum rules obtained after DOSD construction from Choyke and Palik required less normalisation than from French and Tan giving 21.8 and 17.7 respectively prior to normalisation [25, 28]. The constructed DOSD shows relatively little structure when compared to the oxide distributions and interband transitions are not discussed widely in literature, although the paper of Ummels et al. makes remarks concerning the assignment of the peaks seen [29]. Ummels et al. also discuss the differences due to crystal structure on the optical properties.

Magnesium oxide (MgO) is of interest as a current nuclear fuel matrix [30, 31]. It is also of interest as both an electrical and heat insulator. The DOSD was formulated using a combination of data from Williams and Arakawa [32] and Hanson et al. [33]. Other experimental data found cover significantly smaller energy ranges [34, 35]. Optical data, derived from reflectance measurements, from 4 up to 80 eV with interpolation up to the photo absorption cross sections at 100 eV. The features in the ELF data are discussed clearly by Hanson et al. The main points are also reflected in the DOSD: The 2 plasmon resonance peaks, seen in the DOSD at 22.5 and 25.4 eV; interband transitions of the $L_1$
electrons from oxygen to the conduction band, which can be seen in the region 30-40 eV [33]. The structure at slightly higher energies is attributed to the L_{23} electrons from magnesium. The K-edges can be seen most clearly in the effective charge graph inset at the expected energies of 543 eV (for O) and 1.3 keV (for Mg) [36].

Figure 1. Dipole oscillator strength distribution formulated for water (top left), silicon carbide (top right), magnesium oxide (middle left), silicon dioxide (middle right), aluminium oxide (bottom left) and zirconium dioxide (bottom right). The inset graphs show the evolutions of effective charge as a function of photon energy.
Silica is of importance to many industries including the semiconductor and detector industries [37]. As such it has been extensively studied with optical data from many sources available. There are many sources providing optical measurements for both crystalline and alpha crystalline silica [28, 38-40]. The optical data chosen in this study is that described by Ashley and Anderson for crystalline silica [40], which spans from energy 0-40 eV. The energy loss function data correlates well with other sources for crystalline silica. The main peak at 23 eV due to bulk plasmon effect with lower structure attributed to interband transitions by Buechner [41]. As shown in Table 1 the constructed DOSD gives a close agreement of the second sum rule with experiment.

![Graph of the evolution of the electrons affected by an energy transfer to the medium in question.](image)

**Figure 2. Normalised graph of the evolution of the electrons affected by an energy transfer to the medium in question.**

Alumina, in a similar manner to SiO₂, is proposed for use in optical devices [42]. This oxide is also of interest in radiation fields for its use as a structural ceramic material. Optical data for amorphous alumina is taken from French et al. with an energy loss function described for the energy range 6-142 eV from electron energy loss spectroscopy (EELS) data [43]. French et al. also quotes vacuum ultraviolet (VUV) spectroscopic data, however the EELS data are chosen in this study due to a greater energy range. The same structures mentioned by French et al. for the energy loss spectrum can be seen in the constructed DOSD, a plasmon peak at around 26 eV, multiple scattering effects around 50 eV and the L-edge at 78 eV can be seen. The mean excitation energy found from this DOSD is close to literature values, lending credibility to the modifications made, as seen in Table 1.

The formulation of the DOSD for zirconia has been discussed in detail previously. Optical data for this ZrO₂ DOSD is taken from Prieto et al. [22] after comparison with other data showed it to be the most appropriate. This optical data ranges from 0 up to 80 eV. The
water DOSD has also been formulated and discussed in detail by LaVerne and Mozumder [14] using an energy loss function described originally by Ashley [21].

Table 1. Table showing the material properties of importance in this study. Mean excitation energies with a superscript b have been calculated from values of elemental excitation energies and added according to Bragg additivity.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Z</th>
<th>( Z_{\text{eff}} ) at 1 MeV pre-normalisation</th>
<th>( Z_{\text{eff}} ) at 1 MeV post-normalisation</th>
<th>Density (g/cm(^2))</th>
<th>Mean excitation Energy (eV)</th>
<th>Excitation energy from data (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>10</td>
<td>-</td>
<td>10</td>
<td>1</td>
<td>75(^b)</td>
<td>74.8</td>
</tr>
<tr>
<td>SiC</td>
<td>20</td>
<td>21.8</td>
<td>20</td>
<td>3.21</td>
<td>136.23(^b), 150 [44]</td>
<td>128.3</td>
</tr>
<tr>
<td>MgO</td>
<td>20</td>
<td>19.1</td>
<td>20</td>
<td>3.58</td>
<td>128.12(^b)</td>
<td>145.74</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>30</td>
<td>27.9</td>
<td>30</td>
<td>2.65</td>
<td>133.1(^b), 139.2 [45]</td>
<td>132.3</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>50</td>
<td>47.4</td>
<td>50</td>
<td>3.95</td>
<td>133.8(^b), 145.2 [45]</td>
<td>146.9</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>56</td>
<td>-</td>
<td>56</td>
<td>5.68</td>
<td>295(^b), 313 [46]</td>
<td>327</td>
</tr>
</tbody>
</table>

Figure 2 presents the first sum rule normalised to the total number of electrons for all the materials as a function of incident energy. As expected all materials tend towards the expected values at high incident energies. It is also clear that the structure of the DOSD in the optical domain has a large and lasting effect on the evolution of the number of electrons accessible at a given energy.

![Figure 3](image1.png)

**Figure 3.** Normalised mean free path of protons in different materials. The black solid line represents water; dark yellow shows Al\(_2\)O\(_3\) and cyan is MgO. The blue line is the prediction for SiO\(_2\); red is SiC; the dashed black line is ZrO\(_2\).

![Figure 4](image2.png)

**Figure 4.** Mean free path for oxygen ions in silicon carbide. The solid line denotes the mean charge state as described in Equation (8). The black dashed lines are levels of stripping of the ion with the bottom line corresponding to a fully stripped ion and the top a 1+ charge state.

Figures 3 and 4 show the mean free paths (mfp) of protons in various materials and of oxygen in SiC for various charge states respectively. The specific mfp in Figure 3 (each divided by material density, as given in Table 1) shows that the material chosen has an effect on the mean free path, with water giving the highest mfp values and zirconium the lowest. Although density normalised (divided by respective material densities), the order of the mean free paths appears to follow that of the density of the materials, with the
exception of magnesia and silicon carbide, which appear to be switched. The reason underlying this probably falls to the DOSD structure. The figure shows that protons through liquid water will be least likely to ionise the material for a given energy. Protons through zirconia, however, will have the densest track structure.

Figure 4 shows the mean free path of an oxygen ion through silicon carbide, both using the expression to describe the charge state as given in Equation (8), and the prediction of the mean free path assuming an unchanging charge state through the material progressing from a fully stripped to neutral charge. It is clearly shown (and intuitive) that fully stripped ions will have the lowest mean free path, and the densest tracks. This figure illustrates the importance of charge state descriptions for energy loss properties.

![Graph showing energy loss properties of different materials](image)

Figure 5. The differential $Y$ function of 0.5 MeV/u oxygen ions in the oxides and materials of interest in this study (see the key). The most probable energy loss can be seen for this incident ion energy and is clearly material dependent reflecting the different DOSD structures.

Figure 5 shows the differential $Y$ function of 0.5 MeV/u oxygen ions through the oxides and silicon carbide with Table 2 showing the mean energy loss for each inelastic collision of oxygen at different incident energies, and the most probable energy loss for 0.5 MeV/u oxygen ions. The most probable energy loss can also be seen as the maxima in Figure 5 and reflects the DOSD in the materials' features (although not in their absolute values). We expect this property to be material dependent, with energy loss depending on the optical data gathered. This is shown, with no discernible pattern for density or atomic number for the compound in question. The same is true of the mean energy loss per inelastic collision; for every material this value (as it must) increases although the absolute values differ.
Table 2. The first three columns correspond to the mean energy loss per inelastic collision (in eV) for oxygen ions at various different incident specific energies. The final column describes the most probable energy loss (in eV) for oxygen ions at 0.5 MeV/u.

<table>
<thead>
<tr>
<th></th>
<th>0.5 MeV/u</th>
<th>1 MeV/u</th>
<th>10 MeV/u</th>
<th>Most Probable</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>58.8</td>
<td>61.3</td>
<td>70.4</td>
<td>23.0</td>
</tr>
<tr>
<td>SiC</td>
<td>65.0</td>
<td>74.3</td>
<td>90.5</td>
<td>23.5</td>
</tr>
<tr>
<td>MgO</td>
<td>85.2</td>
<td>93.5</td>
<td>113.7</td>
<td>25.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>70.0</td>
<td>76.9</td>
<td>94.2</td>
<td>29.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>78.0</td>
<td>86.3</td>
<td>106.4</td>
<td>26.5</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>61.3</td>
<td>71.6</td>
<td>101.9</td>
<td>15.0</td>
</tr>
</tbody>
</table>

The stopping power of protons, helium ions and oxygen ions were calculated through the materials of interest from the inelastic cross sections according to Equation (6). These predictions were compared, where possible, to experimental data with Figures 6-8 showing the resultant comparisons. No other formalisms were included as this paper seeks to compare the predicted stopping powers using this formalism with available experimental data only. There is a lack of experimental data for any ions in magnesia - our predictions have remained in the figures in order to compare the different oxides. There appears to be some stopping power constructions from Mg and O stopping powers using Bragg additivity [47, 48], however these have not been included due to concerns about the validity of using Bragg additivity to predict stopping power at intermediate speeds [49].

It is known from a previous study using this formalism that, for ion energies below 0.1 MeV/u, the predicted stopping powers do not reflect empirical data [8]. This is partly due to the basis on optical data for the foundation of the formalism, however also due to a lack of improved charge state descriptions, and the absence of the Barkas-Anderson correction in this model. Stopping data here is therefore only compared up to this cut-off energy.

Inspection of Figure 6 shows the good agreement of the formalism for normalised proton stopping powers at high energies with experimental data. Agreement remains close for water to 0.2 MeV and then begins to deviate, although this breakdown occurs at the same point as a wider scatter seen in the experimental data for Bauer [50] and Wenzel [51], this difference is probably due to phase differences with Wenzel’s data showing ice rather than liquid water. For protons there is no SiC or MgO data in the regions for which our code is valid. Silica shows a similar trend to water with a closer agreement to experiment above 0.3 MeV/u falling to an error of 17.5% at 0.1 MeV/u. The error at 0.1 MeV/u for Al₂O₃ is larger than for silica or water at 26.2%. There are several experimental results and all use amorphous alumina, as used in the constructed DOSD [46, 52-57]; therefore it is reasonable to propose that this difference comes from the assumption of unitary charge for the proton. This difference could also be due to errors in the DOSD formation. ZrO₂ has a
relatively good agreement with experiment at high energies. Despite normalisation to the material density of the predicted energy loss properties, there are large differences between some oxides; this reflects the differences in the constructed DOSDs. Most striking is ZrO$_2$ with much lower stopping power results; Figure 1 shows the significant differences of this oxide with the other constructed DOSDs which has an effect on the calculated inelastic cross sections. This can also be seen in the supplementary graphs.

Figure 6. The stopping power of protons in various materials. The formalism presented here is shown using lines for Al$_2$O$_3$ (dark yellow), MgO (teal), SiO$_2$ (blue), SiC (red), ZrO$_2$ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Bauer [57] (●) and [52] (○), Turner [53] (●) and (∙), Reuter [56] (▲), for SiO$_2$ in blue from Bauer [57] (●), for water in black from Wenzel on ice [51] (○), Bauer [50] (●), Shimizu [54](●) and [55] (+), Siiskonen [58] (●) and for ZrO$_2$ in grey from Behar [59] (∙).
Helium ion stopping powers through the materials of interest is shown in Figure 7. Similar trends are seen as discussed for protons. It is interesting to note that there is a great deal of scatter around the silica data, with this formalism even appearing to fit some of the data. It is not the expectation of the authors that this implies the formalism is correct for silica, when it shows large errors for other materials and ions at the same specific energies. However, it does illustrate the importance of multiple experiments for any given dataset. The Bragg peak can be seen to occur at around the same point as experimental data for all materials.

Figure 7. The stopping power of alpha in various materials. The formalism presented here is shown using lines for Al₂O₃ (□), MgO (■), SiO₂ (○), SiC (○), ZrO₂ (○) and water (●). Experimental data is seen for alumina in dark yellow from L’Hoir [72] (○), Mai [60] (□), Santry [61] (●), Thomas [62] (□) and Pascual-Izarra [63] (□) and (●). SiC data is in red from Zhang [64] (●) and [65] (○). Silica data in blue is from Thompson [66] (○) Pascual-Izarra [67] (□) Santry [61] (●) Meyer [68] (□) and Lennard [69] (●). Water is shown black Akhaven-Rezayat (●) Matteson [70] (○) Palmer (●) Haque (○) and Thwaites (●). Finally Zirconia data is shown in grey from Behar [59] (○) and Zhang [71] (●).
For heavy ions, higher order corrections to the energy loss calculations must be taken into account. In particular the Barkas-Anderson correction will become more important at lower energies. This correction is proportional to a $Z^3$ correction to the stopping power and corrects for the difference in stopping between a particle and its antiparticle and acts to increase the predicted stopping power. This can typically introduce an error of several per cent [72]. Whilst there are ways to incorporate this correction into the stopping power this paper seeks to focus on the comparison of different DOSDs on the energy loss properties rather than the formalism construction. Further amendments will be presented in future papers for this correction into our model to predict inelastic cross sections. The proton and helium data, Figures 6 and 7, show the effect this has on stopping, with SiO$_2$ and Al$_2$O$_3$ predictions falling well below the experimental data.

It could be expected that the error for oxygen ions will be larger than for helium and protons, both due to more complex charge state distributions and larger higher order corrections. Inspection of Figure 8 shows this to be the case. At 0.1 MeV/u the error between the prediction of this code and empirical data is as much as 40 % for some of the Al$_2$O$_3$ data. Similarly to helium experiments there appears to be significant scatter in experimental measurements, this is especially noticeable for alumina where at the Bragg peak the error of our data could be considered as little as 5.8 % or as much as 15 % depending on the data chosen. The Bragg peak occurs at the same energy for this prediction and experiment with the exception of silicon carbide, however the experimental data from Janson [73] does not convincingly show a definite Bragg peak at a significantly lower energy. The formalism consistently under predicts experimental data. Error in stopping power predictions could be increased due to the use of different expressions of the charge state of ions. The helium ion formalism used in this work is a tailored effective charge whereas the charge utilised in the calculation of stopping powers for oxygen ions is a mean charge state model as described by Schiwietz and Grande [10]. This attempt to incorporate some target dependence, however, is not empirically fitted, and will only be accurate over the range for which data exists.
4. Conclusions

The DOSD for silicon carbide has been formulated from optical data and photo absorption cross sections. The DOSD for several oxides have also been formed. The resulting distributions have been discussed as well as the DOSDs for zirconium dioxide and water including a comparison of the sum rules from literature. A good agreement is found for all constructed materials’ DOSDs. Energy loss properties have been evaluated using a formalism developed previously. The dependence of mean free path on material type and
charge state of an incident ion has been investigated with a density dependence illustrated. The differential $Y$ function and stopping power of protons, helium ions and oxygen ions was discussed, with differing results obtained for materials. Limitations of the model hinder good agreement with experimental data; however, in some materials, this appears to have less of an effect than previously thought.

Acknowledgements

The research in this article was supported by a research studentship though the EPSRC Nuclear FiRST Doctoral Training Centre.

References


[78] M. Msimanga, C. M. Comrie, C. A. Pineda-Vargas, S. Murray, Experimental stopping powers of Al, Mg, F and O ions in ZrO₂ in the 0.1–0.6 MeV/u energy range, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 268 (2010) 1772-1775.

Supplementary Material

Figure 9. The stopping power of protons in various materials. The formalism presented here is shown using lines for Al₂O₃ (dark yellow), MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Bauer [57] (●) and [52] (○), Turner [53] (●) and (○), Reuter [56] (▲), for SiO₂ in blue from Bauer [57] (●), for water in black from Wenzel on ice [51] (○), Bauer [50] (●), Shimizu [54] (●) and [55] (+), Siiskonen [58] (●) and for ZrO₂ in grey from Behar [59] (●).
Figure 10. The stopping power of alpha in various materials. The formalism presented here is shown using lines for Al₂O₃ (dark yellow), MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from (●), Mai [60] (□), Santry [61] (●), Thomas [62] (○) and Pascual-Izarra [63] (+) and (▪). SiC data is in red from Zhang [64] (●) and [65] (□). Silica data in blue is from Thompson [66] (●) Pascual-Izarra [67] (○) Santry [61] (●) Meyer [68] (□) and Lennard [69] (+). Water is shown black Akhaven-Rezayat (●) Matteson [70] (□) Plamer (●) Haque (○) and Thwaites (+). Finally Zirconia data is shown in grey from Behar [59] (●) and Zhang [71] (□).

Figure 11. The stopping power of oxygen ions in various materials. The formalism presented here is shown using lines for Al₂O₃ (dark yellow), MgO (teal), SiO₂ (blue), SiC (red), ZrO₂ (dashed black) and water (black). Experimental data is seen for alumina in dark yellow from Mizohata [74] (●) and (□) and Pascual-Izarra [63] (●). Silicon carbide data is shown from Janson [73] (●) and from Zhang [75] (●). Silica data is shown from Zhang [76] (●) and zirconia data is shown from Zhang [77] (●) and Msimanga [78] (□). No experimental data was found for water.
Figure 12. Comparison of DOSD constructed or used in this study.
3. Charge Exchange Equilibrium Charge State Fractions in Materials

3.0. Objectives
To evaluate the charge state fractions of light ions in metals and to test the validity of effective charge models in predicting mean charge states.

3.1. Motivation and Aims
The previous section described efforts made to develop a simple formalism for calculating the inelastic cross sections of heavy ions in materials for use in the Monte Carlo simulation of track structures. This approach requires a description of the charge state of a projectile in a material to predict stopping powers from the calculated cross sections. In the absence of charge exchange cross section data, empirical models to describe an ion’s average or effective charge inside a material have been proposed and used. These charge models are inadequate in describing the physical processes changing the charge state of ions in materials. A more accurate approach is to describe the charge state of an ion directly as it passes through a material.

On passage through a material several mechanisms can take place on collision of a projectile with the electrons in a target atom, the result of which is charge cycling [1]. Charge cycling, or charge exchange as it also termed, is the action of an ion picking up and losing electrons on passage through a material. Two simple and separate mechanisms of electron capture and electron loss can be described. Electron capture is the capture by the projectile ion of an electron from the medium, via a radiative or non-radiative process decreasing the charge state of the ion:

$$X^q + e^- \rightarrow X^{q-1}$$  \hspace{1cm} (3.1)

for any $q \geq 0$, allowing for a -1 charge state. This treatment is a simplification and assumes a charge change of 1 is the only possible outcome. Electron loss is the transfer of an electron from the travelling ion to the medium:

$$X^q \rightarrow X^{q+1} + e^-$$  \hspace{1cm} (3.2)

changing the charge state of the ion. It can occur for any ion with $q \geq -1$, again assuming $|\Delta q| = 1$. A detailed exploration of the determination of charge state fractions can be found in Appendix 3.
Figure 3.1 illustrates capture and loss processes using carbon as an example. At intermediate energies, in the range 0.01-0.1 MeV/u, multiple charge states might be expected to occur. The energy at which C\(^{5+}\) undergoes charge exchange processes to +4 and +6 charge states is similar to the energies explored in this study. The probability of charge exchange will be dependent on the incident ion’s mass, atomic number, speed and the number of bound electrons as well as the target’s properties. Charge exchange is not limited to individual interactions, more complicated combinations of multiple simultaneous electron capture and loss events can occur [2]. A fuller description of these processes can be found elsewhere [1-5].

![Figure 3.1. Schematic of electron loss and non-radiative capture for a C\(^{5+}\) ion. The left hand side shows a C\(^{5+}\) ion, the middle diagram depicts electron loss to the material, and the right hand shows non-radiative electron capture.](image)

Charge exchange is observed by passing ions in a given charge state through a thin film (or gas) and measuring subsequent change of charge states. In practice determining direct charge capture and loss cross sections is difficult due to the number of possible outcomes and the number of cross sections which must be measured as well as the requirement that the thickness of film is such that only single interaction occurs: typically < 1 µg/cm\(^2\) (there are few studies at this thickness [6]). Typically another parameter is determined, the equilibrium charge exchange distribution. This is the set of probabilities that the ion is in a given charge state. The equilibrium charge state distribution will occur at larger thickness, where the charge state of ions is determined only by the material and the ion velocity. The capture and loss processes have thus become balanced. An example of charge equilibrium being reached can be seen in Figure 3.2 from Betz [3] for iodine ions in oxygen gas.
Figure 3.2. Equilibrium charge state fractions of 15 MeV iodine ions in oxygen taken from [3]. Solid lines show the trend of data points for each charge state.

The charge state of an ion directly affects the energy loss properties as it passes through a material [1]. In particular the charge state will affect the range and the position of the Bragg peak. Consequently charge exchange studies are important to health physics, notably hadron therapy [7]. Other interested fields include astrophysics, where charge exchange is utilised when regarding helium ions in gas targets to simulate stellar radiation fields [8, 9]. Accelerator Mass Spectrometry (AMS) also uses the charge exchange processes of ions passing through gases in order to function [10].

Radiation chemistry is also concerned with charge cycling through the effects which it has on stopping power. The interaction of (fast) charged particles with matter is seen by Hatano [11] to be one of the most important scientific topics in radiation chemistry. The considerations required for the charge of ions in materials can complicate attempts to form kinetic models or predict chemical yields [12].

Although most charge cycling data exists for ions in gases or carbon foils. Several reviews of charge exchange and charge state equilibration in other materials are available [13-15]. This work focusses on the fields of inelastic cross section prediction (which relates to stopping power and health physics) and radiation chemistry. In particular for this study the charge of an ion will affect the energy lost to the electrons in a material and hence the chemistry of the system. The aim of this project is to investigate the equilibrium charge states of some light ions in solid materials, with materials chosen because of their relevance to the nuclear industry. The feasibility of forming uranium dioxide thin films will be considered and the relationship between material type and the charge state fractions will be
investigated. Another aim of the study will be to examine the validity of effective and mean charge models for light ions.

The following sections detail the possible experimental methods to study charge exchange and outline the approach used in this work.

### 3.2. Previous Work and Possible Options

#### 3.2.1. Thin Films

Measuring charge state distributions requires the ion to pass through the material of interest. This means any study will require the use of thin films or gases. Thin film experiments are the focus of this study and so gas target experiments will not be considered.

A ‘thin’ film is characterised as one less than a couple of micrometres thick. Previous experiments have found that thin film equilibrium has been reached in carbon films with as little as 20 µg/cm² although literature suggests this could be as low as 3 µg/cm² [6]. For charge exchange experiments thin films should be as thin as possible (whilst still allowing charge exchange equilibrium to take place). Films should also be self-supporting and allow ions to pass through them with negligible energy loss. It is imperative for most charge exchange experiments that ions do not stop in the film, as most detectors will measure charge, with no result being ascribed to a neutral 0 charge state.

Thin films have many applications aside from energy loss experiments, notably in optical equipment and electronic circuits (for example in fabricating semiconductors) [16]. The most common method of forming thin films according to Geissel in his recent review [17] is evaporation, however many other possible methods exist [16, 18-20]. In general these can be separated into two methods, evaporation and chemical deposition. Evaporation occurs when a bulk material is heated (usually in vacuum with an electron beam) to form a vapour of the required material. This vapour deposits in a thin film onto a cooler surface above it. Chemical deposition for thin film formation is also possible; however the change of phase from gas to solid film requires some chemical reaction in order for this to occur.

When forming thin films of non-metallic crystalline structures ion channelling must be considered. Ion channelling occurs in single crystals and has been shown to affect both the stopping power and charge exchange properties of an incident ion [21]. This is because the projectile is limited to interacting with mainly conduction (or mainly valence) electrons [22]. This is not representative of ions passing through amorphous materials and therefore is not
desirable for the purposes of this study. Ion channelling can be avoided by not using single crystals.

The thickness of a foil can be determined after or during the formation process. The following are common methods to determine film thickness:

- **X-ray reflectivity.** This method is a non-destructive technique frequently used with amorphous films. The intensity of an x-ray beam is measured at glancing angles on a film [23]. The resulting data is fitted to simulated curves to determine the thickness.

- **SEM (scanning electron microscope).** A cross sectional view of the film can be seen under a scanning electron microscope and the thickness measured from this, assuming this thickness is indicative of the thickness throughout the film [24].

- **Energy loss of alpha particles.** This method detects alpha particles embedded in the substrate under a film [2]. Thickness is found by relating energy loss to the stopping power of alpha particles through the material. This method will not work with a self-supporting thin film unless the film is itself an alpha emitter. Closely related is recoil scattering of heavy ions [25] which uses the same underlying energy loss theory.

- **Quartz crystal monitoring.** This is one of the most frequently used methods to determine thickness deposition [2]. It makes use of the piezoelectric effect in quartz crystals. Passing a voltage across the crystal induces an oscillation. When the film substance is layered onto the quartz this changes the oscillation frequency and therefore thickness can be determined.

- **RHEED (reflection high-energy electron-diffraction analysis).** An electron beam is reflected at grazing angles from a material. Differences in intensity of an electron beam reflected from the film surface are measured [23] and the periodic changes are measured to determine thickness.

- **A more indirect way of measuring thickness uses gravimetric techniques (i.e. weighing the substrate before and after sputtering).** This is commonly used as an additional technique in combination with others [17, 23].

### 3.2.2. Uranium Dioxide Thin Films

This chapter describes work to investigate the feasibility of manufacturing self-supporting thin films of uranium dioxide. Thin films of uranium and uranium oxides have been manufactured previously [18-20] using various different methods, however no reports of self-supporting films have been found. In order to investigate this possibility collaboration was carried out with Dr R. Springell of the Interface Analysis Centre, University of Bristol using Reactive DC Magnetron Sputtering [26].
Reactive DC Magnetron Sputtering operates under ultra-high vacuum and at high temperature. Sputter targets are placed in the bottom of the machine with a plasma formed on their surface. The negatively charged target stage attracts the positive sputtering ions which are deposited on the surface of the target. In this study the target is made of depleted uranium. This can be used to form uranium dioxide by addition of small amounts of oxygen into the chamber during deposition. The machine is capable of forming uranium and uranium containing compounds e.g. oxides, carbides and nitrides on a range of different substrates.

Uranium dioxide is brittle, being an oxide rather than a metal, and therefore self-supporting thin films are difficult to manufacture. The films produced here were as thick as possible to try and make self-supporting films whilst limiting energy loss. Films were of around 1000-1500 Å, corresponding to around 164 µg/cm². For a 1500 Å film there will be an energy loss of 0.25 MeV for 7 MeV Li⁺ ions, as calculated by SRIM from a simulation of over 10,000 incident ions. This calculation was performed using the “monolayer collision steps” calculation in TRIM and assumes threshold displacement energies of 50 eV and 20 eV for U and O in the uranium dioxide respectively [27]. This corresponds to an average energy loss of 3.5 % of the initial energy. This is a fairly negligible energy loss and can be discounted during charge exchange experiments. The growth rate in the chamber is ≈2 Å/sec and films took around 15 minutes to grow. X-ray reflectivity diffraction were used to determine typical film thickness.

Figure 3.3. Mounting chamber for the magnetron sputter at the University of Bristol. Samples mounted upside down to allow uranium ions from below to sputter onto the surface.

The functioning of the magnetron sputter requires that a substrate is used on which to form the thin film. This should be a material into which we can manufacture a hole to allow free passage of our ions through the film, or one which can be removed post deposition. Typical substrates used for UO₂ thin films have been mentioned by G. Lander in conversation: LaAlO₃ [28], CaF₂ [29], and YSZ [30]. Collodion, which Schmitt uses with carbon, can be removed with heat, but this would not work with UO₂, the heat needed to form crystals of UO₂ is well in excess of the boiling temperature of Collodion (160 °C) [31]. The mentioned
substrates are not suitable in this case as they promote the formation of single crystals of UO₂ which are not ideal due to ion channelling effects. In addition they are chemically inert and therefore do not dissolve easily [32]. Silica is a possibility for use, with laser ablation to form a hole in the substrate. However this would require extreme precision in the laser ablating process to avoid going too far and ablating the film. The time required to perfect this method would exceed the time available for this study and was therefore set aside. In addition the heat on the film from the laser may induce oxidation for part of the film from UO₂ to U₃O₈.

The method chosen as having the best chance of success in this case uses a salt crystal as the film substrate. This can be dissolved easily in water and the thin film floated off the substrate entirely and transferred onto a substrate holder. The substrate holder, as seen in the Figure 3.4, is a stainless steel rectangle with a 0.8 cm diameter hole to allow beam to pass through.

![Figure 3.4. Schematics of the supports used for this study. Steel supports were \( \approx 2 \) mm in diameter which is sufficient to stop ions passing through.](image)

A 1 x 1 cm single crystal of KBr salt was used as the material on which 1500 Å UO₂ thin film was deposited. This was then placed on a stainless steel support in a bath of water. As the salt dissolves the UO₂ film rests on the stainless steel frame. The water can then be allowed to drain slowly out of the bath and the film is left on the frame, electrostatic interaction ensuring the film remains attached. Due to the brittle nature of UO₂ this method was not successful, with films breaking immediately as water is drained away. Further attempts were made by reducing the hole diameter to 0.5 mm and putting multiple holes in the same 0.8 cm diameter circle area. This resulted in a stable 20 % coverage of the 0.8 cm diameter hole. However, in order to use these films, every hole that is not covered with UO₂ film must be back-filled with something sufficiently thick to ensure that no beam will pass through.

Despite the positive indications from this experiment, the time required to improve the films in order to perform charge cycling experiments would exceed the time available for this
section of the work. As charge cycling experiments are the key aim for this work, the thin films required for this experiment were purchased.

3.2.3. Experimental Options
Geissel [17], following Betz [3], summarises the basic set-up of all charge state experiments, they comprise three distinct parts. The first stage produces a mono-energetic ion beam in a particular charge state (dispersive). The second stage is the passage of the single charge state through the target equipment. This creates multiple charge state ions on exit through the material. The final stage is analysis of the produced ion charge states (dispersive) [17]. The following section sets out the broad possibilities for ion charge state preparations and analysis. The scattering chamber and thin film apparatus will be described in Section 3.3.

All incident charge state preparation requires a method of acceleration. It is not the aim of this study to describe all the existing heavy-ion accelerator methods. Many studies use tandem accelerators to achieve the energies at which charge exchange becomes important [25, 33], however other types of accelerators have been utilised [34, 35]. The functioning of a tandem accelerator will be described in detail in Section 3.3.

In the case of continuous beam experiments it is necessary to monitor the beam for fluctuations. This is often done with semiconductor detectors [25] although any available, counting beam monitoring device is sufficient.

When the mono-energetic, accelerated beam has passed through the material of interest the generated charge states are quantified in a magnetic spectrograph which separates the ions into charge-specific beams. The separated ions are captured in a simple Faraday cup to register charge [34]. In some cases electrostatic spectrometers are used [36].

![Magnetic Spectrograph ESP-90](image)

Figure 3.5. Schematic of Ishihara and Shima experimental set-up [25]. This is typical of charge exchange studies.
Time of flight methods can also be used to determine charge state fractions. There have been fewer studies of this type. Jamiecsny uses this method coupled with an electrostatic spectrometer that consists of an electrostatic lens system and an electrostatic analyser [36]. In order to be able to separate different charge states as well as ion masses, the energy measurement is combined with a timed measurement of the particles through the instrument.

One limitation of most charge exchange experiments is the inability to measure neutral charge state fractions. At high energies it is unlikely that the ion will be in the 0 charge state. However for lighter ions at low energies this is a possibility and it is a disadvantage to be unable to quantify this charge state. One possibility for measuring this charge state fraction would be producing a beam of neutral atoms and measuring the charge of ions exiting the film. Apparatus at Imperial has been considered for this application but is not explored further in this work. Details can be found in Appendix 4.

The choice of apparatus is somewhat arbitrary for the case of charge cycling: different set-ups should provide the same charge state fractions, however all three sections are necessary in concert to measure charge state fractions.

3.3. Set-Up in this Experiment
This experiment was undertaken at the University of Notre Dame following a previous study detailed in literature by Schmitt et al. [37]. The method is similar to that described by Ishihara and Shima as shown in Figure 5 [25]. The University of Notre Dame has a 10 MV FN tandem accelerator, with a helium ion source (HIS) and a multiple source of negative ions by caesium sputtering (multi-SNICS) and has the Browne-Buchner spectrograph [38] allowing for charge collection.

The helium ion source houses helium gas with a filament as shown in the schematic in Figure 3.6. This filament heats up causing electrons to ionise the source, producing plasma. $\text{He}^{+}$ ions emerge from the chamber and are accelerated at 20 kV through the Einzel lens and then into the lithium vapour region. This allows charge exchange to take place; some -1 ions leave the chamber and are injected into the tandem accelerator. As charge exchange is velocity-dependent the lithium reservoir is kept at 20 kV to maximise the -1 charge state.
The multi-SNICS is capable of holding 40 sample cathodes without requiring reloading. The schematic in Figure 3.7 shows the functioning of a SNICS. The powder pressed sample is loaded into the cathode. The whole region is filled with caesium vapour (from heating the reservoir). The cathode is cooled and the ioniser heated. This allows caesium condensation to form on the cathode. The ioniser ionises the caesium to Cs⁺ ions which are accelerated toward and sputter into the cathode releasing material from the powder. This material travels through the caesium condensate and some pick up electrons to become negatively charged. These negative ions leave the apparatus, held at 80 kV and are injected into the accelerator. The choice of powders required in a SNICS cathode to produce ion beams is not always clear. Advice on cathode sources can be found from the Negative Ion Cookbook [40]. In this case LiOH powder is used to produce the lithium ions required.

Helium and lithium ions have been chosen due to their occurrence in the nuclear industry: in the case of alpha particles due to radiation from nuclear fuel rods themselves, and in the case of lithium from the B(n,α)Li reaction from neutron irradiation of the control rods in a nuclear reactor [41]. This reaction is of great interest not just for nuclear-related fields but in cancer therapy where this effect has been developed over the past 70 years [42]. Heavier ions are more complicated as the charge state fractions bunch together and so resolution in the magnet is more difficult. The graph in Figure 3.8 is from Marion and Young data tables [43] and shows empirical predictions of charge state fractions for lithium and...
carbon atoms. Over the same energy range of 0.01 to 0.5 MeV/u, lithium ions have four dominant charge state fractions compared to five for carbon ions. In addition to this consideration, time constraints determined that solely helium and lithium were studied, with limited beam time at Notre Dame available. Lithium ions were examined in the +2 and +3 charge states and helium in the +2 charge state with energies limited to regions possible in the accelerator and also to areas where multiple charge states can be expected.

Figure 3.8. Marion and Young data tables [43] for lithium and carbon ions. This empirical formalism deems charge state fractions to be target independent.

The 10 MV FN tandem accelerator is shown in the schematic Figure 3.9 along with all the other equipment used in this experiment. A tandem accelerator uses 2 stages of acceleration to achieve higher energies, enabled by a change of charge state at the central terminal through an electron stripping material. This stripping medium is sometimes an inert gas (e.g. argon) but in this case a solid, film carbon stripper is used. The carbon stripper is very efficient at stripping electrons off the ions, however they have a limited lifetime, unlike gas which can be continuously pumped and recycled.
Acceleration is achieved by holding the central terminal at a desired positive voltage. The functioning is very similar to a traditional Van de Graaf generator, with Figure 3.10 showing the charging mechanism. Instead of a continuous belt, the accelerator at Notre Dame uses metal sections between insulating material to carry the charge. This is charged by the electrode, A, held at a large negative potential, which repels electrons on the pellets; these electrons flow through the drive pulley to ground, leaving a charged pellet continuing round the circuit. The voltage is made uniform along the beam line due to 200 gaps with 600 MΩ of resistance between them creating a voltage divider circuit [39]. After the stripper foil the positive ions are accelerated away from positive terminal and exit the tandem with energy

$$E = E(q + 1)$$  \hspace{1cm} (3.3)

The desired charge state can be selected by using the bending magnet to direct the beam of ions in the correct charge state into the beam line.

Inside the scattering chamber the set-up is similar to Schmitt [14]. The scattering chamber, shown in Figure 3.11, consists of a central target ladder with room for four foils at a time, a
Faraday cup and a hole (for free passage of the beam). The chamber also has a silicon detector out of the beam line to measure backscattered beam and to provide a normalisation count. The silicon detector uses a 50 V Bias, Canberra (model 2003b) preamp and an Ortec 572 amplifier with a shaping time of three microseconds and gain of one; measurements were taken from the unipolar output. The count is determined using ORTEC software. Ions pass through the scattering chamber and into the spectrograph where the different ion charges are separated and directed into the Faraday cup in turn by manipulation of the magnetic field strength. For each energy measurement the magnetic field is scanned up and down the range to find the charge state in question. Suppression on the Faraday cups was held at 360 V to stop electron backscatter. Counts are measured from this cup and from the silicon detector in the scattering chamber to calculate the charge state fractions. Measurements were taken multiple times for short time periods to determine beam stability.

Figure 3.11. a) Picture of the ladder used to mount samples. This shows the Faraday cup at the top and two broken foils. b) The scattering chamber, ladder mount is in the centre with silicon detector in the bottom left hand side, beam runs right to left horizontally across the page.

Figure 3.12. a) Schematic of the Brown-Buchner spectrograph [38]. b) Photo of the spectrograph during this experiment.
Charge state fractions, $F_q$, for a given charge, $q$, are determined from the normalised ion count, $C_q$, for each charge state using the equation:

$$F_q = \frac{c_q}{\sum c_q} \quad (3.4)$$

where $C_q$ is obtained from raw data using

$$C_q = \frac{I_q}{q e N_q} \quad (3.5)$$

with $I_q$ being the current from the Faraday cup, $N_q$ the normalisation count of back-scattered ions on the silicon detector and $e$ the electron charge. These charge state fractions can then be combined into the mean charge state as shown in the equation (3.3), describing the average charge state of our ion after traveling through the film:

$$\bar{q} = \sum q F_q. \quad (3.6)$$

As it is the charge state distribution of ions in a material that are of interest, different thicknesses of thin films should be used in order to determine the thickness at which charge state distribution is reached. [44] This experiment was carried out with four different types of foil: 0.1 $\mu$m and 0.25 $\mu$m titanium foil, 0.1 $\mu$m zirconium foil and 0.1 $\mu$m copper foil. Material properties can be found in Table 3.1. In order to verify energy loss will be negligible through these films, TRIM simulations were run for at least 10,000 ions passing through the film in the ‘Monolayer Collision Steps’ mode. The Table 3.2 shows that energy loss will be small for ions at all energies through all materials in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Number (Z)</th>
<th>Density g/cm$^3$</th>
<th>Thickness ($\mu$m)</th>
<th>$\mu$g/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>22</td>
<td>4.51</td>
<td>0.1±0.01</td>
<td>45.1±4.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.25±0.03</td>
<td>112.8±11.3</td>
</tr>
<tr>
<td>Copper</td>
<td>29</td>
<td>8.96</td>
<td>0.1±0.01</td>
<td>89.6±9.0</td>
</tr>
<tr>
<td>Zirconium</td>
<td>40</td>
<td>6.52</td>
<td>0.1±0.01</td>
<td>65.2±6.5</td>
</tr>
</tbody>
</table>
The preliminary results shown in Figure 3.15 are the charge state fractions of lithium ions through the 0.1 μm thick titanium foil. These results clearly show the expected trend of higher mean charge states at higher energies. Some anomalies can be seen in these results, this is particularly clear for lithium ions at 4 MeV however scatter can also be seen at 5 MeV. It was first suggested this could be due to beam passing partially through a broken foil however this would mean double peaks would only be seen on the charge state initially entering the beam, which was not the case. On investigation it became clear these errors were due to a second peak being recorded in the AMS for a given energy. This relates to the geography of the Faraday cups inside the AMS. As can be seen in Figure 3.15 when manipulating the magnetic field strength in order to bring a beam of a given charge state into the Faraday cup it is possible that the beam will instead hit the side of the cup. This will give a peak that is not suppressed and therefore meaningless in value. All measurements from this preliminary run were discounted as it could not be made clear which were taken on the ‘real’ measurement and which on the anomalous peak.

Table 3.2. Results from TRIM calculation for lithium +3 ions in materials, data averaged over at least 10,000 ions.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{in}}$ (MeV)</th>
<th>$E_{\text{out}}$ (MeV)</th>
<th>$E\text{ loss}$ (keV)</th>
<th>% loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu film</td>
<td>7</td>
<td>6.91</td>
<td>90</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.90</td>
<td>100</td>
<td>1.67</td>
</tr>
<tr>
<td>Ti thick film</td>
<td>5</td>
<td>4.90</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.89</td>
<td>110</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.89</td>
<td>110</td>
<td>3.67</td>
</tr>
<tr>
<td>Ti thin film</td>
<td>7</td>
<td>6.86</td>
<td>140</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.84</td>
<td>160</td>
<td>2.67</td>
</tr>
<tr>
<td>Zirconium film</td>
<td>5</td>
<td>4.83</td>
<td>170</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.81</td>
<td>190</td>
<td>4.75</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.79</td>
<td>210</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>6.94</td>
<td>60</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.94</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>Ti thin film</td>
<td>5</td>
<td>4.93</td>
<td>70</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.92</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.92</td>
<td>80</td>
<td>2.67</td>
</tr>
<tr>
<td>Zirconium film</td>
<td>5</td>
<td>4.93</td>
<td>70</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.92</td>
<td>80</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.92</td>
<td>80</td>
<td>2.67</td>
</tr>
</tbody>
</table>
Figure 3.14. Preliminary experimental data on titanium film, showing lithium ion data (January 2014). The anomalous results for 4 MeV and possibly 3 and 5 MeV are seen clearly.

Figure 3.15. Beam incident on Faraday cup inside AMS. a) shows ‘correct’ functioning and b) shows the origin of the false reading seen in Figure 3.14.
References

[42] F. C. Young, J. B. Marion, Nuclear Reaction Analysis graphs and tables, John Wiley and Sons (1968).
3.4. Charge Cycling of Light Ions in Titanium, Zirconium and Copper from an Experimental and Theoretical Perspective

Paper Authors: J. Schofield, J. A. LaVerne, D. Robertson, P. Collon and S. M. Pimblott,

Status: Intending to submit to Physical Review A Journal

Author contributions: First Author on the paper. Took the measurements and analysed the data. Wrote first draft of the manuscript.

Relevance: This work presents the measurements of equilibrium charge state fractions of lithium and helium ions exiting thin films of titanium, zirconium and copper metal. Analysis of the results reveals a dependence on material properties. These new results show good agreement with prior experiments and contribute to mean charge state data for ions through materials.
Charge Cycling of Light Ions in Titanium, Zirconium and Copper from an Experimental and Theoretical Perspective

Jennifer Schofield1,2,3, Jay A. LaVerne3, 4, D. Robertson4, P. Collon4 & Simon M. Pimblott1,2

1 The University of Manchester, School of Chemistry, Oxford Road, Manchester, M13 9PL, United Kingdom
2 The University of Manchester, Dalton Cumbrian Facility, Westlakes Science & Technology Park, Moor Row, CA24 3HA, United Kingdom
3 University of Notre Dame, Radiation Laboratory, Notre Dame, IN 46556, USA
4 University of Notre Dame, Department of Physics, Notre Dame, IN 46556, USA
Jennifer.schofield@postgrad.manchester.ac.uk

Abstract

Charge cycling cross sections of lithium and helium ions are measured for atomic metal films of titanium, zirconium and copper. The experimental data qualitatively agrees with previously documented charge exchange cross sections for carbon thin films and shows the expected increase in the fraction of higher charge states with increasing velocity, over the ion velocity range considered. The material dependence of the measured charge state fractions is investigated for correlation with the material density, electron density, work function and Fermi level. The measured charge state distributions are expressed as a mean charge state and compared with various mean and effective charge formalisms. The effective charge models are demonstrated to be inadequate representations of the measured mean charge states for the ions and films in this study.

Key Words: Charge exchange, Zirconium, Titanium, Copper

1. Introduction

The energy loss properties and attenuation of ions in materials are of importance in many fields of physical [1], chemical [2], material [3] and health [4] sciences, and their prediction has been the focus of numerous theories [5]. The rate of energy loss, i.e. the stopping power, and range of ions in a medium at low and intermediate energies is affected by the charge state of the incident ion [6]. Furthermore, the equilibrium charge state (distribution) of an ion in a material changes as energy is lost and the ion slows down. Cycling of an ion's charge and the change in charge state, therefore, have an impact on the energy loss properties of the ion in the material as well as on dependent phenomena, such as the radiation chemistry of the system where the nonhomogeneous spatial distribution of the energy transfer events and subsequent generation of reactive ions and radicals, affects the observed radiation track chemistry and product yields [7]. Understanding charge exchange of ions in radiation tracks is also important in fields such as astrophysics [8] and health physics and hadron therapy [9].
The data obtained in this study are of general fundamental interest; however, the materials and ions were selected because of their relevance to the nuclear (fission) power industry. Zirconium is the principal component of LWR fuel cladding and copper is the casing of choice for the geological disposal of spent fuel [10], while titanium is employed ubiquitously as a structural metal because of its favourable properties. Helium and lithium ions were chosen because of their low atomic number, \( Z \), and for their many practical occurrences in the nuclear power industry. In the nuclear context, the helium ion is the energetic decay product from uranium and plutonium in spent nuclear fuel, while lithium ions are produced by the \( \text{B}(n,\alpha)\text{Li} \) reaction in the borated water of pressurised water reactors.

As the probability of an ion picking up an electron on passage through a material increases as the ion’s velocity (energy) is lowered, higher charge state fractions are expected to dominate at higher energies. Marion and Young have produced data tables for charge state fractions for ions in materials [11]. This compilation is primarily based on experimental data for light ions in carbon and also theoretical calculations from Armstrong and Zaidins [12, 13]. The approach assumes material independence so the fit can be used for any ion or film type. Very few subsequent studies have tried to address the charge state distribution as a function of ion velocity, but a wide variety of sophisticated models for mean charge states and effective ion charges have been developed [14-17]. Comparison of experimental data with model predictions gives a good indication of the model accuracy.

The following sections detail the experimental approach taken, report the measured charge state fractions and make comparison to both experimental and theoretical methods in the literature.

### 2. Experimental Methodology

The experimental approach used to determine charge state fractions has been described in detail previously [6], only a brief summary follows. The experiments reported here use the same 10 MV FN tandem ion accelerator, scattering chamber and magnetic spectrograph, which is part of an accelerator mass spectrometry (AMS) set-up, as in reference [6]. Figure 1 shows the experimental layout in this project.
The chosen ion is produced using either the NEC multi-cathode Source of Negative Ions by Caesium Sputtering (SNICS source) for lithium ions or the Peabody Scientific duoplasmatron Helium Ion Source (HIS) for helium ions. The sources produce negative ions that are accelerated towards the centre of the accelerator by a positive potential. At this point, the ions pass through a carbon foil that partially strips the electrons from the ion producing a positive ion. The positive ions are then further accelerated from the positive potential of the accelerator to the desired energy. A 90° analysing magnet is used to choose the desired charge state of the ion. Ions examined in this work are: \(^4\text{He}^{2+}\) and \(^7\text{Li}^{2+}\) and \(^7\text{Li}^{3+}\). Following the analysing magnet, the ion beam is focussed into the scattering chamber (under a vacuum of about \(10^{-7}\) Torr). In the scattering chamber, the ion passes through a chosen thin film and undergoes charge exchange. A silicon detector in the chamber measures the scattered beam, which is used as a normalisation tool. After traversing the film, the beam (consisting of several charge states) travels into the magnetic spectrograph where it is split into its component charge states by the magnetic field. Each of the charge states is focussed, in turn, onto a Faraday cup and the charge state fractions are determined from the measured current.

The range of ion energy used in the experiments is restricted by the operating parameters of the accelerator and is limited to the range where reasonable quantities of different charge states are expected after the energetic ion has passed through the thin film. For helium and lithium ions, the energy ranges considered lie between 1.4 and 2 MeV, and 3 and 7 MeV, respectively. This study used two different charge states of lithium ion incident on the films in the scattering chamber, +2 and +3. At higher energies both incident charge states were available from the accelerator and employed, however, at lower energies only...
+2 ions were available due to the charge cycling of electrons from the lithium ions by the carbon stripper within the accelerator.

For charge exchange studies, it is necessary to have foils that are as thin as possible in order to allow for minimal (electronic) energy loss, but that are thick enough to allow charge state equilibrium to be obtained during ion passage through the material [18]. Films of titanium, zirconium and copper were used in the experiments reported. The metal films used were purchased from LeBow company [19] and their properties are shown in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Atomic Number (Z)</th>
<th>Bulk density g/cm³</th>
<th>Thickness µm</th>
<th>Thickness µg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>22</td>
<td>4.51</td>
<td>0.1±0.01</td>
<td>45.1±4.51</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>4.51</td>
<td>0.25±0.025</td>
<td>112.8±11.28</td>
</tr>
<tr>
<td>Zirconium</td>
<td>40</td>
<td>6.52</td>
<td>0.1±0.01</td>
<td>65.2±6.52</td>
</tr>
<tr>
<td>Copper</td>
<td>29</td>
<td>8.96</td>
<td>0.1±0.01</td>
<td>89.6±8.96</td>
</tr>
</tbody>
</table>

Films with a thickness of 0.1 µm were chosen as a compromise between cost, time and suitability; however, titanium films of thickness 0.25 µm were also studied to verify that the films were sufficiently thick to ensure incident ion beams exited with an equilibrium charge state distribution. The thickness was measured by LeBow Company using a quartz crystal microbalance with a maximum error of 10% quoted [19]. The attenuation of the kinetic energy of lithium ions within 0.1 µm films was estimated using TRIM (in the "Monolayer Collision Steps" mode) and energy losses are small at all the incident energies and thickness used in this study.

Charge state fractions, $F_q$, for a given charge, q, are determined from the normalised ion count, $C_q$, for each charge state using the equation:

$$F_q = \frac{C_q}{\sum C_q}$$  \hspace{1cm} (1)

where $C_q$ is obtained from raw data using

$$C_q = \frac{I_q}{qeN}$$  \hspace{1cm} (2)

with $I_q$ being the current from the Faraday cup, $N$ the normalisation count of back-scattered ions on the silicon detector and $e$ the electron charge.

3. Models for Ion Charge

In order to formulate models of energy loss properties, and specifically stopping power, one of the most widely used, albeit inappropriate, methods is an effective ion charge. The concept of an effective ion charge has been developed to describe charge of an ion at a
particular energy in a material. Generally, effective charge models are not target material specific. Most are constructed by compiling stopping powers for many ions over a large energy range and then empirically fitting the data for the ions to that for protons with the same velocity to obtain a multiplication correction (or "fudge" factor) for the ion data.

In other words

\[ S(M, Z, E) = q_{\text{eff}}^2 S(1, 1, \frac{Z}{M}), \]  

where \( S(M, Z, E) \) is the stopping power of a material for an ion of mass \( M \), stripped charge \( Z \) and kinetic energy \( E \), and \( q_{\text{eff}} \) is the fitted effective charge, which depends upon the velocity of the ion as well as its fully stripped charge, \( Z \).

Three empirical effective charge models are considered in this study. They are described in detail in references [15], [14] and [16]. The first is that of Northcliffe, who suggested the effective charge on an ion could be described by the equation:

\[ q_{\text{eff}} = Z \left(1 - 1.85 \exp \left(\frac{-2V}{V_0}\right)\right)^{1/2} \]  

where \( V \) is the velocity of the incident ion and \( V_0 \) is the Bohr velocity. Pierce and Blann extended this approach of relating \( q_{\text{eff}} \) to the Bohr velocity. They obtained a fit by considering 4 ions in 11 different targets including both solids and gases [14], and suggested effective charge could be described by

\[ q_{\text{eff}} = Z \left(1 - \exp \left(\frac{-0.95V}{V_0^2}\right)\right) \]  

including a proportionality to the fully stripped ion charge, \( Z \).

The final model considered here was developed by Ziegler, who compiled a larger dataset comprising hundreds of targets for many different ions [16]. The data set was used to obtain the following expression for effective charge:

\[ q_{\text{eff}} = Z \left(\left(1 - \exp \left(\frac{-0.95V}{V_0^2} - 0.07\right)\right) + \exp \left(\frac{-0.95V}{V_0^2} - 0.07\right) \right) \left(\frac{V_0/V}{2}\right)^2 \ln \left[1 + \left(\frac{2\Lambda V}{a_0 V_0}\right)^2\right] \]  

with \( V_r \) being the relative velocity of the incident ion to that of the electrons in the medium and \( a_0 \) the Bohr radius [16]. \( \Lambda \) is a screening length, describing the electronic distribution around the projectile ion, this separates 'close' and 'distant' collisions. The screening length will change as a function of the number \( N \) of electrons remaining on the projectile and can be described

\[ \Lambda = \frac{N^{2/3}a_0^2}{Z(1 - N/Z)}. \]  

The formalism in Equation (6) is similar to that of Pierce and Blann, relating \( q_{\text{eff}} \) to the relative velocity of electrons in a medium and the ion charge; however, it goes further by including an additional second term incorporating the effect of incomplete shielding of the ion nucleus by any associated electrons i.e. to account for electrons in the medium which penetrate the electronic shells of the incident ion and thereby giving less shielding to the
ion nucleus. This correction is the second term in Equation (6), with the first term being the effective charge for ‘distant’ collisions. This first order perturbation approach is explained in detail in reference [16] and relies on Brandt and Kitagawa’s ‘BK’ theory [20].

For helium, Ziegler has obtained a more specific empirical fit to the compilation of experimental data in which the effective charge is given by

\[ q_{\text{eff}} = Z \left(1 - \exp\left[-\sum_{i=0}^{5} a_i \left(\ln(E_{\text{He}})\right)^i\right]\right)^{1/2} \] (8)

where \( Z = 2 \), and the parameters \( a_i \) are empirically fitted, and \( E_{\text{He}} \) is the energy of the incident helium ion in MeV; The fitted parameters are: \( a_0 = 0.2865 \), \( a_1 = 0.1266 \), \( a_2 = -0.001429 \), \( a_3 = 0.02402 \), \( a_4 = -0.01135 \), \( a_5 = 0.001475 \) [16]. It is clear from Equation (3) that the effective charge does not actually portray the mean charge state of an ion in a material, incorporating other corrections required to change the proton stopping power to reflect the stopping of the required ion.

In addition to effective charges, mean equilibrium charge states have been proposed by various authors including Schiwietz and Grande [17]. When comparing to measured charge states these fits should be superior to effective charge as they are fitted to mean equilibrium charge state data, mostly for captured for ions in carbon (for which there is the largest data-set). Grande and Schiwietz describe the mean equilibrium charge state of projectiles in materials as [17],

\[ q_{\text{mean}} = \frac{Z (0.29x + x^4)}{\frac{v}{1.54}c_2} \] (9)

with the scaling variable

\[ x = c_1 \left(\frac{v}{1.54 c_2}\right)^{1+0.83/Z} \] (10)

Where

\[ c_1 = 1 - 0.26 \exp\left(-\frac{Z_t}{11} - \frac{(Z_t-Z)^2}{v}\right) \] (11)

\[ c_2 = 1 + 0.030 \frac{\bar{v}}{\ln(Z_t)} \] (12)

and

\[ \bar{v} = Z^{-0.543} v / V_0 \] (13)

with \( Z_t \) being the “nuclear” charge of the target material. By definition,

\[ q_{\text{mean}} = \sum_{q=0}^{n} F_q q, \] (14)

so use of the square of this parameter in expressions for stopping power is not a wholly satisfactory representation of the effects of charge exchange of an ion in a material, especially as the empirical expressions are only applicable over a limited energy.

Sigmund recently stated that the empirical methods used to account for the cycling of an ion’s charge lack rigorous theory and that a better method should be found to predict mean charge states [21]. Ideally, ion and material dependent charge cycling cross-sections should be measured and used. If desired to be used in the same way as effective charge,
for instance in the calculation of stopping power, charge as defined by charge exchange experiments, would be described as

\[ q_{\text{eff}} = \sqrt{\sum_{q=0}^{n} q^2 F_q} \]  

(15)

with \( F_q \) the fraction of ions in a given charge state determined by charge cycling cross-sections and \( n \) the number of different charge states for an ion i.e. \( Z \). In other words, the measured experimental stopping power of an ion should be given by

\[ S(M, Z, E) = S(1,1, \frac{E}{M}) \sum_{q=0}^{n} F_q q^2 \]  

(16)

using the notation of Equation (3).

4. Results and Discussion
The measured ion charge state fractions for lithium in titanium films are shown in Figure 2 as a function of lithium ion energy. Only ions of charge state +2 and +3 were observed in the magnetic spectrograph with the proportion of +1 ions produced (in the energy range considered) being negligible [22]. The same is also true for neutral lithium, although this species would not have registered in the magnetic spectrograph. The error bars shown are standard deviations between different experimental values and fluctuate according to beam fluctuations. As the energy (velocity) of the incident ion increases, the proportion of +3 ions increases and that of +2 ions decreases, as expected. This study used two different charge states of lithium incident on the films in the scattering chamber, +2 and +3. The data confirms that the incident charge state has no effect on the charge state fractions of ions exiting the film.

For titanium, two different film thicknesses, 0.1 and 0.25 \( \mu \text{m} \), were studied to check operation in a thickness regime where charge cycling has reached equilibrium. If the ion beam has not reached charge state equilibrium, then the thicker film (0.25 \( \mu \text{m} \)) will give a lower fraction of ions with the same charge as the incident ion and a higher fraction of ions in the other charge state than the thinner film (0.1 \( \mu \text{m} \)). It is important to recognise that thicker samples have a decrease in the mean charge state [23] because of the greater energy loss in the film. TRIM calculations of over 10,000 ions were done to predict the average attenuation of helium and lithium ions in the metals used in this experiment, with all energy losses found to be less than 4.7 %. Changes in the equilibrium distribution due to energy loss can therefore be discounted. Despite larger errors at lower energies due to beam uncertainties, there is a good agreement between the data for the two film thicknesses showing the choice of films of thickness 0.1 \( \mu \text{m} \) is appropriate.

Also shown in Figure 2 are empirical charge state fraction curves obtained by Marion and Young from fitting a compilation of Armstrong and Zaidin’s data [12, 13]. Measured charge state fractions for +2 and +3 ions are in good agreement with these curves.
Figure 2. Effect of incident ion energy on the equilibrium charge state fractions of lithium ions exiting titanium thin films of thickness 0.1 and 0.25 μm. Incident ions initially of charge +2 or +3 were used, the same key is used for both. Open data points correspond to experiments performed with the thinner film and filled data points correspond to experiments performed with the thicker film. Square data points represent the fractions of exiting ions in the +2 charge state (F$_2$) and circles those in the +3 charge state (F$_3$). The solid lines are the charge state fractions predicted by the approach of Marion and Young [11].

Equilibrium charge state fractions for +2 and +3 lithium ions after passage through zirconium films are shown in Figure 3. Having confirmed the equilibrium charge state distribution regime, only a single film thickness of 0.1 μm was considered. The figure shows there is no effect from incident charge state on the measured charge state distribution. The data for the +2 and +3 charge state fractions show the same velocity dependence as demonstrated in Figure 2 by titanium thin films, i.e. the fraction of +3 charge state increases and that of +2 charge state decreases with increasing incident ion energy and. Again, the data are in good agreement with empirical curves of Marion and Young, for carbon films.
Figure 3. Effect of incident ion energy on the equilibrium charge state fractions of lithium ions exiting a zirconium thin film of thickness 0.1 μm. Incident ions initially of charge +2 or +3 were used. Open data points correspond to incident ions with charge state +3 and filled data points correspond to incident ions in with charge state +2. Square data points represent the fractions of exiting ions in the +2 charge state and circles those in the +3 charge state. The solid lines are the charge state fractions predicted by the approach of Marion and Young [11].

Figure 4 shows the measured equilibrium charge state fractions for lithium ions after passing through a copper thin film. Again there is no effect of incident ion charge state on the experimentally measured charge state fractions exiting the film and the proportion of +3 charge state increases and that of +2 decreases with ion energy. The new data presented here is in excellent agreement with the experimental results of a previous study performed on the same apparatus as shown in the figure [6]; however, the measured fraction of +3 ions is somewhat lower, and that of +2 ions is somewhat higher than suggested by the empirical curves of Marion and Young based on empirical data for carbon films.
Figure 4. Effect of incident ion energy on the equilibrium charge state fractions of lithium ions exiting a copper thin film of thickness 0.1 µm. Incident ions initially of charge +2 or +3 were used. The same key is used for both. Filled data points are data from this experiment. Open data points are from reference [24]. Square data points represent the fractions of exiting ions in the +2 charge state and circles those in the +3 charge state. The solid lines are the charge state fractions predicted by the approach of Marion and Young [11].

A compilation of all the data for the Li +3 charge state fraction for the different films considered in this study as well as additional data from the literature, including data for lithium ions incident on carbon films [25, 26] and for lithium ions incident on gold [25] is shown in Figure 5. There is a clear discrepancy with the Marion and Young empirical curve for carbon. If the observed differences were due to a density effect similar to that observed in comparisons of gas and solid [27] then the more dense material, copper in this case, would be expected to have the highest +3 charge state fraction and lowest +2 charge state fraction at a given energy. The opposite effect is observed with copper giving the lowest proportion of +3 lithium ions in the equilibrium charge state distribution. The figure shows a striking material dependence of the +3 charge state fraction, with a decreasing in the order: Ti > Zr > Cu > Au > C.

For the metallic elements study here, this ordering corresponds to increasing bulk density, however, added literature data in Figure 5 for gold films does not support this correlation.
Figure 5. Material dependence on the effect of incident ion energy on the +3 charge state fraction of lithium ions exiting thin film of thickness 0.1 μm. Experiments with titanium films (■), zirconium (●), copper (▼), gold (▲) and carbon (△). Filled points are from the experiments reported here, open points are from Schmitt [6] and half-filled points are from Itoh [26]. The solid line is the charge state fraction predicted by the approach of Marion and Young [11].

Table 2. Bulk density and electrical properties for the materials considered in Figure 4. Free electron density calculated using the Drude method assuming a valency of: Ti=4, Zr=4, Cu=1, Au=1, C=0. Parentheses give data from the CRC handbook for copper and gold [28] and from G. H. Kinchin [29] for carbon. First Ionisation Potential data from Kramida et al. [30].

<table>
<thead>
<tr>
<th>Material</th>
<th>Free Electron Density ($\times 10^{28}$/m$^3$)</th>
<th>Fermi Energy (eV)</th>
<th>First Ionisation Potential (eV)</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium</td>
<td>22.7</td>
<td>13.6</td>
<td>6.83</td>
<td>4.51</td>
</tr>
<tr>
<td>Zirconium</td>
<td>17.2</td>
<td>9.3</td>
<td>6.63</td>
<td>6.52</td>
</tr>
<tr>
<td>Copper</td>
<td>8.4 (8.46)</td>
<td>(7)</td>
<td>7.72</td>
<td>8.96</td>
</tr>
<tr>
<td>Gold</td>
<td>5.9 (5.9)</td>
<td>(5.53)</td>
<td>9.23</td>
<td>19.32</td>
</tr>
<tr>
<td>Carbon</td>
<td>0 (6 x 10$^{-4}$)</td>
<td>0</td>
<td>11.26</td>
<td>2.26</td>
</tr>
</tbody>
</table>

Table 2 lists a number of properties of the materials considered in Figure 5 to explore the possibility that the equilibrium charge exchange and the trend seen is dependent on an
electronic property. Assuming Coulombic interactions of the incident ion with electrons of the material give rise to charge cycling, materials with higher free electron density should give rise to a greater probability of the ion accepting an electron as it travels through the medium and therefore a lower proportion of higher charge states. In this case, the charge state fraction of +3 lithium ions would be expected to decrease in the order

\[ C >> Au > Cu > Zr > Ti, \]

which is the opposite order to that observed experimentally. The Fermi energy, which is the energy difference between the highest and lowest occupied single-particle states at absolute zero, shows a similar (reverse) ordering. In contrast, the first ionisation potential, which is a measure of the ease with which a material releases an electron, suggests the charge state fraction of +3 lithium ions should decrease in the order:

\[ C << Au < Cu < Ti \sim Zr, \]

which is essentially the order observed experimentally. There is clearly some dependence between the fraction of ions in the +3 state (and the +2 state) with the electronic properties of the target material; however the exact nature of this relationship is unclear.

The experimentally determined root mean square charge states for lithium ions in the foils of interest are compared with the three different effective charge models in Figure 6. Although the energy range covered by this experimental study is fairly narrow, it includes the range where the different effective charge formalisms begin to diverge with decreasing ion velocity. All the models considered for the effective ion charge predict lower values than the experimental data set, with the more empirically tailored formalism of Ziegler showing the best agreement with experiment.

Table 3 compares the measured mean equilibrium charge states with those given by the equation of Grande and Schiwietz. As shown predicted mean charge by Grande and Schiwietz are systematically lower than measured. In addition the model mean charge states fall away more quickly than the experimental mean charge states. The Grande and Schiwietz range of validity ends at \( \frac{V}{V_0} = 0.7 \). Lower energy charge state fractions would allow more comment to be made on this discrepancy.
Table 3. Experimentally determined mean charge states of lithium ions passing through the thin films of titanium, zirconium and copper.

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Mean charge state</th>
<th>Grande and Schwietz equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Titanium (0.1 μm)</td>
<td>Titanium (0.25 μm)</td>
</tr>
<tr>
<td>3</td>
<td>2.72±0.07</td>
<td>2.73±0.04</td>
</tr>
<tr>
<td>4</td>
<td>2.83±0.04</td>
<td>2.84±0.05</td>
</tr>
<tr>
<td>5</td>
<td>2.88±0.09</td>
<td>2.88±0.08</td>
</tr>
<tr>
<td>6</td>
<td>2.91±0.06</td>
<td>2.91±0.10</td>
</tr>
<tr>
<td>7</td>
<td>2.92±0.04</td>
<td>2.92±0.06</td>
</tr>
</tbody>
</table>

Figure 6. Comparison of experimentally determined mean ion charge for lithium with the predictions of empirical models for effective ion charge. Experiments are shown for titanium films (■), zirconium (●), and copper (◀). The formalism of Northcliffe, Equation (4) is shown as the solid line, those of the formalism of Pierce and Blann, Equation (5) by the dashed line, and that of the formalism of Ziegler, Equation (6), by the dotted line.

Figure 7 shows measured equilibrium charge state fractions for helium ions in titanium, zirconium and copper as well as the Marion and Young fit for helium ions. The energy range over which it was possible to measure equilibrium charge state fractions for helium...
ions was limited by the lower energy limits of the ion accelerator. At the lowest voltage, the accelerator gives 1.4 MeV helium ions with +1 charge. Figure 7 shows the +1 and +2 equilibrium charge state fractions for helium ions at 1.4 MeV and at 2.0 MeV. At these energies, the helium ions exiting the thin metal film are predominantly in the +2 state. While systematic errors are larger due to low beam currents available, the data reveals a material dependence of the charge state fraction at the lower of the two energies considered. The dependence is same as that observed for lithium ions, i.e. the fraction of ions in the higher charge state decrease in the order

\[ \text{Ti} > \text{Zr} > \text{Cu}. \]

This data is not compared with other films at this time. At the higher energy considered, 2 MeV, there is no distinguishable difference between the charge state fractions in the different materials.

![Graph showing charge state fraction vs energy](image)

**Figure 7.** Effect of ion energy on the charge state fractions of helium ions in titanium (■), zirconium film (●), and copper (▲). The +1 charge state fractions are the lower set of open data points and the +2 charge state fractions are the upper filled set. The solid lines are the charge state fractions predicted by the approach of Marion and Young [11].

The root mean square charge states for the different materials as a function of incident helium ion energy is shown in Figure 8. As expected from the charge state fractions, there is a clear dependence on the material at the lower of the two energies. At the higher energy where the ion beam is almost fully stripped there is no experimentally distinguishable
difference between the different films. The experimental values are compared with the effective charges predicted by Equations (3), (4) and (8), in Figure 8. There is good agreement between the experimental data and the formalism of Ziegler, which is based on an extensive empirical fitting of experimental stopping power data; however, agreement with the other effective charge formalisms is less satisfactory.

Figure 8. Comparison of experimentally determined mean ion charge for helium with the predictions of the three empirical models for effective ion charge. Experiments are shown for titanium films (■), zirconium (●), and copper (▼). The formalism of Northcliffe, Equation (4) is shown as the solid line, the formalism of Pierce and Blann, Equation (5) by the dashed line, and the formalism of Ziegler, Equation (8), by the dotted line.

5. Conclusion

Equilibrium ion charge state fractions have been measured for lithium and helium exiting from titanium, zirconium and copper thin films. The data obtained for copper films are in good agreement with data collected previously using the same experimental set-up and reported in reference [6]. There appears to be a marked material dependence on the material when the ion beam is not fully stripped and this dependence appears to follow the same order as the first ionisation energy of the film material, although further investigation over a wider energy range is required. This dependence is clearer for the heavier lithium ion due to the availability of unstripped charges at the energies investigated.

The root mean square ion charge has been calculated from the experimental data and compared to the effective charge predicted by several empirically based literature models.
Reasonable, but not satisfactory agreement is found with the formalism of Ziegler reported in reference [16]. As is widely acknowledged effective charge is not found to be a suitable representation of mean charge states, however the formalism of Grande and Schwietz is also found to be ineffective at predicting the mean charges for lithium ions in metallic targets at the energies measured in this work.

**Acknowledgements**

The authors thank the NSF Nuclear Structure Laboratory at the University of Notre Dame, which is funded by the United States National Science Foundation, for the use of their facilities. The research described was funded by the Dalton Cumbrian Facility Project, a joint initiative of the Nuclear Decommissioning Authority and The University of Manchester and by the EPSRC as well as by the Division of Chemical Sciences, Geosciences and Biosciences, Basic Energy Sciences, Office of Science, United States Department of Energy through grant number DE-FC02-04ER15533. J. Schofield was supported by a research studentship though EPSRC Nuclear FiRST Doctoral Training Centre.

**References**


4. Hydrogen Radiolysis from Water-Nanoparticle Systems

4.0. Objectives
To determine if silicon carbide (SiC) nanoparticles increase the yield of hydrogen in SiC-water slurries exposed to gamma irradiation compared to the H$_2$ yield in the radiolysis of water. The effect of the water to powder ratio on hydrogen yield was investigated for both alpha and beta phase silicon carbide.

4.1. Motivation
Waste management of used nuclear fuel often includes storage in water for long periods of time, for example the fuel storage ponds at Sellafield [1]. This wet storage allows for cooling of what can often be hot material and also provides effective shielding of alpha and beta radiation. After a given period of time this fuel is removed and at this point it can go down several routes. One of the currently proposed fuel storage routes in the UK is dry-storage, where dried fuel is kept in sealed cans in air conditioned units whilst its activity decays [2]. This dry store may be used for many years. Indeed, Scotland intend for this approach to be the final fate of their radioactive waste [3].

One well publicised challenge encountered with long-term storage is pressurization of cans, which may cause can failure and this can lead to radiation spills and environmental impact. Pressurization of cans can be caused by many different gaseous products [4]:

- Fission gases
- Helium
- Hydrogen generation from corrosion
- Hydrogen generation from radiolysis [1]
- Methane production from irradiation of organics

The main gases produced over longer timescales are considered to be mostly helium but also hydrogen and methane [4, 5].

This work focusses on hydrogen generation from irradiation of materials in contact with water. Radiolytic generation is important to understand for long term dry-storage as, even post drying process; there will be residual moisture on the surface of materials. There is dissociated chemisorbed water on the surface of most oxide materials [6]. The majority of this water can be driven off under heat, however, it will re-adsorb if there is moisture in the environment on return to normal atmospheric temperature and pressure. To understand hydrogen production, it is important to understand how energy from ionising radiation is deposited in water.
Radiolysis of water in aqueous solutions has been extensively studied with many review papers and books [7-10]. When high energy radiation is incident on a water molecule one of two things can happen. The H$_2$O molecule can be ionised or it can become excited, leading to the production of reactive ions and radicals shown in Figure 4.1. As can be seen in the figure there are a number of stable products, among them, molecular hydrogen. The distribution products resulting from a single energy transfer event is called a spur. The molecular hydrogen produced from this radiolysis is believed to derive mostly from recombination of the water cation and non-hydrated electron with the decay of subsequent excited states [11].

![Event Diagram](image)

**Figure 4.1.** Graph illustrating the effects of radiation in water. In the presence of other impurities this scheme becomes exponentially more complicated. These primary yields react further at longer timescales.

The products within a spur interact and, in the case of solely water irradiated with low LET radiation, there is little net production of H$_2$ from a sealed system as a result of back reactions [7]. In the case of a leak or the presence of other chemicals in the water, these back reactions can be prevented. This would lead to an excess of H$_2$ and an ability to measure the primary yield.

The microsecond yields of radiation species depend on the LET of the radiation due to different clustering of spurs. When the LET is high the spurs are closer together, when low they are far apart. The work here on stopping and charge cycling aims to help address understanding this challenging and complex system. The overall outcome in future projects would be a complete prediction of chemical yields for any type of ionising radiation in any material.
Studies have shown that water when exposed to radiation gives a primary hydrogen yield of 0.45 molecules/100 eV \cite{12}. In radiation chemistry this is referred to as the $G$ value. When water is in contact with nanoparticles of oxides, there is a well-documented change in hydrogen $G$ value, for example yields of hydrogen can reach 150 molecules/100 eV for small numbers of water layers on zirconia \cite{6, 13-16}. In many cases during the study of hydrogen generation, bromide is added to scavenge the radical $\cdot OH$ therefore preventing back reaction and giving a measure of the gas produced \cite{17, 18}, although chloride has been used as an alternative anion \cite{13}. LaVerne has shown that 1 mM potassium bromide (KBr) is an acceptable concentration in solutions and indeed that, almost irrespective of dose, the ions are recycled by reducing species and therefore higher concentrations are not required for higher doses \cite{19}. As such 1 mM KBr is used in this project. The radiolytic production of molecular hydrogen from water adsorbed on solid oxides and water-oxide slurries has received much attention. This area was first highlighted by Petrik et al. who observed deviations in the yield from that expected assuming a mixture rule. In Petrik’s review he suggests that the amount of hydrogen released is related to the band gap of the particle studied as well as crystal size and amount of water deposited \cite{20}. He suggests water-oxide interfaces act in three separate ways: oxides that produce excess hydrogen under irradiation (for example ZrO$_2$ and La$_2$O$_3$), oxides that do not change the expected yield (for example SiO$_2$, TiO$_2$ and Al$_2$O$_3$) and oxides which lower the yield of hydrogen (Fe$_2$O$_3$ and CuO). Recently there has been work by various authors on Fe$_2$O$_3$ \cite{21}, TiO$_2$ \cite{22} and Al$_2$O$_3$ obtaining contradictory results suggesting that these predicted trends are not upheld. LaVerne and co-workers have studied in-depth various oxide systems; interest has been focussed on urania (UO$_2$) and zirconia (ZrO$_2$) as these materials are currently in use by the nuclear industry in its fuel and fuel clad respectively \cite{23, 24}. These showed that for small numbers of water layers the yield may be orders of magnitude larger. Laverne has shown that, when in contact with oxide nanoparticles, the yield of hydrogen can rise to as much as 40 molecules/100 eV \cite{24}. In general the mechanism for interfacial excess radiolysis hydrogen production is unknown, although there have been several postulations. Possible mechanisms for excess hydrogen production could be electron-hole recombination, dissociative electron attachment or resonance exciton coupling \cite{10, 20}. Many are in favour of migration of excitons through to the surface of powders causing the excess hydrogen \cite{10, 15, 20}. The process for this excess hydrogen is not understood to date, and will not be something that this project attempts to uncover.
The size of particles is known to affect the amount of hydrogen evolved from a sample. For slurries in particular LaVerne has shown that the particle size can double the yield of hydrogen seen [25]. Smaller sized particles are likely to produce a greater G value with a substantially reduced yield shown for particles larger than 22 nm diameter [15]. Water in contact with other nanoparticles has also been shown to evolve more energy in the system than expected. There are studies of nanoparticles with gold in particular, with reference to biological systems (DNA) which have shown an increase in cell death in cells which have taken up gold nanoparticles. The mechanism for this has been put down to the 'Local Effect Model' and it would be interesting in future to investigate the possibility of an underlying link between these two effects [26].

Thus far only radiolytic hydrogen production in water-oxide nanoparticle systems has been studied. Silicon carbide (SiC) is investigated in this project. SiC is a well-studied semiconductor of great interest for its electrical properties. It has high hardness, thermal conductivity and is chemically inert [27]. These advantageous properties makes silicon carbide important to many industries and has led to it being considered by the nuclear industry for both Gen III+ fuel cladding (TRISO particles) [28] and also cladding of material when considering a geological disposal facility [29]. The Figure 4.2 shows the three most common phases of SiC although there are more than 200 possible polytypes.

![Figure 4.2. The 3 main polytypes of SiC. There are many more polytypes, this is from reference [30].](image)

All the polytypes exhibit similar mechanical properties, however, due to their stacking differences, they can possess very different electronic properties [30]. The stability of the different phases depends on the rate of growth and the temperature. The 3C-SiC phase forms over high temperatures of 1,273 - 3,023 K [31], but is unstable and can become the 6H phase at even higher temperatures (1,626 - 3,946 K) [30]. 3C silicon carbide is referred to as beta-SiC (β-phase). 6H and 4H are the most common phases and both can be
referred to as alpha-SiC (α-phase). In this project 6H is referred to as alpha phase; 3C and 6H are the phases studied.

Both phases have been studied in some respects by the nuclear industry. However, whilst the irradiation conditions of SiC have been studied, there has been little done on its radiolysis. Most work focuses on the structural properties or the change of phases, or amorphisation possible under irradiation [29]. There has also been work on the electrical conductivity change upon irradiation [32]. Perhaps the closest studies have been done on SiC nanowires and photocatalytic hydrogen production [33], however the low-energy UV light is not analogous to the radiation environment encountered in the nuclear context and the mechanism behind hydrogen production is expected to be different. Griffith [34], writes that there is decreased hydrogen production from SiC however provides no reference or extra details. This particular reference probably pertains to hydrogen produced from corrosion rather than radiolysis products. This oversight to fully investigate the radiation chemistry of SiC, when combined with the relative wealth of studies on oxide powders, illustrates the gap filled by this current work.

The aims of this project will be to determine if silicon carbide increases hydrogen yield for water in the presence of radiation. It will determine how much of an effect this has and ascertain if this is a dose-dependent effect or not. The work will investigate if the water/SiC ratio affects this yield. The study also aims to determine if phase changes the amount of radiolysis.

4.2. Methodology for Hydrogen Production Measurement

In order to measure the hydrogen from a SiC-water system it is necessary to irradiate in a closed system, then be able to break that system and measure the hydrogen generated. In this project H\textsubscript{2} analysis is done using a gas chromatography analyser. SiC powder was used: α-phase SiC (99.8 %) and β-phase SiC (99.8 %) were purchased from Alfa Aesar. The density of both polytypes is 3.21 g/cm\textsuperscript{3}. Initial experiments were done with relative humidity chambers to deposit water layers onto SiC powder post-baking, however it was discovered that this process would be too lengthy. This means that small numbers of water layers were not possible in this work. Preliminary H\textsubscript{2} experiments and TPD studies showed the powders to be clean it was decided not to bake them and to use them as received, combining powder with high purity water and 1 mM KBr to create slurries.

Initial analysis was done using a Quantachrome Autosorb 1 and the Brunauer-Emmett-Teller (BET) method in order to determine size of the powders used. This method consists of outgassing a sample of powder (usually about 1 g) and then adsorbing N\textsubscript{2} onto the surface as the sample is placed in a cold sink (in this case liquid nitrogen is used). As the sample is raised and lowered in the cold sink different amounts of nitrogen gas are
adsorbed and the size of the particles can be deduced. The Figure 4.3 shows the general set up of this method.

Figure 4.3. Equipment used in this project, samples are of around 1 g and outgassing is performed under heating (50 °C). The lower left hand cylinder is the sink, the right is the sample holder.

The powders were not sieved or otherwise prepared before analysis. The results in Figure 4.4 show a small amount hysteresis, a possible indicator of porosity in our sample, however in general these samples do not appear to be overly porous. This is beneficial as it means our surface area measurements are more accurate. The surface area and size of the particles correlates well with the size quoted by the manufacturers, as shown in Table 4.1.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Specific Area (m²/g)</th>
<th>Density (g/cm³)</th>
<th>Particle diameter (µm)</th>
<th>Manufacturer quoted area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-α</td>
<td>10.267±0.076</td>
<td>3.2</td>
<td>0.183</td>
<td>9 - 11</td>
</tr>
<tr>
<td>SiC-β</td>
<td>16.275±0.564</td>
<td>3.2</td>
<td>0.115</td>
<td>14 - 19</td>
</tr>
</tbody>
</table>
When preparing samples for H$_2$ analysis the SiC powder is put into glass tubes, 10 cm long, purchased from Soham Scientific, which then has pure water from an Elga water supply (~18.2 MΩ cm$^{-1}$) (with 1 mM bromine ions) added to make up the concentration. An Ohaus Discovery analytical balance is used. Care should be taken to ensure the next steps are performed swiftly after water has been added to the powder. Whilst evaporation is slow, condensation has been observed on top of the the glass when left overnight. This brings challenges when attempting to flame seal the vials without losing sample (an accurate knowledge of amount of sample is necessary for analysis).

Samples are purged with argon gas for 5 -10 minutes to ensure air is removed: less than 5 minutes will cause air to be seen in the sample post-irradiation. This work focusses on slurries, which are well-behaved when purging, although care should be taken not to lose material on the needle when purging slurries with lower water contents (when they start to become paste-like). After adequate purging time, and ensuring a slight positive pressure, the samples are removed from the purging apparatus and flame sealed an example of a flame sealed sample can be seen in Figure 4.5. Flame sealing under a slight positive pressure ensures no air will re-enter the vials during sealing. This is crucial when measuring in the Gas Chromatogram (GC) after irradiation.
When using a slurry mixture it is important to ensure that the powder is as evenly distributed as possible within the aqueous phase (in other words there is a homogeneously heterogeneous phase). In order to ensure a complete mixing, samples are attached to the windmill rotator (see Figure 4.6). This machine was developed by Thomas Donoclift at the Dalton Cumbria Facility (DCF). Samples are rotated at 3 rotations/min. This allows complete mixing for slurries. Below a concentration of around 40 percent these SiC-Water mixtures stop being slurries and become sludge, and then with even lower water content, paste or wet sand. This means they no longer require mixing as there is no sedimentation over the irradiation time period. They continue to be irradiated in the same way to ensure consistent dose rates. Samples are loaded into the cobalt-60 ($^{60}$Co) irradiator for irradiation.

The $^{60}$Co Irradiator is a lead-contained cobalt-60 source set-up as shown in Figure 4.7. Cobalt-60 decays by beta-decay to nickel-60 with a half-life of 5.27 years [35]. As shown in Figure 4.8 this unstable configuration of the nickel-60 isotope then decays by 2 prompt gamma-rays of 1.332 MeV and 1.173 MeV, respectively. The approach of using the decay chain of cobalt has often been used in the gamma irradiation of samples [36]. A $^{60}$Co irradiator is one of the most easily used devices for delivering gamma irradiation. This is due to its 5 year half-life, meaning sources do not have to be replaced often, and
reasonable dose rates can be given. The energy of the gamma rays is suitable to obtain a large dose without needing an extortionate amount of shielding. Samples are placed in the chamber and irradiated by the raising of one or more $^{60}$Co rod. The internal temperature of the irradiator reaches a stable 30 °C during these exposures. The samples in this experiment were irradiated for a given amount of time to obtain a desired dose. Dose rate is determined by Fricke dosimetry.

**Figure 4.7.** Cobalt-60 irradiator at the DCF. Samples are inserted into the chamber and the $^{60}$Co source rises up to irradiate the sample.

**Figure 4.8.** Decay scheme of cobalt-60. Information on the decay scheme was taken from [35].

This ubiquitous dosimetry is a well-known method used in radiation chemistry to quantify the energy absorbed, i.e. the dose, of a sample exposed to radiation. Developed in the 1920s by Hugo Fricke [37], it works by measuring oxidation of a solution of Fe$^{II}$ to Fe$^{III}$ ions on exposure to ionising radiation. When an air-saturated solution of ferrous sulphate is exposed to radiation, the oxidation of the iron ions can be determined from UV spectroscopy. The ferric ions have a strong absorbance peak at 305 µm which is not present for ferrous ions. In order to calculate the dose the following equation is needed

$$ Dose(Gy) = \frac{(9.647 \times 10^6) \Delta \alpha}{\Delta \epsilon \rho G(Fe^{III})} \cdot $$ (4.1)
Here $\Delta \varepsilon$ is the molar extinction coefficient, a temperature-dependent value given as $2201 \text{ mol}^{-1} \text{ cm}^{-1}$ by [7]. $\rho$ is the solution density and $G(\text{Fe}^{III})$ is the yield of Fe$^{III}$ after irradiation. For a 0.4 M H$_2$SO$_4$ solution the yield of iron 3+ is 15.6, the solution density is 1.024 and the path length, described by $l$, is 1 cm. The measured difference in optical absorbance pre and post irradiation is $\Delta a$. Although the half-life of $^{60}$Co is well known and therefore the decay of the source can be predicted [35], it is good practice to re-verify the Fricke measurement at appropriate intervals. In this experiment Fricke was carried out using the sample mount used in the study to ensure an accurate value was obtained.

Gas chromatography was used in this experiment. The GC machine used here is a SRI Model 8610C Gas Chromatogram with a Thermal Conductivity Detector (TCD) for analysis of the gas given off. The TCD works on the principle of differences in thermal conductivity. This universal detector takes gas in through 2 channels, one for reference and one for detection, as shown in Figure 4.9. The gasses pass over a Wheatstone Bridge and if the gasses are the same there is no signal. If the gasses are different then heat will be lost at a different rate on the detection side and there will be a signal [38] as there will be a change in filament temperature and also therefore electrical resistance. The detector works best when the thermal conductivity of the carrier gas and the thermal conductivity of the gas you wish to measure are significantly different. As can be seen from Table 4.2 the thermal conductivity of helium and hydrogen are similar, as are nitrogen, oxygen and argon. In this study, measuring hydrogen zero grade argon gas was used.

**Table 4.2. Table of the thermal conductivities of gases used in GC measurements.** Data from [39] - thermal conductivity will change with temperature but the relative differences are assumed to remain the same.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Thermal Conductivity @ RTP (mW/m°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>185.9</td>
</tr>
<tr>
<td>He</td>
<td>154.6</td>
</tr>
<tr>
<td>Ar</td>
<td>17.8</td>
</tr>
<tr>
<td>O$_2$</td>
<td>25.9</td>
</tr>
<tr>
<td>N$_2$</td>
<td>26.2</td>
</tr>
</tbody>
</table>

There are two main approaches to measuring gases given off in radiation chemistry: headspace injection methods and in-line methods. In this study in-line methods have been used as it is believed they give better accuracy. The headspace injection method, as the name suggests, involves taking gas from the headspace of the experiment and injecting this into the GC. Downsides of this method are that if a small amount of hydrogen is produced in the experiment then, when taking only a small volume of the headspace to analyse, signals can be too small to be detected by the GC. It has also been noted that the septa fitted to the glass vials in this method can produce hydrogen under irradiation, so adding an uncertain background to the readings. Although some people subtract this background from results, the amount of hydrogen produced by rubber septa can vary, as their density and formulation vary from batch to batch. Headspace techniques are also only
capable of analysing the gas phase. The hydrogen produced in this experiment will be produced in the liquid phase and escape into the gas phase.

**Figure 4.9.** Set-up of the GC. When in the ‘OFF’ position, carrier gas bypasses the sample (connection 2 and 10). In the ‘ON’ configuration the carrier gas flows through the sample.

In-line GC analysis can be further broken down into 2 techniques. One technique takes gas directly as it is produced during irradiation and analyses it. This is susceptible to loss of H₂ in the liquid phase and is only able to irradiate one sample at a time. The crush tube technique is the second method and is used here. Crush tube techniques are only really suitable for gamma radiolysis, as alpha and beta radiation will not penetrate through the glass. If these shorter range irradiations are investigated then the first in-line technique should be used with a thin mica window, allowing penetration of the radiation.

The GC in this experiment is fitted with a customised column of 0.25 inch outer diameter (OD), 4 m long, copper tubing packed with 13x molecular sieves. This compensates for the higher flow rate than usual. The GC columns are arranged as shown in the Figure 4.10. This allows attachment of the sample in isolation. Then, when the G valve is ‘ON’, the carrier gas flows through the sample (connected between ports 2 and 10). Figure 4.10 is a set-up of the system used in this project. The glass sample which has been irradiated is inserted into a Tygon tube which is connected via glassware and nylon tubing to the input and output ports (2 and 10 on Figure 4.9 respectively). The sample is purged of air, then the glass tubing is broken and the carrier gas is run through again to measure H₂. Figure 4.11 shows this setup. The GC is operated at 40 °C and 8 psi (giving a flow rate of ~50 ml/min). This crush tube set-up is beneficial as gas bubbles through the water/SiC slurry.
Figure 4.10. a) The GC apparatus with the crush tube apparatus attached. b) Crush tube sample apparatus.

Figure 4.11. Schematic of the crush tube system: Argon (Ar) flows round the system.

Calibration of the GC system is done often as, over time, the Gas Chromatograph can become more, or less, sensitive depending on the column moisture loading and detector filament condition. These factors can be affected by atmospheric conditions of the time (for example excess moisture in the air, or ambient temperature) or if it has recently been baked. Baking is done every couple of months (dependent on use), raising the column temperature up to 200 °C, and serves to drive off water from the column in the GC, increasing the efficiency of the column to separate out gases and therefore the sensitivity of the machine. Calibration is done using a T glass-tube fitted to the IN and OUT ports of the GC. A rubber septum is put over the third end and known volumes of H₂ gas are injected using a set of gas-tight locking valve syringes.
Calibration must be done at different volumes of H$_2$ gas to verify linearity of the detector response. If the response is not linear then there should be an in-depth investigation into why the machine is behaving non-linearly. This GC machine gives a linear response to differing amounts of hydrogen injected, see Figure 4.12. The fitted straight line equation passes through the origin and has the equation:

$$\text{Area on PeakSimple} = 15.8823 \times \text{Volume Hydrogen (mL)}.$$  \hspace{1cm} (4.2)

![Graph showing the linear relationship between GC area and hydrogen volume.](image)

**Figure 4.12.** Gas chromatograph response from different amounts of hydrogen. The residual chi-squared value from this fit is 4.65.

A preliminary set of experiments was carried out to ascertain the correct dose to ensure a reading from the GC. Ensuring there is a good output from the GC is more important when considering smaller water % as there will be less hydrogen generated. A dose of around 12.5 kGy was chosen, as it was determined hydrogen can be measured even at low water percentages. This preliminary run also ensured that no air was found within an empty vessel, and that no air was found with a sample of just powder (lending credibility to the method used here of not baking powder prior to using). Irradiation of organics can give rise to H$_2$ and also methane. The yield of water (with Br) was also calculated to ensure that this system can reproduce the value found in literature. A yield of 0.461 molecules/100 eV was found. This correlates well with literature and lends credibility to this technique. The chosen dose was also varied for a chosen slurry (water %) in order to investigate the effect of dose on hydrogen emitted from the sample. A response is not expected as previous studies have shown no dependence with oxides [40]. Finally, the signal is collected on the PeakSimple system, an example of which is in Figure 4.13, which allows simple data analysis post-calibration.
This experiment should allow us to investigate hydrogen produced under irradiation of SiC slurry samples. The main downsides of the method will be discussed in Section 5.

Particle characterisation was also an important aspect of this work. Methods used in this work in addition to the BET methodology described earlier include SEM, XPS, XRD, FTIR and TPD. These machines were used by both myself and S. C. Reiff at the University of Notre Dame in order to conduct a preliminary analysis, with S. C. Reiff conducting a secondary confirmation in order to produce the published paper. An outline of each technique is found below with final results in the following paper.

As mentioned the Brunauer-Emmett-Teller (BET) methodology was used to determine the surface area and estimated particle size of the powders.

Temperature Dependent Fourier Transform Infrared spectrometry (TD-FTIR) is an effective way of studying the water adsorbed onto surfaces. Light is reflected off a surface and any change in the wavelength is indicative of bonds on the surface interacting with this incident light.

Powders are put into the cell, shown below, which is capable of heating up to 500 °C. Infrared spectra can be taken at any point in the reflective mode. Incident rays (IR) are reflected off the top of the surface of the powder and then directed back into the machine. Normally IR spectra are taken in the transmission mode as, with transparent liquids and solids, one can more conveniently take spectra throughout the whole material and not just the surface. Since we are considering non-transparent materials this was not feasible. In fact, difficulty with reflectance can be encountered when the material is dark coloured, as both the silicon carbide $\alpha$- and $\beta$-phase are. When this occurs KBr must be used to dilute the material in order to detect a spectrum. The machine used here is a Bruker Vertex 70 Diffuse Reflection Infrared Fourier Transform (DRIFT) spectrometer.
Temperature programmed desorption is used to indicate what kind of molecules are adsorbed onto the surface of powders. This is done by placing powder samples inside a vacuum and heating up to 500 °C in increments of 2 °C/min using a Watlow 989 temperature controller. Gases of physisorbed particles are given off and can be measured in the mass spectrometer attached to the apparatus. The masses measured are m/z=14, 15, 16, 18, 28, 32, 40 and 44. 18 indicates the presence of water and together with organics, m/z=14, 15, 16, 44 (CH$_2$, CH$_3$, CH$_4$, CO$_2$), it is of the most interest to this study. By evaluating the amount and time when the gases are emitted, the energy of the binding of those particles to the powder surface can be determined. This is of most interest for water adsorbed onto the surface as it illuminates if there is any chemisorbed water. This is water which is not normally liberated under gamma irradiation and so does not usually contribute to hydrogen production.

X-ray photoelectron spectroscopy (XPS) is an accurate surface characterisation method used to evaluate the oxidation state of the surface of our powders. This method, as depicted in Figure 4.15, works by having the sample under vacuum and irradiating with X-rays whilst measuring emitted electrons at the same time. This provides information about the first 10 nm of sample (due to the penetration depth of X-rays). This technique is very surface sensitive and will accurately provide oxidation states, it can determine if any other phases are present on the surface of our sample which might affect its behaviour under irradiation. It also helps determine if the preparation method has removed contaminants such as hydrocarbons from the powders.
Figure 4.15. Schematic of energy level where electron is ejected during XPS.

The PHI VersaProbe is used here, from the Materials Characterisation Facility at Notre Dame, using weighted aluminium Kα X-rays of energy 1.486 keV. Both full scans and higher resolution scans over relevant core electron levels can be performed and atomic concentrations can also be calculated from the areas of these peaks.

Scanning electron microscopy imaging (SEM) is used in conjunction with several of the other methods to evaluate particle size and formation. This was only an overview to combine with BET measurements. Figure 4.16 is an image of a typical particulate for SiC α-phase and for SiC β-phase. Both are spherical, however SiC β-phase is clearly less well formed. When comparing the size of these particles (50 μm) seen in the SEM with BET measurements (0.2 μm) it is clear that these must be several particles clumped together to give a larger mass. An image of singular grains was not taken in this study, however in SiC β-phase (which has larger grain size) the feathering around the spherical mass could correspond to singular grains.

Figure 4.16. SEM images of typical SiC powder. SiC α-phase is shown on left, β-phase is on the right.
References

4.3. Radiolytic Hydrogen Generation at Silicon Carbide - Water Interfaces

Paper Authors: J. Schofield; S. C. Reiff; S. M. Pimblott; J. A. LaVerne

Status: Published in Journal of Nuclear Materials

Thesis Page Number: 117

Author contributions: First Author on the paper and measurement of radiolytic hydrogen production; analysed this data. Wrote first draft of this section of the manuscript and the introduction and conclusions. The characterisation of SiC powders presented in this paper was prepared by S. C. Reiff.

Relevance: This paper presents measurements of hydrogen production from irradiated slurries showing that silicon carbide acts in the same way as some oxides and produces excess H$_2$. This is the first study of this kind. This yield of excess hydrogen is small, but comparable with recent iron and copper oxide results.
Radiolytic hydrogen generation at silicon carbide–water interfaces

Jennifer Schofield a, b, Sarah C. Reiff c, Simon M. Pimblotta, b, ** Jay A. LaVerne c, *

a School of Chemistry, The University of Manchester, Manchester M13 9PL, UK
b Dalton Cumbrian Facility, The University of Manchester, Westlakes Science & Technology Park, Moor Row CA24 3HA, UK
c Radiation Laboratory and Department of Physics, University of Notre Dame, Notre Dame, IN 46556, USA

HIGHLIGHTS

• SiC–water interfaces were irradiated with γ-rays and 5 MeV He ions.
• Hydrogen production from SiC–water slurries was greater than that for pure water.
• Raman spectroscopy shows conversion of the α-phase SiC to the β-phase.
• He ion radiolysis resulted in the formation of SiO2 on the surface.

ARTICLE INFO

Article history:
Received 21 August 2015
Received in revised form
16 November 2015
Accepted 18 November 2015
Available online 23 November 2015

ABSTRACT

While many of the proposed uses of SiC in the nuclear industry involve systems that are assumed to be dry, almost all materials have dissociated chemisorbed water associated with their surface, which can undergo chemistry in radiation fields. Silicon carbide α-phase and β-phase nanoparticles with water were irradiated with γ-rays and 5 MeV 4He ions followed by the determination of the production of molecular hydrogen, H2, and characterization of changes in the particle surface. The yields of H2 from SiC–water slurries were always greater than expected from a simple mixture rule indicating that the presence of SiC was influencing the production of H2 from water, probably through an energy transfer from the solid to liquid phase. Although the increase in H2 yields was modest, a decrease in the water mass percentage led to an increase in H2 yields, especially for very low amounts of water. Surface analysis techniques included diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), nitrogen absorption with the Brunauer – Emmett – Teller (BET) methodology for surface area determination, X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Little change in the SiC surface was observed following radiolysis except for some conversion of β-phase SiC to the α-phase and the formation of SiO2 with He ion radiolysis.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Silicon carbide (SiC) has been suggested for many different applications in the nuclear industry, including use as the clad for new nuclear fuels for light water reactors [1], incorporation into the matrix of Gen III+ fuel materials [2], and the encapsulation of high level waste for long term storage [3]. This popularity is due to its high temperature stability [4], good thermal conductivity [5,6], and oxidation resistance at high temperatures [7]. SiC exists as 3 main polytypes, 6H-SiC (SiC α-phase), 3C-SiC (SiC β-phase) and 4H-SiC. Much work has been done on examination of SiC properties in the context of its use as a nuclear material [8,9]. There have been reports on α-phase and β-phase SiC polytypes for nuclear industry applications, including their behavior under irradiation [10] and transformation between types [4], however, the study of SiC has very much remained in the domain of material science and little work has been published on its radiolysis in realistic environments [1].

In the absence of a long term disposition solution, the nuclear industry is facing extended periods of interim storage for used fuel and consequently dry storage following cooling in a water pond is being investigated and under serious consideration for adoption. Many of the proposed uses of SiC in the nuclear industry involve systems that are relatively dry [1]. However, almost all materials
have dissociated chemisorbed water associated with their surface [11]. In addition, accidents and other mishaps can lead to the introduction of water onto nuclear materials. Waste storage containers may be designed to be dry, but the probability of such containers coming into contact with ground water at some point in the future is not negligible.

Several studies have shown that the radiolysis of water in contact with solid interfaces has very different radiation chemistry than observed in bulk water [12–17]. The transfer of energy, charge, or mass through the solid–water interface may lead to significant modifications to the surface as well as enhanced degradation of the water. Systematic studies on the radiolysis of SiC–water interfaces will aid future nuclear engineering and used fuel management endeavors.

This work investigated the radiolysis of water in association with the surface of SiC nanoparticles to determine how each component affected radiolytic changes in the other. Adsorbed water on SiC and SiC–water slurries were examined in order to obtain the relative dependence of radiolytic yields on the amount of each phase. Water radiolysis was monitored by observing the variation in the yield of molecular hydrogen, \( \text{H}_2 \). The surfaces of SiC were characterized before and after radiolysis using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), nitrogen adsorption using the Brunauer–Emmett–Teller (BET) methodology for surface area determination, X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Irradiations were performed with \( \gamma \)-rays and accelerated 5 MeV \(^4\)He ions to mimic the radiation typically associated with nuclear materials.

2. Experimental

2.1. Sample preparation and analysis

Silicon carbide, \( \alpha \)-phase SiC (99.8%) and silicon carbide, \( \beta \)-phase SiC (99.8%) were purchased from Alfa Aesar and used as received. The density of both polytypes is 3.21 g/cm\(^3\). The Brunauer–Emmett–Teller (BET) methodology was used to determine the surface area and estimated particle size of the powders using a Quantachrome Autosorb-1. Water and other contaminants present on the surface were analyzed using two complimentary techniques: temperature programmed desorption (TPD) and temperature dependent diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). The TPD measurement was performed on a sample of between 50 and 100 mg deposited in a custom cell. The cell was heated from room temperature to 500 °C at a rate of 2 °C/min, while the gases desorbing from the sample were monitored using a Pfeiffer Prisma quadrupole mass spectrometer. The mass to charge ratios measured were 14, 15, 16, 18, 28, 32, 40, and 44. A background scan was taken using an empty cell and was subtracted from the sample measurement. The DRIFT was obtained using in situ measurements of samples heated up to 400 °C using a Bruker Vertex 70 with a Harrick Praying Mantis high temperature cell. Prior to DRIFT measurements samples of SiC were mixed with KBr. Two mixtures were measured for each phase, one with 10% and one with 1% SiC by mass. Mixtures of KBr had to be used because the pristine samples absorbed too much light.

Surface analysis was performed using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The Raman spectroscopy measurements were taken using a Jasco Micro-Raman Spectrometer MRS-5100. In this configuration, the beam diameter on the sample is estimated to be around 1 μm with a 10 μm sampling depth. A 532 nm laser was used for the measurements with a power of 0.2–0.3 mW and resolution of 3.53 cm\(^{-1}\). XPS measurements were taken using a PHI VersaProbe II X-ray photoelectron spectrometer with a monochromatic Al-Kα X-ray source, photon energy of 1486.6 eV, and a hemispherical electron energy analyzer. Wide scans over the binding energy range from 1486 to 0 eV were taken with a pass energy of 187.85 eV and an energy step of 0.4 eV. High resolution scans were taken for each element of interest with a pass energy of 23.5 eV and energy steps of 0.05 eV. Multiple 200 μm diameter spots were analyzed on each sample and the sampling depth is estimated to be less than 10 nm. Charge neutrality was maintained on the surface by floating the sample chamber with 10 eV Ar\(^{+}\) ions and low-energy electrons during measurement. Under these conditions, the resolution for the wide range scans was 2.43 eV and was 0.58 eV for the elemental regions scans as determined using the full width at half maximum, FWHM, for the Ag 3d\(\text{S}2\) peak from a sputtered silver foil.

X-ray diffraction (XRD) measurements were taken using a Bruker D8 Advance DAVINCI Powder X-Ray Diffractometer equipped with a Cu-Kα X-ray source. Scans were taken over a range of two-theta values from 20° to 80°, with a 0.05° step. To prevent radiation damage to the surface during the measurement, samples were rotated at a rate of 15 revolutions per minute.

2.2. \( \text{H}_2 \) production and gamma irradiation

Silicon carbide does not adsorb water easily onto its surface and no \( \text{H}_2 \) could be observed under normal irradiation conditions. Therefore these carbides were not baked to remove adsorbed water and slurries were investigated instead. The amount of water was varied as a function of the mass from 10 to 97.5%. Water was obtained from an Elga Water system, and mixed with 1 mM KBr. The addition of KBr is used to scavenge \( \cdot \text{OH} \) radicals that are produced during the radiolysis of water, which would otherwise react with \( \text{H}_2 \), resulting in a lower yield.

Radiolysis with \( \gamma \)-rays was performed using a self-contained Foss Therapy Services Inc. 812 \(^{60}\)Co source located within The University of Manchester Dalton Cumbrian Facility. Temperatures inside the source reach 35 °C so little macroscopic heating was observed. The dose rate was nominally about 107 Gy/min as determined using the Fricke dosimeter. This dosimeter is strictly valid for only water or aqueous solutions; however, both the elements Si and C have relatively low atomic numbers and the absorption of gamma rays is expected to be very similar to that of the O in water and no further correction was made to the dosimetry. The sample cells were 10 cm long and 10 mm diameter Pyrex tubes. Samples were prepared by purging the SiC powders under argon to positive pressure and then flame sealing the tubes. In order to ensure homogeneous mixing of the slurries, samples were irradiated at a constant distance from the source while turning at 3 rotations/min, which was sufficient to ensure complete mixing.

The production of \( \text{H}_2 \) from empty glass vials after purging was lower than the detection limit when irradiated for times comparable with those of the samples. The yield of \( \text{H}_2 \) with aqueous KBr solutions using this methodology gives a value of 0.46 molecules/100 eV, which agrees well with previous results [18]. The SiC powder irradiated without water (purged with argon) gave no detectable \( \text{H}_2 \), which indicates clean surfaces on the powders.

Samples were irradiated up to 12.5 kGy with the \( \text{H}_2 \) produced measured using a SRI 8610C gas chromatograph coupled with a thermal conductivity detector (TCD) [12]. Carrier gas, 99.999% argon, was passed through a constant flow regulator, an injection septum, a four-way valve connected to a sample injection loop, and into a column consisting of 13 × molecular sieve. Following irradiation, the sample cells were inserted into Tygon tubing, connected in-line to the GC, flushed with the argon carrier gas, and then cracked open allowing any gases produced during the irradiation to be swept away and detected by the GC. Calibration was performed by injecting pure gases with a gas-tight microliter syringe. The
sensitivity for detection of H₂ was 1 μL and all errors associated with H₂ determination are about 5%.

2.3. Irradiations with γ-rays and He ion for surface analysis

Irradiations of SiC with γ-rays to produce samples for surface analysis were performed using a self-contained Shepard ⁶⁰Co source located at the University of Notre Dame Radiation Laboratory, which had a nominal dose rate of 179 Gy/min as determined using Fricke dosimetry. Sample cells consisted of 10 mm diameter Pyrex tubes about 10 cm long that were flame sealed following freezing, pumping with vacuum and thawing 3 times, to remove any air from the samples. Following irradiation, the sample vials were cracked open and the samples were deposited on SEM stubs for surface analysis.

Heavy ion irradiations were performed with 5 MeV ⁴He ions obtained using the facilities of the Nuclear Science Laboratory at the University of Notre Dame. The beam diameter was approximately 6.4 mm, with a beam current of 1.5 nA charge. Energy loss to the machine exit window was determined using standard range tables and fully stripped ions were used for irradiations [19]. Samples for He ion irradiation were prepared by pressing SiC powders into a carbon tab attached to an SEM stub and were irradiated to 1/10³⁵ ions/cm². The SEM stub and exit window were connected electrically, and current from them was integrated to give the ion fluence.

3. Results and discussion

3.1. Characterization of SiC surfaces

Water adsorbed on the surface of solid oxides typically dissociates to form OH groups [11,16]. The characterization of the surface of the SiC powders was undertaken to determine how water adsorption occurs on SiC. The specific surface area for α-phase SiC was 10.3 ± 0.6 m²/g and for β-phase was 16.3 ± 0.1 m²/g using the BET methodology. Multiple scans were used to determine the standard deviations. From these surface areas, the average particle diameters were estimated as 183 and 115 nm for the α-phase and β-phase SiC powders, respectively, assuming spherical particles. An
isotherm for each phase is shown in Fig. 1. The shape of the isotherms as well as the lack of hysteresis between the adsorption/desorption curves suggest that the particles are either macroporous or nonporous.

TPD and DRIFT measurements were made to analyze the water and other contaminants present on the SiC surface. The TPD measurements for water are shown in Fig. 2. Curves for the other gases monitored were orders of magnitude less than that for the desorption of water. The desorption curves are broad but three peaks at 135 °C, 261 °C, and 480 °C can be fit for α-phase SiC, and two peaks at 155 °C and 384 °C can be fit for β-phase samples. The desorption energies calculated using Redhead’s method are 1.3, 1.7, and 2.4 eV for the α-phase samples and 1.3 and 2.1 eV for the β-phase samples [20]. This result suggests that there are multiple bonding sites available on the SiC surfaces for chemisorbed water, which has a desorption energy greater than 0.35 eV [21]. DRIFT spectra for each sample were measured at room temperature; following heating to 100 °C, 200 °C, 300 °C, and 400 °C; and again after cooling to room temperature giving the results shown Fig. 3. For comparison, a reference curve of water ice at 10 K is also displayed [22]. Neither SiC phase shows peaks indicating the presence of surface water at room temperature. However, following heating a broad inverse reflection peak around 3475 cm⁻¹ is present, suggesting that water is being lost from the surface. The water peak at room temperature is not visible due to the high amount of KBr present, which was required because pure SiC absorbs almost completely in the infrared. The peak at 3475 cm⁻¹ disappears when the sample is cooled to room temperature, indicating that the water is reabsorbed on the surface. This water must be the chemisorbed water observed in the TPD spectra that desorbs at the higher temperatures. The α-phase SiC sample has a main peak at 870 cm⁻¹ from the Si–H bond, with a shoulder at 790 cm⁻¹ from the Si–C bond and at 950 cm⁻¹. Other peaks are also visible at 1300, 1540, and 1620 cm⁻¹. Previous work on SiC films have identified vibrations from the Si–C bond [23–29] at 780 cm⁻¹, the Si–H bond [23,25] at 860 cm⁻¹, the Si–CH₃ bond [25,29] at 980 cm⁻¹, the Si–O bond [28] at 1020 cm⁻¹, and from work on silicon nitride films, the Si–O bond [26,30] at 1040–1060 cm⁻¹. Additional modes which were reported in the previous works [23–28] were not observed in these samples. The β-phase SiC sample had a main peak at 920 cm⁻¹, with smaller peaks at 760 and 620 cm⁻¹. A previous
The location and sizes of the peaks are not observed to change during the heating experiments, suggesting that except for the loss of water the SiC surfaces are stable during heating.

### 3.2. Production of H₂ with γ-ray radiolysis

The most obvious probe of the variation in the radiolysis of water in the presence of SiC is the production of H₂. This gaseous product is relatively unreactive and easy to measure in mixed-phase systems. Systems of physisorbed water would not give observable amounts of H₂ so slurries with various amounts of water were used. The yields for H₂ with 70% water by mass are shown in Fig. 4 as a function of the dose. These results show that the yields of H₂ are not dependent on the total dose to the system. Variation of the dose rate also did not affect the production of H₂. The presence of the solid SiC interface does not lead to any spontaneous or catalytic water decomposition. Variation in the relative amount of SiC and water gives information on the interactions occurring at the interface in radiolysis. The yields of H₂ are shown in Fig. 5 as a function of the water mass percentage in the system. Each experiment was performed four times and the error bars represent one standard deviation. Errors in H₂ determination are sometimes more dependent on sample reproducibility than in H₂ measurement. Fewer data were collected for the β-phase since this system was not expected to behave much differently than the α-phase. Yields can be reported with respect to the total energy deposited in the whole system (water and SiC) as in the upper plot or with respect to the water alone, as in the lower plot. In all cases, the yields of H₂ with SiC present are higher than would be expected for pure water. This result implies either a transfer of energy from the carbide into the water for a given sample or modification of the sensitivity of adsorbed water to radiation. Although the yields of H₂ are small, they are comparable to recent studies using iron [14] and copper oxide [15] slurries with water. These small yields suggest that the carbide surfaces are
relatively inefficient at transferring "radiation damage" to the water. Similar results were observed with iron oxides [14]. Very little is known about the mechanism for the transfer of energy through the bulk and interface, but previous studies with ZrO₂ suggested that it is due to an exciton [13]. Calculations seem to indicate that exciton energies in SiC are only a few eV, which would be too small to break a typical water bond [32].

Observations of the H₂ yields with respect to the energy deposited only in the water give a better representation of the effect of SiC on the water radiolysis. The yields of H₂ with a-phase SiC increases from 0.46 molecules/100 eV for pure water to about 0.87 molecules/100 eV at 60% water and then remains constant until 10% water. This result suggests that there is a relatively constant amount of energy being transferred from the SiC to the water phase and the yield appears to increase because the amount of energy directly deposited in the water is decreasing. However, there appears to be a rather large increase in H₂ yields as the amount of water decreases below 10%. This lower limit is quite reproducible. Experimental difficulties precluded the extension of the data to much lower water content, but the trend in the data with decreasing water content suggests that a high yield of H₂ is expected from SiC with a few associated water layers.

3.3. Changes to the SiC surface

Powder X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy were used to analyze the SiC powder surfaces and bulk before and after irradiation with He ions and γ-rays. The XRD patterns (not shown) confirmed the correct diffraction patterns for α-phase and β-phase SiC following comparison with the particle diffraction file database [33] as well as with previously reported diffraction patterns for α-phase SiC [31,34,35] and β-phase SiC [36,37]. No significant changes in the diffraction patterns were observed following irradiation, indicating that the bulk crystalline structure is unchanged at the doses used in this work.

Samples of SiC were also characterized using Raman spectroscopy and the spectra are shown in Fig. 6. The pristine α-phase sample has peaks at 154, 244, 769, 791, 950, 972, 1515 cm⁻¹, while the β-phase pristine sample has peaks at 793, 1354, 1513, 1586, and 1615 cm⁻¹. The peaks at 1354 and 1586 cm⁻¹ are due to graphitic or
amorphous carbon present on the 𝛽-phase SiC sample [38,39]. These peaks are in good agreement with previously reported Raman spectra of 𝛼-phase [29,39–41] and 𝛽-phase [31,39,40,42,43] SiC samples [26,44]. No peak around 480 cm⁻¹, due to the presence of the Si–Si bond [26] was observed for either sample. Following irradiation with 𝛾-rays and He ions, no changes are observed in the 𝛼-phase SiC sample. For the 𝛽-phase sample, the 𝛾-ray irradiated sample shows an increase in the relative intensity of the graphic carbon peaks and one of the sampled locations on the He ion irradiated samples showed additional peaks at 152, 243, 764, and 965 cm⁻¹ suggesting that it was converted to 𝛼-phase SiC. The near similarity in H₂ yields observed for both phases suggests that this phase conversion has little to do with H₂ production; however, further experiments may offer more clarity. A previous study where SiC was irradiated with 4 MeV Au ions reported the loss of crystalline structure in the SiC samples and the formation of Si–Si bonds, which was found to be dependent on the dose given to the sample. However, none of the He ion irradiated samples showed the formation of the Si–Si bond, which could be due to the lower stopping power of the He ion than the Au ion leading to less local damage to the SiC surfaces.

X-ray photoelectron spectroscopy is an extremely surface sensitive technique, providing analysis of the chemical composition and chemical bonding occurring in the top 10 nm of a sample. The lower resolution wide scans showed the presence of carbon, oxygen, and silicon atoms in the SiC samples. High resolution scans for those elements for 𝛼-phase SiC are shown in Figs. 7–9 and for both the 𝛼-phase and 𝛽-phase SiC. The atomic concentrations of carbon, silicon, and oxygen were calculated based on the relative areas of the C 1s, Si 2p, and O 1s peaks and relative sensitivity factors for the PHI VersaProbe at those photoelectron energies. The calculated atomic concentrations are given in Table 1. For both the 𝛼-phase and 𝛽-phase samples, the amount of carbon decreases following irradiation. During irradiation, showing the formation of SiO₂, especially for He ion irradiation. The contribution of the Si–Si peak was observed to increase, particularly for the He ion irradiated samples suggesting that following the ion irradiation that parts of the surface are oxidized to SiO₂.

Errors in atomic concentration are estimated at ±5%.

### 4. Conclusions

Changes in 𝛼-phase and 𝛽-phase SiC nanoparticle surfaces were observed following radiolysis with 𝛾-rays and with 5 MeV He ions. Adsorbed water was characterized using TPD and DRIFT to show that little physisorbed water was on the SiC surfaces and the chemisorbed water desorbed on heating. Slurries of SiC with varying amounts of water were also examined and the yield of H₂ was found to be higher than that expected using a simple mixture rule, and its yield increases with decreasing amount of water. This result indicates that there is some transfer of energy between the SiC and water in radiolysis. Bulk crystal structure was not observed to change following irradiation with 𝛾-rays or He ions. However, Raman spectroscopy of the SiC surface suggests that the 𝛽-phase can be converted to the 𝛼-phase in He ion radiolysis. XPS analysis of procedure using the C–C bond. The C–C bond was low in concentration and appeared as a shoulder, making it difficult to locate the exact position for charge calibration. The other spectra, O 1s and Si 2p, were shifted accordingly. For both the 𝛼-phase and 𝛽-phase samples, the C–C peak had the largest contribution to the C 1s spectrum in the pristine sample; however, following irradiation the contributions dropped dramatically as can be seen in Table 2. This decrease suggests that irradiating the surfaces with both 𝛾-rays and He ions removed some of the carbon contamination present on the SiC surfaces. The C–Si contribution either increased or stayed the same, as was the case for He ion irradiated 𝛼-phase SiC. The contributions of the carbon-oxygen peaks were initially less than 5% of the total, and remained as such following radiolysis.

The Si 2p spectra show contributions from the Si–C bond at 100.5 eV and the Si–O bond in SiO₂ at 102.2 eV [34,45]. No lower binding energy peak for a Si–Si bond was present in any of the samples. There is good agreement between the calculated concentrations of the C–Si bond and the Si–C bond, listed in Table 2; however, there is a discrepancy in the comparison of the Si–O and O–Si bonds with the values calculated in the O–Si bonds being higher. Both phases of SiC had about a 10% increase in the Si–C bond following irradiation with 𝛾-rays, and had only slight increases for He ion irradiation. The contribution of the Si–O peak was observed to decrease, particularly for the He ion irradiated samples suggesting that following the ion irradiation that parts of the surface are oxidized to SiO₂.

The O 1s spectra are fit with two peaks, a main one at 532.0 eV for the O–Si oxide layer [34,45], and a higher binding energy shoulder around 533.4 eV, due to H₂O present on the surface [46], which is only present in the pristine samples. Following irradiation, the H₂O peak is no longer visible in the spectrum suggesting the loss of the water layer during irradiation with both 𝛾-rays and He ions. The concentration of the O–Si peak is observed to increase during irradiation, showing the formation of SiO₂, especially following He ion irradiation.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Atomic composition for 𝛼-phase and 𝛽-phase SiC samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>𝛼-phase SiC – pristine</td>
<td>Carbon (%)</td>
</tr>
<tr>
<td>𝛼-phase SiC – 𝛾-ray irradiated</td>
<td>45</td>
</tr>
<tr>
<td>𝛼-phase SiC – He irradiated</td>
<td>37</td>
</tr>
<tr>
<td>𝛽-phase SiC – pristine</td>
<td>64</td>
</tr>
<tr>
<td>𝛽-phase SiC – 𝛾-ray irradiated</td>
<td>54</td>
</tr>
<tr>
<td>𝛽-phase SiC – He irradiated</td>
<td>41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Peak atomic concentrations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>Si 2p</td>
</tr>
<tr>
<td>(S_{\text{C}–\text{Si}}) (%)</td>
<td>(S_{\text{C}–\text{C}}) (%)</td>
</tr>
<tr>
<td>282.6 eV</td>
<td>284.7 eV</td>
</tr>
<tr>
<td>(x)-phase SiC – pristine</td>
<td>24</td>
</tr>
<tr>
<td>(x)-phase SiC – 𝛾-ray irradiated</td>
<td>32</td>
</tr>
<tr>
<td>(x)-phase SiC – He irradiated</td>
<td>23</td>
</tr>
<tr>
<td>(\beta)-phase SiC – pristine</td>
<td>14</td>
</tr>
<tr>
<td>(\beta)-phase SiC – 𝛾-ray irradiated</td>
<td>21</td>
</tr>
<tr>
<td>(\beta)-phase SiC – He irradiated</td>
<td>24</td>
</tr>
</tbody>
</table>
the SiC surfaces indicated that following irradiation the contribution from the C–Si bonds had increased and that there was a loss of the H2O peak suggesting that water and impurities were removed from the surfaces during the irradiations. With He ion radiolysis, the formation of SiO2 oxide was observed on both x-phase and β-phase SiC.

**Acknowledgments**

The authors thank Prof. Michael Wiescher for making available the facilities of the Notre Dame Nuclear Structure Laboratory, which is supported by the U.S. National Science Foundation. The authors also acknowledge the Center for Sustainable Energy at Notre Dame (cSEND) Materials Characterization Facilities for the use of the PHI VersaProBle II X-ray Photoelectron Spectrometer, Jasco Micro-Raman Spectrometer NRS-5100, and Bruker D8 Advance DAVINCI Powder X-Ray Diffractionmeter. Support of the National Science Foundation through MRI award 1126374 is acknowledged for the Raman Spectrometer NRS-5100, and Bruker D8 Advance DAVINCI Materials Characterization Facilities for the use of the PHI also acknowledge the Center for Sustainable Energy at Notre Dame.

**References**


5. Remarks on the Body of Work and Future Directions

The work presented in this thesis investigates the electronic effects of ionising radiation on solid materials of interest to the nuclear industry. This work has produced a novel formalism to predict electronic collision cross sections using a DOSD of the material in question, has analysed charge state fractions of lithium and helium through new materials and ascertained the production of excess hydrogen from silicon carbide-water slurries. The aims of this work have been successfully achieved.

5.1. Inelastic Cross Sections and Energy Loss Properties

5.1.1. Summary

The two papers presented here describe the formalism developed in this work for the construction of electronic collision cross sections in terms of the dipole oscillator strength distribution of a material and the construction of various dipole oscillator strength distributions. Both papers predict energy loss properties including the stopping power of protons, helium and oxygen ions in materials, and compare these to experimental results in order to evaluate the validity of this model for predicting energy loss by ions in matter.

The first paper presents the formalism developed for calculating inelastic cross sections and energy loss properties of ions in material along with development of the DOSD for zirconium dioxide as well as a comparison of energy loss properties to experimental data. In addition, various different models for the effective ion charge are investigated. This paper successfully showed that the formalism is capable of predicting energy loss properties at higher energies than the Bragg peak - however comparison of the results to experimental data show that the model breaks down at lower energies, around 0.1 MeV/u. The possible reasons behind this failure are explored including limitations in the basis of the model and the exclusion of higher order (e.g. Barkas) corrections.

The effect of ion charge is explored in depth in the first paper and is shown to have an effect, not on just the stopping power predicted, but also on the ion energy at which the maximum of the Bragg peak occurs. A preferred model for effective ion charge is not recommended in the absence of charge exchange cross sections. However, when predicting stopping power, the effective charge model proposed by Ziegler should be superior to other approaches. In the first paper effective charge models proposed by Ziegler are used.

In the second paper the mean charge model developed by Schiwietz and Grande is used, which provides a better fit to experiment for heavier ions. One benefit of using empirically
fitted effective charges obtained from stopping power data rather than the mean charge predicted by Schwietz and Grande is that some effects such as higher order corrections may be partially accounted for by comparing against stopping power data. However this approach is not acceptable when calculating other energy loss properties and particularly the inelastic cross sections.

The second paper describes the formation of DOSDs for silicon carbide and various solid oxides and the calculation of the energy loss properties of ions in the materials. This adds to the current materials for which electronic collision cross sections are available for Monte Carlo track structure simulations. The dependence of energy loss properties on the material type is explored in some depth.

Both papers clearly define the limits of validity of the model; these are above 0.1 MeV/u up to tens of MeV/u. At higher energy the difference between calculation and experiment is ~1 % rising to around 10-20 % as energy decreases to the energy of the Bragg Peak. Most developed programs according to Paul have 5-10 % errors at various energies, and this formalism is approaching this level [1]. Some effects which are known to change the energy loss properties of ions are not considered in the formalism as they fall outside the range of validity, for example elastic cross sections (giving energy loss properties for interactions with the target nucleus) and relativistic nuclear reactions.

5.1.2. Limitations

Higher order effects are not explicitly considered in this first iteration of the formalism. The Barkas-Anderson and Bloch corrections are the corrections due to the particle/anti-particle nature of the incident projectile (i.e. the sign of the incoming charge), and shell effects of the target, respectively. The formalism developed inherently compensates for the Bloch effect but not the Barkas-Anderson effect. Whilst it is possible to include the Barkas-Anderson effect into the treatment of stopping powers as a correction term [2], it is unclear how to incorporate these corrections into the inelastic cross sections (the focus of this study).

The nuclear contribution to stopping power is not considered in this model but is expected to be extremely small at the velocities considered in this work. Nuclear stopping is hard to obtain as experimental data since nuclear collisions often occur with large angular changes. Theory usually assumes decoupled electronic and nuclear collisions with negligible quantum and many-body effects: descriptions can be found in [3, 4]. Although the theory will not be discussed in detail here it is possible to use a semi-classical model posed by Ziegler [4] to give a description of nuclear stopping for an ion of mass $M$, charge $Z$ and incident energy $E$ into a target of mass $M_t$ and atomic number $Z_t$, as:

$$S_n(E) = \frac{\ln(1+1.1383E)}{2E[0.01322e^{-2/222}+0.19593e^{-5}]}$$  \hspace{1cm} (5.1)
where the reduced energy $\varepsilon$ is given by the description

$$\varepsilon = \frac{32.53 M_e E}{Z_1 (M+M_1)(Z^{23}+Z_e^{23})}.$$  \hspace{1cm} (5.2)

This approach is valid for a reduced energy less than $30 \text{ eV/u}$. Figure 5.1 shows the stopping power due to nuclear collisions and due to electronic collisions for lithium ions in ZrO$_2$, but the former only becomes an important contribution to the stopping power at energies below tens of eV. Models predicting energy loss properties at extremely low velocities must consider these nuclear collisions; these often utilise molecular dynamics models rather than Monte Carlo track structure simulations [5].

![Figure 5.1](image_url)

**Figure 5.1.** The nuclear and electronic contribution to stopping power as calculated for a proton in ZrO$_2$. The effect of nuclear collisions only occurs below the energy at which our code breaks down.

Another topic not considered in this work is the possibility of nuclear reactions. These will only occur at relativistic speeds of hundreds of MeV/u [3]. The losses which can occur at these energies can be large and were the model to be increased to include this range of energies, nuclear reactions would have to be considered.

As mentioned, crystalline materials can experience channelling effects. This is due to a part of the beam aligning with the crystal structure. This leads to less angular scattering and a reduction in energy loss [3]. The effect is small as Coloumbic interaction can act over the long-range required in these cases. Although this is still a field requiring considerable effort to understand the large, complex existing datasets, there are reports to suggest that charge equilibrium and energy loss properties can be affected [6]. The materials studied here were chosen for their use in the nuclear industry and in most of these cases the oxide will not be
used in a crystalline form with bulk density, but is amorphous and porous of much lower density. Therefore this effect will not be of great importance for this work.

5.2. Equilibrium Charge State Distribution of Ions Through Materials

5.2.1. Summary
The paper presented in Section 3 presents the measured equilibrium charge state fractions of lithium and helium ions in titanium, copper and zirconium. The relationship between the materials properties and the charge state fractions for light ions was investigated. This work presents new findings for charge state fractions of lithium and helium ions through titanium and zirconium thin films and confirms work done previously by Schmitt [7] for lithium ions through copper metals.

The charge state fractions' dependence on material properties was investigated. A correlation to the first ionisation potential was observed but an acceptable explanation of this is not currently available; this correlation should be explored in future experiments.

It has been postulated by Schmitt [7] and others that there is also a dependence of the equilibrium charge state distribution on the projectile electronic structure. It is suggested that as the ion becomes more ionised there is a shift in the mean charge measured, i.e. when electrons start being lost to the medium from the $L$ shell of the ion [8]. Thus we would not see this for helium ions. We do not see a dependence of this kind for lithium although this may be due to insufficient energy range [7].

5.2.2. Limitations
One of the limitations of measuring charge exchange fractions is that, as described in Appendix 3, they do not elucidate charge state cross sections. A normalising path length or cross section is still required to enable charge state fractions to be converted into charge state cross sections. An educated guess as to the characteristic path length of these interactions could be made from literature: for both protons in water, and carbon ions in carbon, charge exchange cross sections are of the order of $10^{-15}$ m$^2$ as given by Rudd [9] and Nikjoo [10] respectively.

In order to illustrate the difficulties in collecting charge exchange cross sections, an attempt was made to collate helium charge state fractions in water vapour. Helium and water vapour were chosen as the projectile and target respectively for their ubiquitous nature in nuclear power generation and also the large body of literature associated with both. Proton charge cycling cross section data have been collated previously by Pimblott from data provided by Rudd [9]. Data collection proved difficult and although attempts have been made, a full description was not been possible. The collated charge state cross sections are shown in Figure 5.2. This is not sufficient to run a Monte Carlo simulation of helium ions in water.
Figure 5.2. Charge cycling cross sections for helium in water vapour. Type of charge exchange is noted in the inset legend. Data in red is from Rudd [11], data in blue is from Greenwood [12] and data in black is from Seredyuk [13].

The work presented in this paper does not discuss whether the charge state as measured in this, and similar, experiments is truly the charge of the ion within the material i.e. the charge state is measured after exiting the solid. This issue has been debated extensively in literature, with some postulating that a higher mean charge is measured than actually occurs in the materials due to Auger electron emission on exit [3, 14]. This effect is suggested to be smaller for lighter ions and therefore the current method is probably acceptable even with this effect [15]. There has been an effort by some to avoid this and measure the charge state of ions before any emission. This has been attempted by measuring emerging H+ from water adsorbed on the front of surfaces under ion irradiation [16]. The underlying mechanism for these measurements is not yet understood, however further work could explore this area.

Further limitations of these measured charge state fractions stem from constraints on equipment. The energy of ions produced by the accelerator at Notre Dame is too high in some cases to capture lower charge state fractions, and this was particularly the case for helium ions, as seen in the paper only two energies were measured. This could only be improved by using a smaller accelerator. The ability for a second peak to be measured for ions coming into the AMS and hitting the Faraday cup on an un-suppressed surface caused inaccuracies with the first set of measurements undertaken in this work. This limitation significantly increases the time needed for measurement taking and should be changed.
This could be avoided by adding a metal sleeve onto the Faraday cup to avoid beam entering anywhere other than the top of the cup. Finally, calculation of charge state fractions using this method is reliant on the silicon detectors for normalisation of the beam. The limits on these detectors are well understood, however an improved method might involve a more precise understanding of the current in real time.

5.3. Hydrogen Production in Materials

5.3.1. Summary
The paper presented in Section 4.5 shows the radiolytic hydrogen produced for silicon carbide powder slurries under gamma irradiation. The paper also describes the characterisation of alpha and beta phase silicon carbide powders and the changes seen under differing LET radiation fields. The work presented here is new, with oxides having been the predominant focus of previous studies on hydrogen yields of nano-materials in aqueous solutions [17]. The presented results show that it is not just oxides that can elicit enhanced hydrogen production.

The G(H₂) measurements shown in this paper are for alpha phase - 6H, and beta phase - 3C, silicon carbide nanoparticles. Whilst these are the most common and most studied polytypes of silicon carbide there are many more (see Section 4). Even the alpha phase can correspond to either the 4H or 6H polytype depending on the source. Only small differences were seen with these two phases but it is unclear if all polytypes will behave similarly.

5.3.2. Limitations
Using the method described in Section 4.2 there is the possibility of loss of sample during purging of the glass vial (necessary in order to eliminate O₂ from the sample). Although efforts are taken to minimise this by careful insertion of the needle into slurries, it is impossible to avoid altogether. This introduces a small error in the calculation of the mass of the sample into the results, which would not be seen from a fully powder or fully liquid phase sample. It is estimated that this error is below the accuracy of the Gas Chromatograph measurements and is therefore not expected to have an effect on the results presented here.

Some of the characterisation results in the paper suggested that water should be present on the surface of the silicon carbide powders. There is also literature detailing some interaction of water with the surface of SiC [18, 19]. During the course of this project silicon carbide powder was taken straight from the vial and irradiated dry (at RTP). The resulting analysis showed no detectable hydrogen in the Gas Chromatograph, suggesting that the amount of water is extremely small, or does not interact with radiation in the same way as small numbers of water layers on oxides to produce excess hydrogen.
It has been suggested that LET of incident radiation could affect the generation of radiolytic hydrogen as shown by LaVerne and Tandon for gamma and alpha irradiation of ZrO$_2$ nanoparticles [20]. The different types of radiation absorbed by nanoparticles is not a variable taken into account in this experiment. However it would be interesting further work to verify if 5 MeV helium ions produce a yield of hydrogen which fits with the hypothesis of LaVerne and Tandon that at this energy powder composition is unimportant.

5.4. Future Directions

5.4.1. Energy Loss and Inelastic Cross Sections

This inelastic formalism does predict energy loss at high and intermediate energies however there are improvements to be made, for example attempting to mitigate the breakdown at lower energies and incorporating the Barkas-Anderson correction.

Attempting to mitigate the breakdown at low energies is not a simple change and may in fact prove to be fatal for the theory behind the formalism. As described in Section 2 this breakdown is due to the fundamental method used. We are taking optical data, which inherently has no momentum transfer involved in its acquisition, and then extending this to allow for momentum transfer. This leads to the model inaccurately predicting energy loss data at low incident ion energies when there are more likely to be large momentum transfers to the material. There are few ways to mitigate this breakdown apart from incorporating different formalisms at lower energies. Changes to the dielectric response function could improve the calculated energy loss properties however this would decrease the models ease of construction and use, requiring analysis of the optical data far above that done for this model [21].

There are papers detailing the implementation of the Barkas-Anderson correction into stopping power models however not into the inelastic cross sections [2]. Future development of this formalism should account for this correction in the inelastic cross section. It is expected this will improve the error seen around the energy of the Bragg peak.

Future work could explore improvements into the way the charge of the ion is expressed in the formalism. Currently an effective charge or a mean charge is used when calculating energy loss properties, as has been discussed extensively in this work. Effective charges could be made more ‘ion specific’ which may improve the result for stopping power, as Ziegler has shown with his highly empirical helium ion effective charge. Improving mean charge state empirical databases, such as Schwietz and Grande’s, could improve the mean charge state model. However, this is an undertaking to be completed by many academics over a period of years. The best improvement would involve using charge
exchange cross sections to calculate charge states for an ion at a given energy. Further measurements of these cross sections would benefit this work.

Perhaps the most important development of this code will be the use of calculated inelastic cross sections in the calculation of Monte Carlo track structure simulations. This would be done using a code developed by Pimblott to predict the track structure of electrons in materials, described in reference [22]. Monte Carlo simulation is a powerful tool to elucidate stochastic energy loss properties, and allows better descriptions of dose, range distributions and kinetics of chemical reactions to be developed. Once electronic collision cross sections and charge exchange cross sections are available then this Monte Carlo model can be easily and swiftly implemented.

5.4.2. Charge Exchange Cross Sections
Further work to obtain charge exchange cross sections would involve the continuation of measurement of cross sections for a wide range of both ions and materials, since it is clear that both the incident ion and the target material have an effect on the charge state obtained. The work in this thesis details some kind of relationship between material properties and charge state fractions. Further equilibrium charge state cross sections would serve to increase certainty (or disprove) the correlation found here for charge state fractions on the material on which the ion is incident. Work of this type is far too vast for one piece of work; rather it is for many researchers to undertake – which can then be collated. Future directions from this work could involve further collaboration with the University of Notre Dame to measure the charge state fractions of heavier ions.

The validation of current work is confirmed by Schmitt’s copper charge state fractions [23]. A further method for validation would be use of a different set-up to measure charge state fractions. This would verify that any results obtained are true representations and uncover any intrinsic bias in the current method. There have been experiments performed using time of flight techniques (TOF) which would serve this purpose, for example Jamecsny has evaluated charge states of neon and argon ions through gold [24].

Future work could involve development of a model to predict charge exchange cross sections. This overcomes the requirement for collating large databases. There has been previous work on this by Nikjoo who describes a Monte Carlo model to predict carbon ion charge exchange cross sections in water [10]. This compares well with the available data for carbon ions in water and neon but is awaiting further development. These models would negate the need for a description of the charge exchange of every ion in every material. Further initial work could include this preliminary cross section data in the formalism developed here.
Most charge cycling cross section experiments are performed on metal films or carbon. This is due to the difficulty in forming thin films of other materials, for example oxides. In the course of this project UO$_2$ thin films were attempted (see Section 3). From this attempt it can be concluded that UO$_2$ films (and by proxy other similarly brittle oxide films) are possible to form, however they require extra support such as a TEM film substrate behind the material film in question.

Furthermore this support should be thick enough to stop any ions penetrating through it. A support not of sufficient thickness to stop ions means ions passing through will undergo charge cycling and will confuse the measurement. It is not a simple matter of deconvolution since the resulting beam will be an unknown combination of both the thin film charge state fractions and the thin film + support charge state fractions. Deconvolution could certainly be performed if complete descriptions of the support film’s charge state fractions were known, by comparison to the charge state fractions found in combination. However, this would mean any backing would have to be a thin film. Further to this the combination of film and backing would also have to be a ‘thin film’. In practice this could not work, the support either being too thick to evade energy loss on passage through both the thin film and support or too flimsy to act as any kind of support.

5.4.3. Hydrogen Production on Silicon Carbide Particles

Whilst it might be interesting academically to investigate different phases of SiC to elucidate if phase differences correspond to large differences in H$_2$ generation, it would be more appropriate to look at different silicon carbide compounds. As described in Section 4 silicon carbide is of interest to the nuclear industry because of its radiation stability. Some of the uses include TRISO fuel where uranium is bound up with SiC and carbon [25]. An interesting further investigation would be to look at particles of all UO$_2$, SiC and C all together. This would add to the complication of the system, with 3 different materials, however the results would be more meaningful when comparing them to real life applications. It would also be interesting to look at other non-oxide semiconductor powders in use in the nuclear industry or of interest to other industries (e.g. silicon nitride).

In the same vein changes should be made to the water content in this experiment to better reflect in-reactor make-up or atmospheric conditions. The bromide added during this experiment is necessary in a closed system in order to prevent back reactions. The experiment can be run without this, however results are sometimes less reliable. In its place additions such as boron to imitate in-reactor water, or microbes to simulate atmosphere could be investigated.

The greatest limitation of this experiment is the potential loss of material when preparing the sample. An improvement to the equipment would be using a different method of preparing the samples. The Dalton Cumbria Facility research group is preparing a vacuum
set-up to evacuate tubes and adsorb water onto the surface of the powder. Although not yet operational it will allow samples to have a known volume of water adsorbed. This will have the added bonus that any measured gas in the Gas Chromatogram (i.e. oxygen or hydrogen) will be from irradiation. There are downsides to this method, slurries will not be able to be prepared and the number of water layers may be difficult to quantify given the small volumes in this preparation. Despite the downsides this would be a good direction for future work.

This experiment used powder of around 0.1 µm diameter. This is relatively large for experiments of this type. In LaVerne’s article [26] it is suggested that oxides of this size will not give results for this size of particle. However this paper shows hydrogen production in a consistent manner. It would be interesting to investigate whether smaller particle sizes give rise to larger amounts of hydrogen, as is the case with oxide powders. Larger sizes should also be considered, to evaluate if a limiting size occurs. It is anticipated this will become a surface area consideration. Once particles are too large then the energy transfer mechanism allowing excess hydrogen to be created will not be available as the surface of the particle is smaller.
References

Appendix 1. Kinematic Bounds and Construction of Inelastic Cross Section Formalism

The following details the kinematic bounds required to consider a heavy ion in a collision with electrons in a medium. Following this the construction of the formalism to calculate inelastic cross sections and energy loss properties in this research is presented.

Kinematics
An incoming ion of mass $M$ travelling with velocity $V$ in a medium will interact with the (bound) electrons in the materials, see Figure 1. After an (electronic) inelastic interaction we can express the result as below, with an electron from the system being given momentum $v_2$ and the incoming ion losing energy to both the electron and a quantity we label here as ‘binding’ energy to the system. In this formalism we use reduced mass of the ion $M = M/m$, and also reduced units $m = h = e = 1$.

![Figure 1. The electronic inelastic collision process of a heavy ion with mass M with an electron in the medium.](image)

According to conservation of energy we have:

$$\frac{MV^2}{2} = \frac{Mv_1^2}{2} + \frac{v_2^2}{2} + \gamma'$$  \hspace{1cm} (1)

When considering the electron and conservation of momentum we might consider 4 different scenarios. However only two of these are physically possible if the binding energy is understood to be greater than zero, $\gamma' > 0$. Therefore for the bounds of momentum on the electron are:

$$0 < M(V - v_1) \leq v_2 \leq M(V + v_1)$$  \hspace{1cm} (2)

Depending on whether the direction of $v_1$ is positive or negative. These limits are extrema; there is a possibility of angular dependence which will give intermediate values. It is also worth pointing out that $v_2 = p$ in this case as this work uses reduced units.

We can also define an energy loss of

$$\gamma = \frac{M}{2} (V^2 - v_1^2) > \gamma'$$  \hspace{1cm} (3)

And it is also pertinent here to re-express $v_1$ as this will be necessary in later calculations.
\[ v_1 = \sqrt{\frac{V^2 - 2y}{M}} \]  

(4)

The momentum inequality of equation (2) can be expanded by inserting our equation for \( v_1 \) in terms of \( V \) and \( \gamma \), and re-stating \( v_2 = \sqrt{2(\gamma - \gamma')} \):

\[
0 < M \left( V - \sqrt{V^2 - \frac{2y}{M}} \right) \leq \sqrt{2(\gamma - \gamma')} \leq M \left( V + \sqrt{V^2 - \frac{2y}{M}} \right)
\]  

(5)

Then the inequality can be squared, divided by 2 and \( \gamma \) can be subtracted to find the following expression:

\[
-\gamma < \frac{M^2}{2} \left( 2V^2 - 2V \sqrt{V^2 - \frac{2y}{M}} - \frac{y}{M} \right) \leq -\gamma' \leq \frac{M^2}{2} \left( 2V^2 + 2V \sqrt{V^2 - \frac{2y}{M}} - \frac{y}{M} \right) - \gamma
\]  

(6)

We can then simplify by cancelling the 2 and multiplying the whole inequality by -1 we can therefore express the bounds on ‘binding energy’ as:

\[
\gamma - M^2 \left( V^2 + V \sqrt{V^2 - \frac{2y}{M}} - \frac{y}{M} \right) \leq \gamma' \leq \gamma - M^2 \left( V^2 - V \sqrt{V^2 - \frac{2y}{M}} - \frac{y}{M} \right) < \gamma
\]  

(7)

So now a maximum binding energy contribution can be defined from equation (7)

\[
y_{\text{max}}' = \gamma - M^2 \left( V^2 - V \sqrt{V^2 - \frac{2y}{M}} - \frac{y}{M} \right) < \gamma
\]  

(8)

This is necessarily less than \( \gamma \). This is the maximum amount of energy that can be lost to the system in an inelastic collision between the ion and a bound electron. A minimum value of the binding energy can be found from the left hand side of the inequality in equation (7):

\[
y_{\text{min}}' = \gamma - M^2 \left( V^2 + V \sqrt{V^2 - \frac{2y}{M}} - \frac{y}{M} \right)
\]  

(9)

In order to find the limits on energy loss, \( \gamma \), the inequality for the binding energy can be rearranged. This requires an expansion of the square root term in this equality, which can be done if we understand that \( \gamma \ll \frac{MV^2}{2} \) the energy loss in this case will be much less than the initial kinetic energy. We are impacting a very large ion on a small electron; the ion isn’t going to lose much energy even if it gives the electron a lot of speed.

In this case we say that \( \sqrt{V^2 - \frac{2y}{M}} = V \sqrt{1 - \frac{2y}{MV^2}} \) so the term \( \frac{2y}{MV^2} \) will be small. We can apply Taylor expansion on this \( \sqrt{1 - \frac{2y}{MV^2}} = \left( 1 - \frac{2y}{MV^2} \right)^{1/2} \) expression. Taylor expansion means this becomes:

\[
\left( 1 - \frac{2y}{MV^2} \right)^{1/2} = 1 + \frac{1}{2} \left( -\frac{2y}{MV^2} \right) + \frac{1}{2} \left( -\frac{2y}{MV^2} \right)^2 = 1 - \frac{y}{MV^2} - \frac{y^2}{2M^2V^4}
\]  

(10)

This expression can now be put back into the inequality in equation (7):

\[
\gamma - M^2 \left( V^2 + V \left( 1 - \frac{y}{MV^2} - \frac{y^2}{2M^2V^4} \right) - \frac{y}{M} \right) \leq \gamma' \leq \gamma - M^2 \left( V^2 - V \left( 1 - \frac{y}{MV^2} - \frac{y^2}{2M^2V^4} \right) - \frac{y}{M} \right)
\]  

(11)
Take $V^2$ out of the brackets and simplify to give the limits on the binding energy as:

$$\gamma - M^2 V^2 \left(2 - \frac{2\gamma}{MV^2} - \frac{\gamma^2}{2M^2V^4}\right) \leq \gamma' \leq \gamma - M^2 V^2 \left(\frac{\gamma^2}{2M^2V^4}\right)$$  \hspace{1cm} (12)

This can be simplified further:

$$\gamma - 2M^2 V^2 + 2My + \frac{\gamma^2}{2V^2} \leq \gamma' \leq \gamma - \frac{\gamma^2}{2V^2}$$  \hspace{1cm} (13)

Taking the right hand side of this inequality we can define a quadratic expression from which we can find an equation for energy loss. This is found to be:

$$\gamma = V^2 \pm V\sqrt{V^2 - 2\gamma'}$$  \hspace{1cm} (14)

This allows us to define: $\gamma < V^2 + V\sqrt{V^2 - 2\gamma'} = \gamma_{\text{max}}$. We can use the right hand side of equation (13): $\gamma' \leq \gamma - \frac{\gamma^2}{2V^2}$, to define a region in the energy-energy plane which is valid for our inelastic collision. This is shown in Figure 2 and completes the kinematic considerations necessary for implementing this formalism.

**Figure 2. Energy-energy bounds which are valid in the case of an ion impacting on a bound electron.**

**Formalism for calculation of energy loss properties**

In order to develop this model we define first the probability of an ion undergoing an energy loss per unit distance. As shown by Ritchie [1], this can be described as

$$\tau(E, \gamma) = \frac{Z^2}{4\pi\varepsilon} \int \text{Im}[-1/\varepsilon(p, \gamma)]dp/p$$  \hspace{1cm} (15)

where $\text{Im}[-1/\varepsilon(p, \gamma)]$ is the imaginary part of the reciprocal of the complex dielectric response function for the material. It is more useful in the context of this work define the
electronic collision cross section: \( \sigma(E) = \frac{1}{N} \int \tau(E, \gamma) d\gamma \) corresponding to the probability of an energy loss even from this interaction, with the \( N \) number density of molecules in the medium.

The model developed here hinges on an approximation, first suggested by Ashley, to extend an energy loss function from the optical domain into one which can be used to predict material responses from particles. This approximation is:

\[
\text{Im} \left[ \frac{1}{\epsilon(p, \gamma')} \right] = \int \frac{\gamma'}{\gamma} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] \delta \left( \gamma - \left( \gamma' + \frac{p^2}{2} \right) \right) d\gamma'
\]

where \( \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] \) is the energy loss function formed from optical data. This can be into the equation (15) for the probability \( \tau(E, \gamma) \):

\[
\tau(E, \gamma) = \frac{Z^2}{\pi E} \int \frac{\gamma'}{\gamma} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] \delta \left( \gamma - \left( \gamma' + \frac{p^2}{2} \right) \right) d\gamma' dp/p
\]

In order to evaluate this equation the function must be integrated with respect to \( p \), this requires first changing the integration bounds. As \( v_2 = \sqrt{2(\gamma - \gamma')} \) and \( v_2 = p \) we can say that \( p^2/2 = (\gamma - \gamma') \) and we can take the natural log of both sides, leaving us with:

\[
\ln(p) = \frac{\ln(2)}{2} + \frac{\ln(\gamma - \gamma')}{2}
\]

When differentiating this we are left with: \( \frac{d\ln(p)}{d\gamma} = \frac{1}{2} \frac{dp}{p} \) we can also say trivially that \( \frac{d\ln(p)}{d\gamma} = \frac{1}{p} \frac{dp}{d\gamma} \)\( \frac{dp}{p} \). This means that the \( dp/p \) term becomes \( \frac{1}{2} \frac{dy}{\gamma - \gamma'} \) making the probability:

\[
\tau(E, \gamma) = \frac{Z^2}{\pi E} \int \frac{\gamma'}{\gamma} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] \delta \left( \gamma - \left( \gamma' + \frac{p^2}{2} \right) \right) d\gamma' \frac{1}{2} \frac{dy}{\gamma - \gamma'}
\]

The integrals can be treated in whichever order is preferred since they are symmetrical which we see from the work on the kinematics and Figure 2. This is helpful since the Dirac term relates to energy loss rather than binding energy. The shifting property of the Dirac is such that:

\[
\int f(x) \delta(x - T) dx = f(T)
\]

Therefore the probability becomes:

\[
\tau(E, \gamma) = \frac{Z^2}{2\pi E} \int \frac{\gamma'}{\gamma} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] d\gamma'
\]

Which when simplified becomes:

\[
\tau(E, \gamma) = \frac{Z^2}{2\pi E} \int \frac{\gamma'}{\gamma} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] d\gamma'
\]

The cross sections is of more interest in this work. This is simply \( \frac{1}{N} \int \tau(E, \gamma) d\gamma \) or in other words:

\[
\sigma(E) = \frac{1}{N} \frac{Z^2}{2\pi E} \int \frac{\gamma'}{\gamma} \text{Im} \left[ \frac{1}{\epsilon(0, \gamma')} \right] d\gamma'
\]
Now with an understanding of the limits on this integral we can calculate the cross section. The total inelastic cross section is calculated by integrating over the whole of the energy plane. Equation (23) can be re-expressed:

$$\sigma(E) = \frac{Z^2}{2\pi EN} \int_{y_{\text{min}}}^{y_{\text{max}}} \text{Im} \left[ \frac{1}{e(0,y')} \right] \int_{y_-}^{y_+} \frac{1}{y-y'} \, d y'$$

(24)

When first considering the energy loss integral (the right hand side term), this can be integrated to obtain:

$$\int \ln \left( \frac{y-y'}{y} \right) \, dy'$$

(25)

Which, when evaluated becomes:

$$\ln \left( \frac{y_{\text{max}}-y_1}{y_{\text{min}}-y_1} \right)$$

(26)

It is therefore necessary to define what $y_+$ and $y_-$ are. In the case of calculating the total area under our energy-energy curve then the definitions are quite simple, since $M \gg m$:

$$y_+ = v^2 \left( 1 + \sqrt{1 - 2y' / V^2} \right)$$

(27)

$$y_- = v^2 \left( 1 - \sqrt{1 - 2y' / V^2} \right)$$

(28)

This means the total inelastic cross section for an ion of incident energy $E$ is:

$$\sigma(E) = \frac{Z^2}{2\pi EN} v_{\text{max}} \text{Im} \left[ \frac{1}{e(0,y')} \right] \int_{y_{\text{min}}}^{y_{\text{max}}} \ln \left( \frac{1+\gamma s(1-s)}{1-\gamma s(1+s)} \right) \, d y'$$

(29)

with $a = y' / V^2$ and $s = \sqrt{1 - 2y' / V^2}$. The maximum/minimum possible values for the binding energy are also known in this case. These are $y_{\text{max}} = V^2 / 2$ and $y_{\text{min}} = 0$. As can be clearly seen in Figure 2.

If we want to evaluate the cumulative cross section then, if we have an energy below $V^2$, we are able to use the same equation with appropriate limits. But for energies above this we have to approach the problem slightly differently. We can either evaluate the entire cross section $\sigma(E, E_{\text{max}})$ and then subtract the cross section area from the energy to the higher limit (the singly hashed area in the Figure 1). Or we can take energy up to the $V^2$ then evaluate the cross section from this to the energy required. When choosing the first option, for energies $0 \leq E' \leq V^2$, we define the integral for cross section with $y_+ = E'$:

$$\sigma(E, E') = \frac{Z^2}{2\pi EN} v_{\text{max}} \text{Im} \left[ \frac{1}{e(0,y')} \right] \int_{y_{\text{min}}}^{y_{\text{max}}} \ln \left( \frac{1+\gamma s(1-s)}{1-\gamma s(1+s)} \right) \, d y'$$

(30)

We consider $y_- = V^2 \left( 1 - \sqrt{1 - 2y' / V^2} \right)$ so we can re-express the energy loss integral as:

$$\sigma(E, E') = \frac{Z^2}{2\pi EN} v_{\text{max}} \text{Im} \left[ \frac{1}{e(0,y')} \right] \ln \left( \frac{(E' - y') V^2 \left( 1 - \sqrt{1 - 2y' / V^2} \right)}{V^2 \left( 1 - \sqrt{1 - 2y' / V^2} \right) E'} \right) \, d y'$$

(31)

134
Which can be re-expressed as

\[
\sigma(E, E') = \frac{2^2}{2\pi E N} \int_{r_{\min}}^{r_{\max}} \text{Im} \left[ -\frac{1}{\varepsilon(0, \gamma')} \right] \ln \left[ \frac{(b-1)(1-s)}{(1-s-a) \gamma} \right] d\gamma'
\]

where \( b = \frac{E'}{\nu^2}, \ a = \gamma' / \nu^2 \) and \( s = \sqrt{1 - 2\gamma' / \nu^2} \).

References
Appendix 2. Energy Loss Properties FORTRAN code

This appendix presents the code used in this work. Started by S. M. Pimblott prior to the start of this PhD, changes have been made by the Author throughout the code, with particularly significant modifications to the subroutines ‘nuclear’ and ‘Zeff’.

```fortran
program cross_sectn
  
c  Program to evaluate Heavy Ion cross-sections
  
  include 'param.h'
  
c  parameter (maxe = 99)
  
  implicit double precision (a-h,o-z)
  
dimension ea(0:600)
  character*1  ans
  character*64 oscfile, yfile, charge
  
  common/bins/ea
  common/consts/avn,pi
  common/param/rho,wmol,zmed
  common/parion/aw,zhi,charge
  
write(6,*) 'Constants'

  pi = 3.14159265
  
  Avogadro's number
  avn=6.02252e23
  
write(6,*) 'Program set up'
  
Energy bins
  call ebins
  
write(6,*) ' Initial conditions'

  iin = 5
  
write(6,*) ' Heavy ion atomic weight '
  read(iin,*) aw
  
write(6,*) ' Heavy ion charge '
  read(iin,*) zhi
  
write(6,*) ' DOSD file '
  read(iin,'(A64)') oscfile
  call oscfunc(oscfile)
  
charge exchange
  read(iin,'(A64)') charge
  
goto 10
  
write(6,*) ' Inelastic cross-section file '
  read(iin,'(A64)') yfile
  
write(6,*) ' Does the Yfile exist ? '
  read(iin,'(A1)') ans
  
ans='N'
  if((ans.eq.'Y').or.(ans.eq.'y'))then
    call yread(yfile)
  
ext
```

136
do i=45,maxe
  if((i.lt.40).or.(i.gt.100)) stop 'error'
  eincident = 10.0**(0.1*dble(i))
call ycalc(eincident)
end do

call ywrite(yfile)
c end if
c
write(6,*)' Differential Y functions'
call difedist
c
write(6,*)' Mean free path'
call mfp
continue

c
write(6,*)' Stopping power : equation'
do i=45,maxe
  eincident = 10.0**(0.1*dble(i))
call let(eincident)
end do
continue

c
write(6,*)' Stopping power : single collision'
call stop_pwr
continue

subroutines

subroutine let(ehi)

implicit double precision (a-h,o-z)
dimension rlet(0:100)
dimension xos(0:2000), yos(0:2000)
common/consts/avn,pi
common/param/rho,wmol,zmed
common/osd/xos,yos
common/stpr/rlet
common/parion/aw,zhi,charge

am = 9.1091e-28
pm = 1.67265e-24
c = 2.997925e10
cc = 1.60219e-12
ee = 4.80298e-10
e=ehi*am*avn/(aw)
ratm = 1./(am*avn/aw)
dens=avn*rho/wmol
call Zeff(ehi, effz)

chi = pi * ee * ee * ee * zhi * zhi * effz * effz / cc

Define energy bounds
Maximum energy loss
emax = 4. * e

E/2
eby2 = 2. * e

write(6,*)' Stopping power : Method 1 '

elim = emax
sum = 0.0
xold = xos(1)
yold=0.0
j=2

wmax = 0.5*eby2
do while (xos(j).le.wmax)
wp = xos(j)
write(6,*) wp, e
y = yos(j) * funcm( wp, eby2 )
sum = sum + 0.5 * (xos(j)-xold) * (y + yold)
yold = y
xold = xos(j)
j = j+1
end do

if(xos(j).gt.wmax)then
grad = (yos(j)-yos(j-1))/(xos(j)-xos(j-1))
const = yos(j-1) - grad*xos(j-1)
y = grad*wmax + const
y = y * funcm( wmax, eby2)
sum = sum + 0.5 * (wmax-xos(j-1)) * (y + yold)
yold = y
xold = wmax
end if

prerlet = sum

beta2 = 1.0-1.0/((1.0+(e*cc)/(am*c*c))*(1.0+(e*cc)/(am*c*c)))
ekin = 0.5 * am * c * c * beta2

ie = nint(log10(ehi)*10.)
call nuclear(ehi,stopadd)
rlet(ie) = dens * prerlet * chi / ekin
300 continue
return
end

subroutine ycalc(ehi)

implicit double precision (a-h,o-z)
dimension ea(0:600), yf(0:600,0:100)
dimension sigin(0:100), xsectn(0:600)
dimension xos(0:2000), yos(0:2000)
common/bins/ea
common/consts/avn,pi
common/osd/xos,yos
common/insectn/sigin
common/yxsectn/yf
common/parion/aw,zhi,charge

am = 9.1091e-28
pm = 1.67265e-24
c = 2.997925e10
cc = 1.60219e-12
ee = 4.80298e-10

c write(6,*) ' Effective charge'
call Zeff(ehi, effz)

chi = pi * ee * ee * ee * ee * zhi * zhi * effz * effz / cc

c ie = nint(log10(ehi)*10.0)

c write(6,*) ' Reduced energy'
e = ehi * am * avn / (aw)

c write(6,*) ' Define energy bounds '

Maximum energy loss:
emax = 4. * e
call eindex(emax, imax)
if(emax.lt.ea(imax)) imax = imax - 1
if(emax.gt.1.e6) then
  stop 'emax'
end if

c E/2

eby2 = 2. * e
call eindex(eby2, iby2)
if(eby2.lt.ea(iby2)) iby2 = iby2 - 1

c write(6,*) ' Total cross-section : Method (1)'

c elim = emax
sum = 0.0
xold = xos(1)
yold = 0.0
j = 2

c wmax = 0.5 * eby2

do while (xos(j).le.wmax)
  wp = xos(j)
  y = yos(j) * funcn(wp, eby2)
  sum = sum + 0.5 * (xos(j) - xold) * (y + yold)
  yold = y
  xold = xos(j)
  j = j + 1
end do

c if((xos(j-1).lt.wmax).and.(xos(j).gt.wmax)) then
  grad = (yos(j) - yos(j-1))/(xos(j) - xos(j-1))
  const = yos(j-1) - grad*xos(j-1)
  y = grad*wmax + const
  y = y * funcn(wmax, eby2)
  sum = sum + 0.5 * (wmax - xos(j-1)) * (y + yold)
  yold = y
  xold = wmax
end if

c sigin(ie) = sum

c 100 continue

c write(6,*) ' Cumulative cross-section '

c 0 < E' < v2

do i = 1, iby2
  wmax = ea(i)*((1.0-ea(i))/emax)
  sum = 0.0
  xold = xos(1)
do while (xos(j).le.wmax)
  ycold2 = y
  wp = xos(j)
  func = funcp(ea(i), wp, eby2)
  y = yos(j) * func
  add = 0.5 * (xos(j)-xold) * (y + yold)
  sum = sum + add
  yold = y
  xold = xos(j)
  j = j+1
end do
if((xos(j-1).lt.wmax).and.(xos(j).gt.wmax))then
  grad = (yos(j)-yos(j-1))/(xos(j)-xos(j-1))
  const = yos(j-1) - grad*xos(j-1)
  func = funcp(ea(i), wmax, eby2)
  y = y * func
  add = 0.5 * (wmax-xos(j-1)) * (y + yold)
  sum = sum + add
  yold = y
  xold = wmax
end if

xsectn(i) = sum
if(sigin(ie).le.0.0)then
  yf(i,ie) = 1.0
else
  yf(i,ie) = xsectn(i)/sigin(ie)
end if
end do
3E/4 < E' < E
do i = iby2+1,imax
  wmax = ea(i)*(1.0-ea(i)/emax)
  sum = 0.0
  xold = xos(1)
  yold=0.0
  j=2
  do while (xos(j).le.wmax)
    ycold2 = y
    wp = xos(j)
    func = funcq(ea(i), wp, eby2)
    y = yos(j) * func
    add = 0.5 * (xos(j)-xold) * (y + yold)
    sum = sum + add
    yold = y
    xold = xos(j)
    j = j+1
  end do
  if((xos(j-1).lt.wmax).and.(xos(j).gt.wmax))then
    grad = (yos(j)-yos(j-1))/(xos(j)-xos(j-1))
    const = yos(j-1) - grad*xos(j-1)
    func = funcq(ea(i), wmax, eby2)
    y = y * func
    add = 0.5 * (wmax-xos(j-1)) * (y + yold)
    sum = sum + add
    yold = y
    xold = wmax
  end if
xsectn(i) = sum
if(sigin(ie).le.0.0)then
  yf(i,ie) = 1.0
else
  yf(i,ie) = 1.0-xsectn(i)/sigin(ie)
end if
end do

do i = imax+1,600
  yf(i,ie) = 1.0
end do

continue

beta2 =1.0-1.0/((1.0+ (e*cc)/(am*c*c))*(1.0 +(e*cc)/(am*c*c)))

ekin = 0.5 * am * c * c * beta2

sigin(ie) = sigin(ie) * chi / ekin

return
end

------------------------------------------------------------------
subroutine ebins

implicit double precision (a-h,o-z)
dimension ea(0:600)
common/bins/ea

do i=0,600
  ea(i)=10.0**(dble(i)*0.01)
end do

return
end

-------------------------------------------------------------------
subroutine eindex(e,ie)

implicit double precision (a-h,o-z)
dimension ea(0:600)
common/bins/ea

ie=int(log10(e)*100.)
return
end

---------------------------------------------------------------------
subroutine nuclear(ehi,stopadd)

implicit double precision (a-h,o-z)
common/consts/avn,pi
common/param/rho,wmol,zmed
common/parion/aw,zhi,charge

a0 = 5.29e-09
rede=32.53*wmol*ehi/(zmed*zhi*(aw+wmol)*(zhi**0.23+zmed**0.23))

if (rede.le.30) then
  stopa=log(1.+1.1383*rede)
  stopadd=stopa/(2*(rede+0.1321*rede**0.21226+0.19593*rede**.5))
else if (rede.gt.30) then
  stopadd=log(rede)/(2*rede)
end if

return
end

-----------------------------------------------------------------------
subroutine mfp

include 'param.h'
implicit double precision (a-h,o-z)
dimension rmfp(0:100)
dimension signin(0:100)
common/consts/avn,pi
common/insectn/signin
common/lambda/rmfp
common/param/rho,wmol,zmed

dens=avn*rho/wmol

do i=45,maxe
    if(sigin(i).gt.0.0)rmfpi(i)=1.0/(dens*sigin(i))
    write(1,1002)10.0**(0.1*dble(i)),sigin(i),rmfpi(i)
end do

close(1)
return
end

-----------------------------------------------
subroutine stop_pwr

include 'param.h'
implicit double precision (a-h,o-z)
dimension y(0:600,0:100)
dimension ea(0:600), rmfp(0:100)
dimension rlet(0:100)
common/bins/ea
common/yxsectn/y
common/lambda/rmfp
common/stop/rlet

c
iin=3
open(iin,file='cross_stop.res',status='unknown')

do i=45,maxe
    e = 0.5*(ea(j)+ea(j-1))
    en = en+e*(y(j,i)-y(j-1,i))
    en2 = en2 + e*e*(y(j,i)-y(j-1,i))
end do

if(rmfp(i).gt.0.0)then
    stopp=en/rmfp(i)
else
    stopp=0.0
end if

fano = en2/en - en
epi = 10.0**(0.1*dble(i))
call Zeff(epi, effz)
write(iin,2000) epi, stopp, rlet(i), effz
2000   format(5(2x,e11.4))
end do

close(iin)
return
end

-----------------------------------------------------------------------
subroutine yread(yfile)
include 'param.h'

implicit double precision (a-h,o-z)
dimension y(0:600,0:100), sigin(0:100)
character*64 yfile
common/ylsectn/y
common/insectn/sigin

ii=3

open(ii, file=yfile, status='unknown', access='direct', form='unformatted', recl=4816)

do i=45,maxe
    read(ii,rec=i)(y(j,i),j=0,600),sigin(i)
end do

close(3)
return
end

-----------------------------------------------------------------------

subroutine ywrite(yfile)

include 'param.h'
implicit double precision (a-h,o-z)
dimension y(0:600,0:100), sigin(0:100)
character*64 yfile
common/ylsectn/y
common/insectn/sigin

ii=3
open(ii, file=yfile, status='unknown', access='direct', form='unformatted', recl=4816)

do i=45,maxe
    write(ii,rec=i)(y(j,i),j=0,600),sigin(i)
end do

close(3)
return
end

-----------------------------------------------------------------------

subroutine oscfunc(osfile)

implicit double precision (a-h,o-z)
dimension ea(0:2000)
dimension xi(0:2000), x1(0:2000)
dimension yi(0:2000), y1(0:2000)
character*15 title
character*64 osfile
common/osd/x1,y1
common/param/rho,wmol,z

ii=3

open(ii, file=osfile, status='unknown')

read(ii,'(A15)')title
read(ii,*)z
read(ii,*)wmol
read(ii,*)rho
read(ii,*)etac
read(ii,*)eo2
read(ii,*)max
read(ii,*)l1
read(ii,*)l2
read(ii,*)l3
read(ii,*)l4
read(ii,*)l5
read(ii,*)l6
do i=1,max
    read(iin,*)xi(i),yi(i)
end do

close(3)
do i=0,600
    ea(i)=10.0**(dble(i)*0.01)
end do
imax = 600
i = 1
j = 0
ind = 1
do while ((j.le.imax).and.(i.le.max))
    if(ea(j).lt.xi(i))then
        x1(ind) = ea(j)
        grad = (yi(i)-yi(i-1))/(xi(i)-xi(i-1))
        const = yi(i-1) - grad*xi(i-1)
        y1(ind) = grad*ea(j) + const
        j = j+1
        ind = ind+1
    else if(ea(j).ge.xi(i))then
        x1(ind) = xi(i)
        y1(ind) = yi(i)
        ind = ind+1
        i = i +1
    end if
end do
return
end

c----------------------------------------------------------------------------
function funcm(eprime,e)
implicit double precision (a-h,o-z)
a=eprime/e
if(a.lt.0.5d0)then
    s=sqrt(1.0d0-2.0d0*a)
    funcm=-log(1.0-a-s) + log(1.0+s)
else
    funcm = log(1.0)
end if
return
end

c----------------------------------------------------------------------------
function funcn(eprime,e)
implicit double precision (a-h,o-z)
a=eprime/e
s=sqrt(1.0d0-2.0d0*a)
if(a.lt.0.5d0)then
    funcn=(1.0/eprime)*((log(1.0-s)+log(1.0-a+s)-log(1.0-a-s)-log(1.0+s)))
else
    funcn=log(1.0)
end if
return
end

c----------------------------------------------------------------------------
function funcp(eprime,wprime,e)
implicit double precision (a-h,o-z)
a=wprime/e
b=eprime/e
s=sqrt(1.0d0-2.0d0*a)
funcp=(1.0/e)*(1.0/a)*(log(b-a)-log(b)+log(1.0-s)-log(1.0-a-s))
function funcq(eprime,wp rime,e)
    implicit double precision (a-h,o-z)
    a=wprime/e
    b=eprime/e
    s=sqrt(1.0d0-2.0d0*a)
    funcq=(1.0/e)*(1.0/a)*(-log(b-a)+log(b)+log(1.0-a+s)-log(1.0+s))
    return
end

subroutine difedist
    implicit double precision (a-h,o-z)
    dimension y(0:600,0:100)
    dimension ea(0:600)
    dimension sigin(0:100)
    character*1 ans
    character*64 file
    common/bins/ea
    common/yxsectn/y
    common/insectn/sigin
    open(2,file='ave.dat', status='unknown')
    write(6,*) ' Particle energy ?'
    read(5,*) pe
    i = nint(log10(pe )*10.)
    write(6,*) ' Filename ?'
    read(5,50) file
    50 format(a64)
    iin=3
    open(iin,file=file,status='unknown')
    ave = 0.
    do j=1,600
        en = 0.5*(ea(j)+ea(j-1))
        de = (ea(j)-ea(j-1))
        dyde = (y(j,i)-y(j-1,i))/de
        if(j.gt.1)ave = 0.5*(en-enold)*(en*dyde+enold*dydeold)+ave
        enold=en
        dydeold=dyde
        write(iin,2000) en, dyde, en*dyde
    end do
    2000 format(3(2x,e11.4))
    write(2,*) pe, ave
    close(iin)
    write(6,*) ' Again ?'
    read(5,51) ans
    51 format(a1)
    if((ans.eq.'y').or.(ans.eq.'Y')) goto 100
    close(2)
    return
end
subroutine Zeff(ehi, effz)
implicit double precision (a-h,o-z)
common/consts/avn,pi
common/param/rho,wmol,zmed
common/parion/aw,zhi,charge
conversion factors from SI to CGS
am = 9.1091e-28
pm = 167265e-24
c = 2.997925e10
cc = 1.60219e-12
ee = 4.80298e-10
a0 = 5.29e-09
hbar = 1.05445e-27
vf = (hbar/am)*((3.*pi*avn*rho*zmed/wmol)**0.3333)
Ion velocity
v = sqrt((2.0*cc*ehi*avn)/aw)
v0 = ee * ee / hbar
if(v.ge.vf)then
  vr = v*(1.+0.2*((vf/v)**2))
else if (v.lt.vf) then
  vr = 0.75*vf*(1.+2.*v*v/(3.*vf*vf)-(1./15.)*(v/vf)**4.)
end if
zhi3d=zhi**0.3333
zhi23rd=zhi**0.66667
yr=v0*zhi23rd
yr=vr/yr
Northcliffe
gammaN = (1.0-1.85*exp(-2*v/v0))**0.5
P & B
gammapb = (1.0-exp(-0.95*yr))
Bloom and Sauter
gammabs = (1.0-exp(-6.35*sqrt(ehi*1.e-6/aw)/(zhi**0.6667)))
Ziegler et al. vol 1 for He2+
he0=1.0
he = dmax1(he0,ehi*1.d-3)
b = log(he/aw)
a = .2865+0.1266*b-0.01135*b**4+0.001475*b**5
heh = 1.-exp(-dmin1(30.d0,a))
effzhe = heh**0.5
Ziegler for heavier ions
effzz=(1.0-exp(-0.95*(yr-0.07)))
hNzi=zhi*(1.0-effzz)
if (hNzi.le.1.) then
  hlamdazi=(3.*a0)/(2.*zhi)
else if (hNzi.le.2.) then
  hlamdazi=(3.*a0)/((2.*zhi)-0.6)
else if (hNzi.gt.2.) then
  ratiozi=hNzi/zhi
  zhi3d=zhi**0.3333
  ratio23dzi=ratiozi**0.6667
  underzi=1.-(ratiozi/7)
  hlamdazi=(0.48*a0*ratio23dzi)/(zhi3d*underzi)
end if
hiddzi = (2.0*hlamdazi*vf)/(a0*v0)
hdzi = 1. + (hiddzi*hiddizi)
gammazi= effzz + (1.-effzz)*(v0/vf)**(v0/vf)*0.5*log(hdzi)
Schiwietz et al. 2001 and 2004

\[ vmpers=sqrt(2*ehi*cc*avn/(aw*10000)) \]

\[ vb=2.19*(10^{10}) \]

if (zhi.le.2) then
  if (vmpers/vb.gt.2) then
    \[ scp=(vmpers/vb)*(zhi^{(-0.543)}) \]
    \[ c1=1-(0.26*exp(-((zmed/11.))*exp(-((zmed-zhi)**2)/9.))) \]
    \[ c2=1+(0.030*scp*log(zmed)) \]
    \[ xsg=c1*((scp/c2)/1.54)**(1+1.83/zhi) \]
    \[ gammasg=2*((8.29*xsg+xsg**4)/((0.06/xsg)+4.+(7.4*xsg)+xsg**4)) \]
  else
    gammasg=0
    write(6,*) 'ratio too small'
  end if
else if (zhi.gt.2) then
  if (vmpers/vb.gt.0.4) then
    \[ scp=(vmpers/vb)*(zhi^{(-0.543)}) \]
    \[ c1=1-(0.26*exp(-((zmed/11.))*exp(-((zmed-zhi)**2)/9.))) \]
    \[ c2=1+(0.030*scp*log(zmed)) \]
    \[ xsg=c1*((scp/c2)/1.54)**(1+1.83/zhi) \]
    \[ gammasg=((8.29*xsg+xsg**4)/((0.06/xsg)+4.+(7.4*xsg)+xsg**4)) \]
  else
    \[ scp=(vmpers/vb)*(zhi^{(-0.543)}) \]
    \[ c1=1-(0.26*exp(-((zmed/11.))*exp(-((zmed-zhi)**2)/9.))) \]
    \[ c2=1+(0.030*scp*log(zmed)) \]
    \[ xsg=c1*((scp/c2)/1.54)**(1+1.83/zhi) \]
    \[ gammasg=((8.29*xsg+xsg**4)/((0.06/xsg)+4.+(7.4*xsg)+xsg**4)) \]
    write(6,*) 'ratio too small'
  end if
end if
eff = 1.
if(charge.eq.'N')then
effz=gammaN
else if (charge.eq.'pb') then
effz=gammapb
else if (charge.eq.'bs') then
effz=gammabs
else if (charge.eq.'zi') then
effz=gammazi
else if (charge.eq.'he') then
effz=effzhe
else if (charge.eq.'sg') then
effz=gammasg
else
  write(6,*) 'true charge'
effz=eff
end if
return
end
Appendix 3. Charge Exchange Cross Sections

If single-collision cross sections are assumed ($|\Delta q| = 1$) then the variation of charge of an ion passing through a material can be described as a series of differential equations

$$\frac{dF_q}{dx} = \sum q' \sigma_{q' q} F_q(x) - \sigma_{q q'} F_q(x)$$  \hspace*{1cm} (1)

where $F_q$ is the fraction of ions in the $q$ charge state after passage through $x$ thickness of a material. $\sigma_{q' q}$ is the probability that ions in the $q'$ will exchange electrons to become $q$ and $\sigma_{q q'}$ is the probability that ions will start in the $q$ state and transition to the $q'$ state after passage through the material. This is valid for the range $-1 \leq q \leq Z$ for an ion of atomic charge $Z$.

For a system with just 2 possible charge states this differential equation (1) becomes simple to solve. For the case of hydrogen only the 0 and +1 charge states will be populated above a few hundred keV, therefore equation (1) can be re-stated for the fraction of neutral ions after passing through a thin film

$$dF_0 = (\sigma_{10} F_1 - \sigma_{01} F_0) dx$$ \hspace*{1cm} (2)

Since we only have two possible charges we can redefine $F_1 = 1 - F_0$ and therefore solve to find $F_0$

$$\int_{F_0 \rightarrow 0}^{F_0} \frac{dF_0}{(\sigma_{10} - F_0)[\sigma_{10} + \sigma_{01}]} = \int_0^x dx$$ \hspace*{1cm} (3)

$$F_0 = e^{-(\sigma_{10} + \sigma_{01})x} \left( F_0 \rightarrow 0 - \frac{\sigma_{10}}{\sigma_{10} + \sigma_{01}} \right) + \frac{\sigma_{10}}{\sigma_{10} + \sigma_{01}}$$ \hspace*{1cm} (4)

where $F_0 \rightarrow 0$ is the fraction of ions that do not change from the neutral state on passage through the film. As this case concerns only two charge states this allows us to define

$$F_1 = e^{-(\sigma_{10} + \sigma_{01})x} \left( \frac{\sigma_{10}}{\sigma_{10} + \sigma_{01}} - F_0 \rightarrow 0 \right) + \frac{\sigma_{01}}{\sigma_{10} + \sigma_{01}}$$ \hspace*{1cm} (5)

Where we apply equilibrium conditions ($x(\sigma_{10} + \sigma_{01}) > 1$) the exponential term will become negligible and the charge state fractions can be expressed

$$F_0 = \frac{\sigma_{10}}{\sigma_{10} + \sigma_{01}}$$ \hspace*{1cm} (6)

$$F_1 = \frac{\sigma_{01}}{\sigma_{10} + \sigma_{01}}$$ \hspace*{1cm} (7)

$$\frac{F_0}{F_1} = \frac{\sigma_{10}}{\sigma_{01}}$$ \hspace*{1cm} (8)

The case of ions with more charge states is more complex and will not be shown here although for more information see [1, 2]. A full description of charge state cross sections would allow charge state fractions to be determined, however the opposite does not hold as is clear from equation (8).
References
Appendix 4. The Possibilities of Measuring Neutral Charge States

One of the limitations of charge cycling experiments is the measurement of neutral charge states. This can prove challenging in an accelerator which produces positive ions. Experimenters are frequently left in a position where they must ascribe a nil measurement to the neutral beam portion of charge states which is not an ideal solution. Protons have either a charge state 0 and +1 (and -1 which only occurs so rarely as to be discounted in this experiment). This makes them uniquely suited to overcoming this in charge cycling experiments, giving only a binary signal after traversing through the thin film. In collaboration with P. Petrov at Imperial an idea was in development to use their patterning machine to produce neutral beams.

The machine at Imperial uses an RF source (of up to 150 V) to produce a plasma of the desired gas. This plasma is contained by a grid at one end set to +500 V allowing only energetic ions to pass through. There is a second grid set at -200 V to accelerate the ions onto the sample (Direction grid). The ions are neutralised after passing a high current filament. To verify this has resulted in a neutral beam, a plate is put in front of the sample and the current is measured with a milliammeter (shield). As the filament current is raised the resulting beam current will become neutral. The proposed apparatus is shown below in Figure 1. The maximum potential of the limiting grid is 1 kV and the area of the beam is 5 cm, with the holder for the sample being 3 cm².

![Figure 1. Basic set-up of the patterning chamber at Imperial. Whilst not ideal this could be useful to produce neutral beams.](image)

There are some problems which we have identified with the set-up. We would need to be sure all the ions are neutralised and we are truly seeing a neutral beam. For this we would use two pico-ameters for our experiment rather than the 1 milli-ammeter already attached. We would also put in a magnetic field to deflect any convoy electrons. Imperial has never used hydrogen in its machine which would be a problem for us. The sample would also need to be insulated from the rest of the machine, as shown below in Figure 2.
This could be done with polymer glue or perhaps etched silicon carbide. Imperial also cannot use UO$_2$ in their machine.

![Diagram of a scientific apparatus with labels: shutter, Aluminium with gold, Thin film, Insulating mount, and pA.]

**Figure 2. The changes that would need to be made to the apparatus at Imperial.**

This challenge was considered as an opportunity to use as a proof of principle with helium and carbon films. However due to time-constraints this project was never taken further. This would be a good PhD project for someone interested in charge exchange methods as it is novel and will access low energies where we expect to see elevated low charge state fractions.
Figure 1. Pertaining to Section 3.3. An example of the output from the silicon detector used in the normalisation of the beam during charge exchange experiments at Notre Dame.
Figure 2. Pertaining to Section 4.2. An example of the XRD changes seen pre and post irradiation of SiC powders with He ions. Little change is seen with this irradiation.
Appendix 6. List of Conferences, Posters and Presentations

The following details in chronological order the conferences attended, and the posters and presentations given during the research period, in addition to the awards received by the Author.

**Winter School Nuclear FiRST** (January 2012)

**Materials challenges for nuclear fission seminar** (November 2012)

**Energy network conference** (November 2012) - *Poster and group Presentation*

**Winter Schools Nuclear FiRST** (January 2013) - *Prize for best Poster*

**Nuclear Materials: the role of thin films/Actinide thin film meeting** (March 2013)

**Miller Conference on Radiation Chemistry** (March 2013) - *Poster*

**Winter Schools Nuclear FiRST** (January 2014) - *Presentation*

**EmiT emerging Technology Conference** (April 2014)

**Gordon Conference on Radiation Chemistry** (July 2014) - *Discussion leader for the Gordon Research Conference and Poster*

**Winter Schools Nuclear FiRST** (January 2015) - *Presentation*

**Miller Conference on Radiation Chemistry** (March 2015) - *Invited speaker and Baxendale Bursary Award.*

**End of Year School of Chemistry PhD talks** (May 2015) - *Prize for best Presentation in Computation section*