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Influence of the Cr^{5+} ion on the magnetic properties of YbCrO_4 oxide

E. Jimenez^{a,*}, P. Bonville^b, J.A. Hodges^b, P.C.M. Gubbens^c,
J. Isasi^a, R. Saez-Puche^a

^aDpto. Q. Inorganica, Fac. C. Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040-Madrid, Spain

^bCEA Saclay, DSM/DRECAM, Service de Physique de l'Etat Condensé, 91191 Gif-sur-Yvette, France

^cInterfacultair Reactor Instituut, TUDelft, Mekelweg 15, 2629 JB-Delft, The Netherlands

Abstract

The magnetic properties of the YbCrO_4 oxide have been studied by both bulk magnetic measurements and ^{170}Yb Mössbauer spectroscopy. Ferrimagnetic ordering is shown to be present below 25 K, driven by the exchange within the chromium sublattice. In the saturation state, the magnetic moment is $0.55 \mu_B$ for Yb^{3+} , and presumably $1 \mu_B$ for Cr^{5+} , the two sublattices being antiferromagnetically coupled. The anisotropic Yb–Cr exchange polarises the Yb^{3+} sublattice below 25 K, so as to force the Yb magnetic moments to lie in the hard magnetic a – b plane.

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Rare earth chromates constitute a subgroup of the family of compounds of general formula RXO_4 , where R(III) =rare earth, while X(V) symbolises the following ions: V(V), As(V), P(V) and Cr(V) [1]. Few studies have been performed so far in the mentioned chromates [2]. We have focused on the magnetic properties of the zircon-type YbCrO_4 oxide. Basing on the existing studies on the isomorphous YbVO_4 , YbAsO_4 and YbPO_4 compounds, the influence of the Cr^{5+} ion on the overall magnetic properties of the YbCrO_4 can be thoroughly assessed.

In a first stage, we measured the magnetic susceptibility of the sample as a function of temperature to determine its magnetic ordering temperature, turning out to be 25 K. Subsequently, the magnetisation was recorded as a function of the external magnetic field up to 1 T at different temperatures. Fig. 1 collects the data corresponding to 35 and 20 K. While the magnetisation varies linearly with the magnetic field at 35 K, a

hysteresis loop has been obtained at 20 K. This fact confirms the previously obtained value for the magnetic ordering temperature, as well as the presence of ferro- or ferrimagnetic interactions in the YbCrO_4 oxide. Both the remanence and the coercivity field increases with decreasing temperature, from $0.4 \mu_B$ and 675 Oe at 20 K to $0.55 \mu_B$ and 3250 Oe at 2 K, respectively.

The Mössbauer spectra on the ^{170}Yb isotope were measured between 4.2 and 30 K. Some selected spectra are represented in Fig. 2. An extra absorption has been detected near the centre of the spectrum coming from an impurity phase, the Yb_2O_3 oxide, whose known spectrum has been included in Fig. 2 as a dashed line. Its substantially high Debye temperature, when compared with the one corresponding to the YbCrO_4 compound, can probably be the cause for its seemingly large Mössbauer percentage, which amounts to 35(10)%.

The YbCrO_4 Mössbauer spectra comprise only a quadrupolar contribution between 25 and 30 K, with a quadrupolar coupling constant: $\alpha_Q = 3.5 \text{ mm/s}$. Below 25 K, a mixed magnetic-quadrupolar hyperfine pattern is clearly present, thus supporting the previously

*Corresponding author. Tel.: +34-91-3944353; fax: +34-91-3944352.

E-mail address: ejmelero@quim.ucm.es (E. Jimenez).

Fig. 1. Variation of the YbCrO₄ magnetisation with the external magnetic field at 20 and 35 K.

Fig. 2. ¹⁷⁰Yb Mössbauer absorption spectra of the YbCrO₄ oxide. The dashed line represents the spectrum of the impurity phase Yb₂O₃.

determined ordering temperature. In local tetragonal symmetry (D_{2d} in this case), the principal axis (z -direction) of the electric field gradient tensor is along the four-fold symmetry axis, i.e. the crystallographic c -axis. The fitting procedure of the spectrum at 4.2 K yields a hyperfine field of 55 T, corresponding to a saturated Yb magnetic moment of $m_0 = 0.55 \mu_B$, which is

significantly reduced with respect to the theoretical value of $g_J J = 4 \mu_B$. Moreover, the hyperfine field is perpendicular to the c -axis.

In the zircon-type YbXO₄ compounds, an isolated Kramers doublet can be attributed to the crystal field ground state of the Yb³⁺ ion [3]. Such doublet can be described by an effective spin $S = \frac{1}{2}$ and a spectroscopic g -tensor which, in the case of axial symmetry, has two components g_z and $g_{\perp}$ defined by

$$g_z = 2g_J |\langle \psi | J_z | \psi \rangle|,$$

$$g_{\perp} = 2g_J |\langle \psi | J_x | \psi' \rangle|,$$

where $|\psi\rangle$ and $|\psi'\rangle$ are the Kramers conjugate states of the doublet. The 4f quadrupole coupling parameter is given by (if one neglects the usually small lattice charges contribution): $\alpha_Q = B_Q \langle \psi | 3J_z^2 - J(J+1) | \psi \rangle$, where $B_Q = 0.276$ mm/s for the ¹⁷⁰Yb³⁺ ion. In local tetragonal symmetry, the crystal field eigenfunctions can be mixtures of either the $|+5/2\rangle$ and $|-3/2\rangle$ states, or of the $|+7/2\rangle$ and $|-1/2\rangle$ states, where $|m\rangle$ stands for $|J=7/2; J_z=m\rangle$. From the measured values of α_Q and $g_{\perp} = 2m_0/\mu_B = 1.1$ at 4.2 K, the approximate wavefunction for the ground state is

$$|\psi\rangle = 0.87|J = \frac{7}{2}; J_z = \frac{7}{2}\rangle + 0.49|J = \frac{7}{2}; J_z = -\frac{1}{2}\rangle.$$

This wavefunction, in turn, results in a value for the longitudinal component of the g -tensor of $g_z = 5.8$. These values are relatively close to those obtained for the Yb³⁺ ion in YbVO₄: $g_z = 6.46$ and $g_{\perp} = 0.77$, and in YVO₄: $g_z = 6.08$ and $g_{\perp} = 0.85$ [4]. Surprisingly, in the magnetically ordered state, the Yb moments do not lie along the easy c -axis but in the a - b plane, which constitutes a hard magnetic plane. Therefore, it must be concluded that the Yb–Cr exchange imposes the direction of the Yb magnetic moments, i.e. it is anisotropic, the Cr⁵⁺ ion having an isotropic g -tensor.

We can now address the question of the nature of the Yb–Cr coupling, i.e. whether it is ferro- or ferrimagnetic, basing on the measured remanence moment at 2 K. The saturated moment of the Cr⁵⁺ ion is $2S = 1 \mu_B$ (if no covalency effects are present in the Cr–O bond), while that of the Yb³⁺ ion depends on the orientation of the magnetic field. For a polycrystalline sample, the saturated magnetisation of an extremely anisotropic doublet (i.e. $g_{\perp}/g_z \ll 1$) averaged over all orientations is $\frac{1}{4}g_z\mu_B$. Using this result for Yb in YbCrO₄ ($g_{\perp}/g_z \approx 0.2$), we obtain: $1.45 \mu_B$. This implies that the experimental remanence moment at 2 K, of $0.55 \mu_B$ per formula unit, would correspond to a ferrimagnetic structure, the Yb–Cr coupling being antiferromagnetic.

Comparatively, the YbVO₄ oxide displays a three-dimensional antiferromagnetic ordering along the c -axis with a Néel temperature of 93 mK, and an ordered Yb³⁺ magnetic moment of $3.1 \mu_B$ [5]. The remarkable differ-

ence in the magnetic ordering temperature between the isostructural YbCrO_4 ($T_C=25\text{ K}$) and YbVO_4 ($T_N=93\text{ mK}$) oxides, coupled with a different sign of the magnetic interactions and the alignment of the Yb^{3+} magnetic moments along the a – b plane in the YbCrO_4 oxide, points to the dominant role that the Cr^{5+} magnetic ion plays in determining the overall magnetic ordering temperature, as well as polarising the magnetic moments of the Yb^{3+} ions along a hard direction of magnetisation.

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