Influence of the Cr\textsuperscript{5+} ion on the magnetic properties of YbCrO\textsubscript{4} oxide

DOI:
10.1016/j.jmmm.2003.11.216

Document Version
Final published version

Link to publication record in Manchester Research Explorer

Citation for published version (APA):

Published in:
Journal of Magnetism and Magnetic Materials

Citing this paper
Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights
Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy
If you believe that this document breaches copyright please refer to the University of Manchester’s Takedown Procedures [http://man.ac.uk/04Y6Bo] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.
Influence of the Cr\textsuperscript{5+} ion on the magnetic properties of YbCrO\textsubscript{4} oxide

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

\textsuperscript{a}Dpto. Q. Inorganica, Fac. C. Quimicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040-Madrid, Spain
\textsuperscript{b}CEA Saclay, DSM/DRECAM, Service de Physique de l’Etat Condensé, 91191 Gif-sur-Yvette, France
\textsuperscript{c}Interfacultair Reactor Instituut, TUDelft, Mekelweg 15, 2629 JB-Delft, The Netherlands

Abstract

The magnetic properties of the YbCrO\textsubscript{4} oxide have been studied by both bulk magnetic measurements and \textsuperscript{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\textsuperscript{3+}, and presumably 1 \(\mu_B\) for Cr\textsuperscript{5+}, the two sublattices being antiferromagnetically coupled. The anisotropic Yb–Cr exchange polarises the Yb\textsuperscript{3+} sublattice below 25 K, so as to force the Yb magnetic moments to lie in the hard magnetic \(a-b\) plane.

© 2004 Elsevier B.V. All rights reserved.

PACS: 75.50.Gg; 76.30.Kg

Keywords: YbCrO\textsubscript{4}; Zircon-type structure; Magnetic ordering; Mössbauer spectroscopy

Rare earth chromates constitute a subgroup of the family of compounds of general formula RXO\textsubscript{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\textsubscript{4} oxide. Basing on the existing studies on the isomorphic YbVO\textsubscript{4}, YbAsO\textsubscript{4} and YbPO\textsubscript{4} compounds, the influence of the Cr\textsuperscript{5+} ion on the overall magnetic properties of the YbCrO\textsubscript{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\textsubscript{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 \textsuperscript{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\textsubscript{2}O\textsubscript{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\textsubscript{4} compound, can probably be the cause for its seemingly large Mössbauer percentage, which amounts to 35(10)\%.

The YbCrO\textsubscript{4} Mössbauer spectra comprise only a quadrupolar contribution between 25 and 30 K, with a quadrupolar coupling constant: \(\chi_Q = 3.5\) mm/s. Below 25 K, a mixed magnetic-quadrupolar hyperfine pattern is clearly present, thus supporting the previously
In the zircon-type YbOX₄ 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

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

$$g_\perp = 2g_I|\langle \psi | J_\perp | \psi \rangle |,$$

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):

$$\delta Q = B_3 \langle J^2 - J(J+1) \rangle |\langle \psi | J_z | \psi \rangle |,$$

where $B_0 = 0.276 \text{ mm/s}$ for the $^{170}\text{Yb}^{3+}$ ion. In local tetragonal symmetry, the crystal field eigenfunctions can be mixtures of either the $|+\frac{5}{2}\rangle$ and $|+\frac{3}{2}\rangle$ states, or of the $|+\frac{7}{2}\rangle$ and $|-\frac{1}{2}\rangle$ states, where $|m\rangle$ stands for $|J=\frac{7}{2}, J_z=m\rangle$. From the measured values of $\delta Q$ and $g_\perp = 2m_0/\mu_B = 1.1$ at 4.2 K, the approximate wave-function for the ground state is

$$|\psi \rangle = 0.87|J=\frac{7}{2}, J_z=\frac{7}{2}\rangle + 0.49|J=\frac{5}{2}, J_z=\frac{5}{2}\rangle.$$

This wave-function, 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 Cr³⁺ 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 Cr³⁺ 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 $\frac{1}{2}g_I\mu_B$. 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$_4$ ($T_C=25$K) and YbVO$_4$ ($T_N=93$ 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.

References