

Large magnetocaloric effect and magnetic properties of polymorphic RCrO_4 (R=rare earth) oxides

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RCrO_4 oxides, where R=rare earth, crystallize at ambient conditions with the tetragonal zircon-type structure, *S.G.* $I4_1/amd$. [1] Recently, we have succeeded to synthesize the scheelite polymorphs (*S.G.* $I4_1/a$) for most of the R elements, by treating the zircon phases at 40 kbar and 813 K. [2, 3] These scheelite high pressure forms are quencheable after releasing the pressure, and TGA and X-ray diffraction data reveal a reversible transition from scheelite polymorph to zircon at 700 K. The coexistence of two paramagnetic ions in these phases, namely Cr^{5+} and R^{3+} , constitutes a very interesting scenario to study 3d-4f magnetic interactions. In this sense, most of the zircon-type RCrO_4 oxides behave as ferromagnetic, while the scheelite polymorphs are antiferromagnetic. The change in the sign of the magnetic interaction can be explained by considering the changes in both distances and bond angles of Cr-O-R pathway through which the superexchange interactions take place. [4]

Neutron diffraction studies have been used to determine the nuclear and magnetic structures for these zircon and scheelite RCrO_4 polymorphs. The analysis of the data reveals the onset of new reflections below the estimated Néel temperature from the previous magnetic susceptibility data corresponding to the scheelite phases. The magnetic structure for these scheelite RCrO_4 oxides can be described with a propagation vector $\kappa = [0\ 0\ 0]$, where the moments of R^{3+} and Cr^{5+} are aligned along the *c*-axis or confined in the *ab*-plane of the tetragonal structure depending on the nature of the R element, Figure 1. [4, 5] This behavior has been confirmed from heat capacity measurements where the onsets of λ -anomalies at the ordering temperatures are almost coincident with those determined from magnetic susceptibility and neutron diffraction analysis, see Figure 2. A detailed analysis of the zircon and scheelite structural types is included in this work to explain the different magnetic behavior showed by these two polymorphic phases allowing establishing relationships structure-magnetic properties.

Very recently it has been reported that the zircon RCrO_4 (R= Ho and Dy) phases show large values of the magnetocaloric parameters that make of these oxides potential refrigerant materials to be used for the liquefaction of hydrogen. [6] It is noting that the field induced magnetization in the case of the scheelite polymorphs yields magnetic moments larger than in the case of the homologous zircon phases and hence the magnetocaloric effect is expected to be larger for the scheelite polymorphs in comparison with the zircon ones. In this work a preliminary study has been done in order to determine the magnetocaloric parameters of the two polymorphic phases of TbCrO_4 and HoCrO_4 . In this sense the isothermal entropy change, ΔS_T , as a function of temperature has been calculated for magnetic field variations from the measurements of magnetization versus field at different temperatures. Both

magnetocaloric parameters, ΔS_T and the adiabatic temperature change, ΔT_{ad} , have also been evaluated from the entropy functions at different fields obtained from the heat capacity data.

Figures:

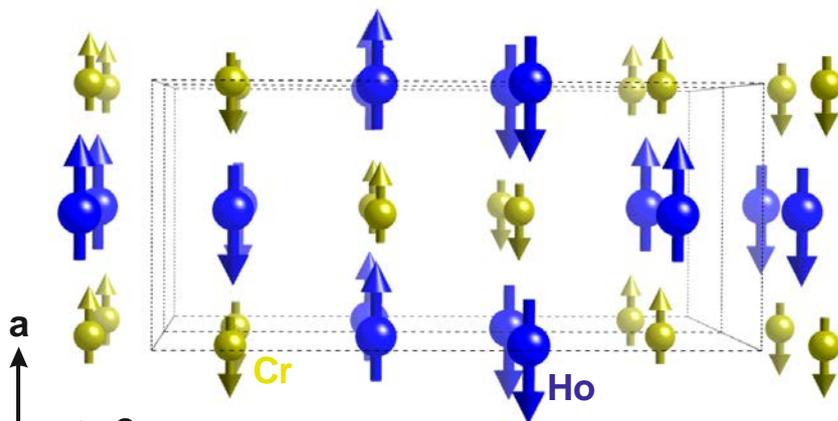


Figure 1. Magnetic structure of HoCrO_4 -scheelite

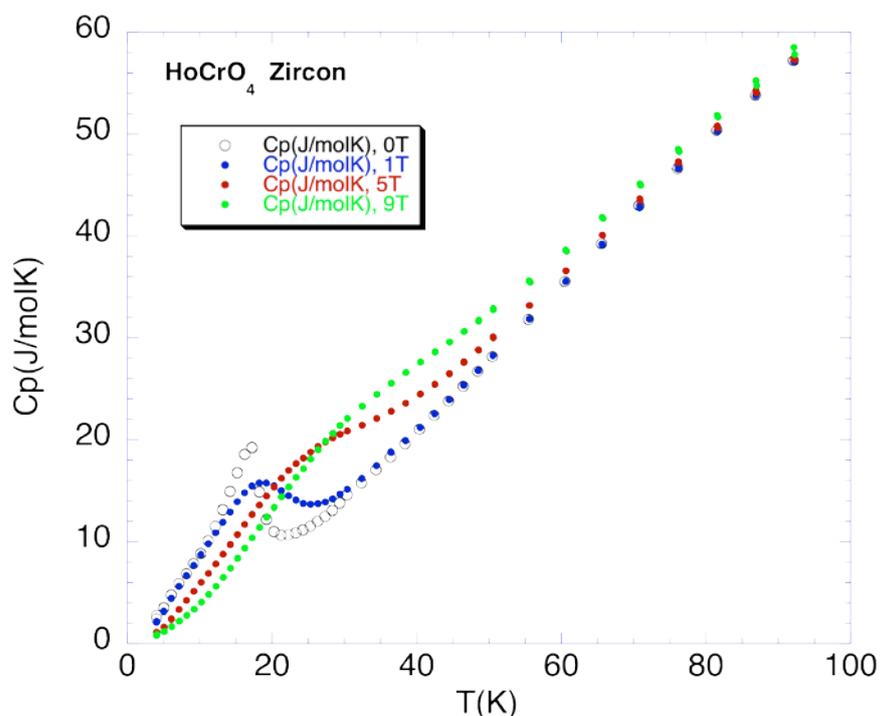


Figure 2. Heat capacity of HoCrO_4 -zircon under different magnetic fields

References

- [1.] R. Sáez Puche, E. Jimenez, J. Isasi, M.T. Fernández Diaz and J.L. Garcia Muñoz (2003) *J. Solid State Chem.* 172 , 161-170.
- [2.] E. Climent Pascual, J. Romero, J.M. Gallardo, R. Sáez Puche (2007) *Solid State Sci.* 9, 574-579.
- [3.] M. Rabie (2013) PhD. Thesis, Universidad Complutense Madrid.
- [4.] E. Climent Pascual, J.M. Gallardo, R. Sáez Puche, M. Castro, N. Taira, J. Romero L.C. Chapon (2010) *Phys. Rev. B* 81, 174419-174425.
- [5.] A.J. Dos santos-García, E. Climent-Pascual, J.M. Gallardo-Amores, M.G. Rabie, Y. Doi, J. Romero de Paz, B. Beuneu, R. Sáez-Puche (2012) *J. Solid State Chem.* 194 , 119-126.
- [6.] A. Midya, N. Khan, D. Boi, P. Mandal (2013) *Appl. Phys. Lett.* 103, 092402-092407.