JOURNAL OF
Materials
CHEMISTRY

Magnetic behaviour of β-Li_3CrO_4

Susana García-Martín,[a,b] **Anthony R. West,**[b] **José L. Martínez**[c] **and Regino Sáez-Puche***[a]

[a]*Departamento de Química Inorgánica, Facultad de C.C. Químicas, Universidad Complutense de Madrid, Madrid-28040, Spain*
[b]*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Scotland, UK AB24 3UE*
[c]*Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco, E-28049 Madrid, Spain*

Magnetic susceptibility and magnetization as a function of temperature and applied field of β-Li_3CrO_4 have been measured. The material is paramagnetic in the temperature range 100–15 K with an effective moment of 1.70 μ_B and $\theta = 2.6$ K. Below 15 K, ferromagnetic interactions in the chromium sublattice are observed with a saturation magnetic moment of 0.8 μ_B and T_c *ca.* 10 K. The results are explained taking into account the crystal structure of the oxide and the oxidation state of the chromium.

Materials with crystal structures related to both the high and low temperature forms of Li_3PO_4[1,2] are of interest as Li^+ ion conducting solid electrolytes.

Although stable oxides of Cr^V are relatively rare, Li_3CrO_4 containing Cr^V has been prepared as a pure and stable compound. Single crystals of the high temperature γ-Li_3CrO_4 polymorph have been grown[3] and the low temperature β-Li_3CrO_4 has been synthesized by two different routes.[4] This low temperature β-phase crystallizes with the basic wurtzite structure type in which one set of tetrahedral sites, T_+ or T_-, is fully occupied, with cation ordering as shown in Fig. 1.

β-Li_3CrO_4 has been used as the starting point to synthesize ranges of γ-solid solutions in the three systems: β-Li_3CrO_4–Li_4YO_4 (Y = Si, Ge, Ti) which constitute a new group of Li^+ ion conductors and mixed conductors in the LISICON family.[5,6] In addition, β-Li_3CrO_4 shows electrochemical activity and is able to reversibly intercalate *ca.* 1 mol of Li ions per formula unit.[7] Preliminary magnetic susceptibility data[4] showed that β-Li_3CrO_4 is paramagnetic down to 15 K but at lower temperatures, appears to behave as a ferromagnet.

The main purpose of this work is to present a detailed evaluation of the magnetic properties of β-Li_3CrO_4 using magnetic susceptibility and magnetization measurements as a function of temperature and magnetic field.

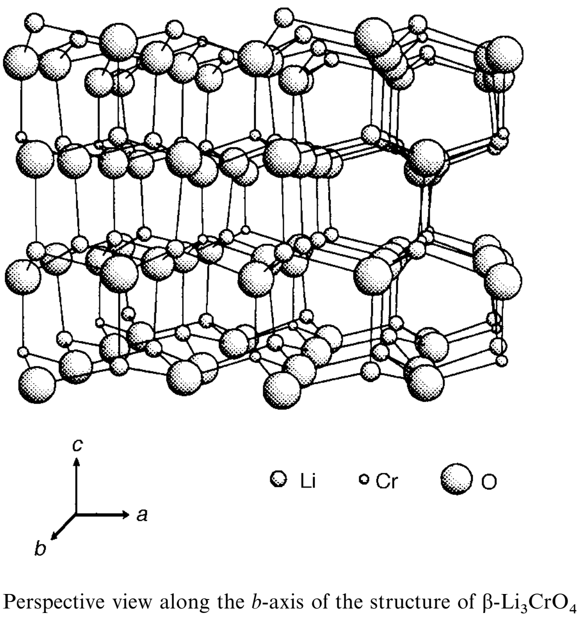

Fig. 1 Perspective view along the *b*-axis of the structure of β-Li_3CrO_4

Experimental

β-Li_3CrO_4 can be prepared by two different ways involving either oxidation of Cr_2O_3 or better, reduction of CrO_3.[4] In this study, the material was synthesized using the latter method, by reacting stoichiometric amounts of Li_2CO_3 and CrO_3 at 700 °C in a Au foil boat in flowing Ar, as described in ref. 4. The product was characterized by powder X-ray diffraction using a STOE STADI/P diffractometer with a position sensitive detector (PSD) and Cu-Kα_1 radiation and found to be phase-pure β-Li_3CrO_4, isostructural with β-Li_3PO_4.[4]

Magnetic susceptibility measurements at typical magnetic fields of 1 kOe were performed in a Quantum Design SQUID magnetometer in the temperature range 2–100 K. The set-up was calibrated with Hg[Co(SCN)$_4$] and metallic palladium. Magnetization measurements and hysteresis loops were made up to 9 T in a Quantum Design extraction magnetometer PPMS at different temperatures.

Results and Discussion

Fig. 2 shows the temperature dependence of the magnetic molar susceptibility of β-Li_3CrO_4. The susceptibility obeys a

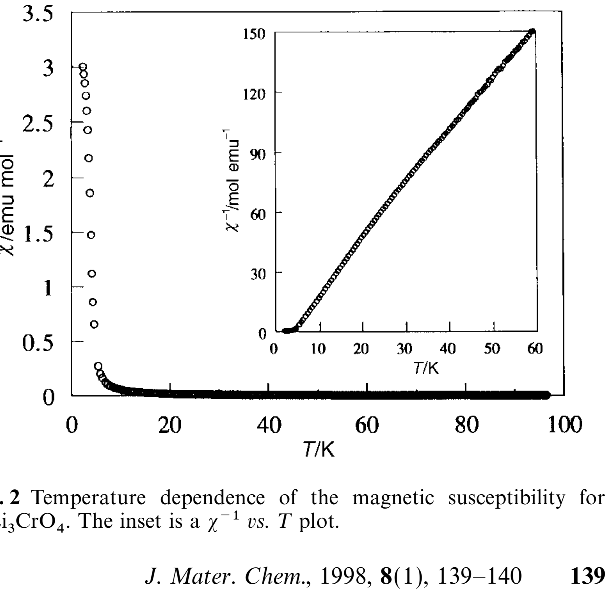

Fig. 2 Temperature dependence of the magnetic susceptibility for β-Li_3CrO_4. The inset is a χ^{-1} *vs.* *T* plot.

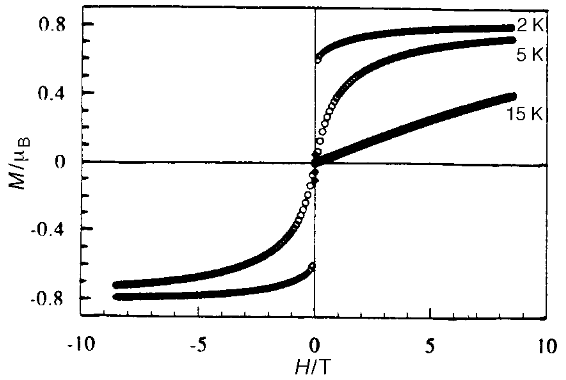

Fig. 3 Magnetization *vs.* magnetic field plots obtained at different temperatures for β-Li_3CrO_4

Curie–Weiss behaviour in the temperature range 15–100 K, Fig. 2 inset, and the mean effective magnetic moment calculated from the slope of the straight line has the value 1.70 μ_B, which is slightly lower than that, 1.73 μ_B, calculated considering the spin-only contribution for Cr^V with $S=1/2$.

This discrepancy can be explained taking into account that the crystal field ground term of Cr^V in tetrahedral coordination is ^2E. It is well known that this ^2E term is mixed, *via* spin–orbit coupling, with the higher-lying excited T_2 crystal field term, giving rise to a magnetic moment depending on orbit-coupling λ and $10Dq$.[8] Since Cr^V has one unpaired electron, the λ value should be positive and this justifies the value of 1.70 μ_B found for this oxide.

The sharp increase of susceptibility below 15 K and the positive value of the Weiss constant, $\theta=2.6$ K, Fig. 2 inset, indicate the existence of ferromagnetic interactions in the chromium sublattice.

Fig. 3 shows the magnetization *vs.* magnetic field curves up to 9 T at three different temperatures. Below 15 K, non-linearity was clearly observed, confirming the presence of ferromagnetic interactions. At the lowest temperature studied, 2 K, the saturation magnetic moment takes the value of 0.80 μ_B which is very close to that expected for Cr^V with one unpaired electron. This slightly lower moment as compared to the theoretical one might be due to partial covalence effects on the chromium–oxygen bond and/or some small disorder between the chromium and lithium sublattices. From both magnetic susceptibility and magnetization data, the Curie temperature is estimated to be around 10 K.

The weakness of these ferromagnetic interactions can be understood from a consideration of the crystal structure of β-Li_3CrO_4.[4] As mentioned above, it has a wurtzite superstructure, it can also be described as a 3D vertex-linked array of $[MO_4]$ (M = Li, Cr) tetrahedra with the Li and Cr cations ordered in such a way, Fig. 1, that the $[CrO_4]$ tetrahedra are completely separated from each other by the diamagnetic $[LiO_4]$ tetrahedra producing a significant dilution of the chromium sublattice. The superexchange interactions are clearly very complex and the pathways, include the sequences Cr^{5+}–O^{2-}–Li^{+}–O^{2-}–Cr^{5+}, involve three diamagnetic atoms. These pathways are aligned along the three crystallographic axes and no evidence of low-dimensional order can be inferred from an inspection of the crystal structure.

Fig. 3 displays the magnetization *vs.* magnetic field plots. The reversibility of the magnetization indicates that this oxide is a very soft ferromagnetic material with remanence and coercitive field values close to zero.

We thank CICYT (Project Mat 95–0809) for financial support.

References

1 J. Zemann, *Acta Crystallogr., Sect. B*, 1960, **13**, 863.
2 C. Keffer, A. Mighell, F. Mauer, H. Swanson and S. Block, *Inorg. Chem.*, 1967, **6**, 119.
3 G. Meyer, D. Paus and R. Hoppe, *Z. Anorg. Allog. Chem.*, 1974, **408**, 15.
4 M. A. K. L. Dissanayake, S. García-Martín, R. Sáez-Puche, H. H. Sumathipala and A. R. West, *J. Mater. Chem.*, 1994, **4**, 1307.
5 M. A. K. L. Dissanayake, R. P. Gunawardane, H. H. Sumathipala and A. R. West, *Solid State Ionics*, 1995, **76**, 215.
6 H. H. Sumathipala, M. A. K. L. Dissanayake and A. R. West, *J. Electrochem. Soc.*, 1995, **142**, 2138.
7 S. García-Martín, A. D. Robertson, M. A. K. L. Dissanayake and A. R. West, *Solid State Ionics*, 1995, **76**, 309.
8 F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*, Chapman and Hall Ltd, London, 1973.

Paper 7/05569B; *Received* 31*st July*, 1997