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Structural, Magnetic and Mössbauer Studies of the Mixed- Metal Molecular Ferromagnet Compounds $NBu_4[MCr(C_2O_4)3]$ (Bu═$(CH_2)_3CH_3$, M═Mn, Fe)

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STRUCTURAL, MAGNETIC AND MÖSSBAUER STUDIES OF THE MIXED-METAL MOLECULAR FERROMAGNET COMPOUNDS $NBu_4[MCr(C_2O_4)_3]$ (Bu=$(CH_2)_3CH_3$, M=Mn, Fe)

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Abstract An X-ray study of a single crystal of the $NBu_4[MnCr(C_2O_4)_3$ composition reveals a layered structure with an ordered arrangement of Mn^{2+} and Cr^{3+} ions. According to the data of the orientation dependence of magnetization at 4.5 K, the magnetic easy axis is aligned along the crystal *c*-axis. Mössbauer data analysis of isostructural $NBu_4[FeCr(C_2O_4)_3]$ powdered material gives, on the contrary, the evidence of strong confinement of Fe^{2+} spins to the crystal basal plane. The ferromagnetic system which arises here is a quasi-2D system in terms of the nature of its exchange interactions.

INTRODUCTION

Recently a group of Japanese researchers have synthesized a family of new metal-complex ferromagnets with the general formula $NBu_4[MCr(C_2O_4)_3]$, where $M=Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}; NBu^{4+} is the tetra(n-butyl) ammonium ion, and $(C_2O_4)^{2-}$ is the oxalate ion.[1] Working from a comparative evaluation of the parameters of the superexchange interaction in an M^{2+} - $(O_2C_2O_2)^{2-}$ - Cr^{3+} chain, Tamaki et.al.[1] suggested that these new compounds are 3D ferromagnets. A valid test of this suggestion requires comparing the results of structure analysis and magnetic measurements on single crystals of these compounds.

In this paper we are reporting an X-ray study of the structure of a single crystal of the compound $NBu_4[MnCr(ox)]_3$. We also measured the magnetization as a function of the applied magnetic field for various orientations of the crystal. To obtain more information about electronic and dynamic structure of the system, Mössbauer studies of $NBu_4[FeCr(ox)_3]$ powdered material have been performed.

EXPERIMENTAL

The $NBu_4[MnCr(C_2O_4)_3$ single crystals were grown by slow interdiffusion of aqueous solutions of a mixture of NBu_4Br with $MnCl_2$ and $K_3[Cr(C_2O_4)_3]$ $3H_2O$ in an argon atmosphere for two weeks. Powdered materials were obtained by the method discribed in Ref.1.

X-ray diffraction data were collected on a KM-4 four-circle diffractometer using monochromized Mo K_α radiation. In the experiment, measurements were made of 570 independent reflections with $I > 3\sigma$, $\sin\theta / \lambda < 0.595$ Å^{-1}.

Magnetization *vs* magnetic field measurements were carried out with PARC M4500 vibrational sample magnetometer. The ferromagnetic transition points were determined by *ac* magnetic susceptibility measurements.

Mössbauer spectra have been taken using variable temperature continious flow helium cryostat and liquid helium bath cryostat supplied with a superconducting magnet. The applied magnetic field was parallel to the gamma ray propagation direction.

RESULTS AND DISCUSSION

The molecular structure of the $NBu_4[MnCr(ox)_3]$ crystal was solved and refined in space group R3c with the AREN X-ray software package. The lattice parameters of the hexagonal cell are $a = b = 9.414(5)$ Å, $c = 53.662(6)$ Å with $V = 4125$ Å^3 and $d_{calc} = 1.485$ g·cm^{-3}. The carbon atoms of the cation are disordered; we have not succeeded in determining their positions accurately.

Figure 1 is a 3D image of the arrangement of atoms in the cell. For simplicity the NBu^{4+} cation is represented by a nitrogen atom and the four carbon atoms bound to it. The metal ions are located in trigonally distorted octahedra represented by oxygen ions from $(ox)^{2-}$ groups. Each metal ion of a given species is bound by three $(ox)^{2-}$ groups to three ions of a different species and forms a layer in the form of a hexagonal network, in a manner similar to that modelled in one version of the structure in Ref.1.

The nitrogen atoms of the NBu_4^+ cations are on threefold axes forming a plane below a network of the nearest anion layer at a distance of 3.32 Å. One of the butyl groups around a threefold axis (the *c*-axis) penetrates into a void in a neighboring $[MnCr(ox)_3]$ layer; the three others are directed towards Mn^{2+} ions of the opposite layer. This configuration probably creates a difference between the Mn and Cr sites and promotes an ordered arrangement of these ions in the crystal. The Cr-O distances are 1.97(2) Å and 2.03(2) Å, and the Mn-O distances are 2.14(2) Å and 2.15(2) Å. Each

metal ion of a given species in an anion layer has only a single nearest neighbor: an ion of another species in a layer below or above the given layer, at a distance of 8.95 Å.

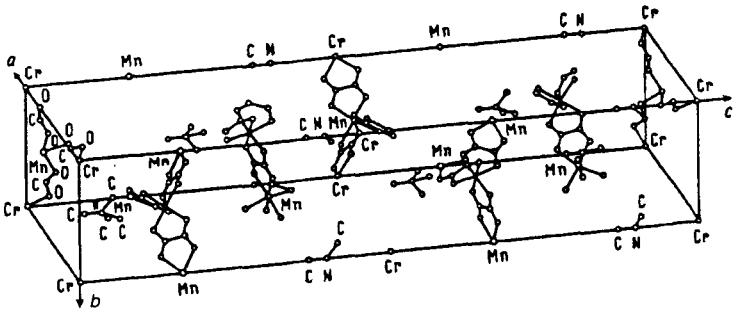

FIGURE 1 Three dimensional image of the arrangement of atoms in the cell. For clarity, some of the atoms are not shown.

By virtue of the structural order of the magnetic ions, a ferromagnetic order of the spins thus becomes possible due to Mn^{2+}-$(ox)^{2-}$-Cr^{3+} superexchange interactions within a layer and a weak interlayer Mn^{2+}-Cr^{3+} exchange at a distance of about 9 Å. It can be concluded that this magnetic system is a quasi-2D system. A positive sign of the direct and indirect exchange in the d^5 - d^3 pair is in agreement with the semiempirical Goodenough-Kanamori rules.[2]

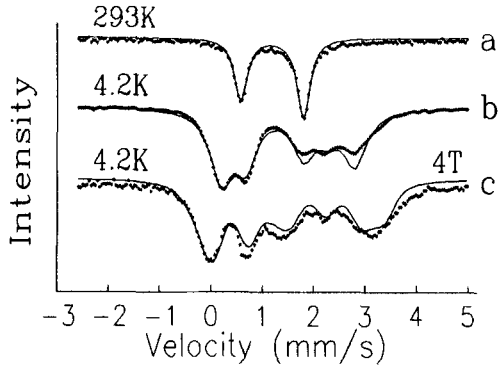

FIGURE 2 Mössbauer absorption spectra of $NBu_4[FeCr(ox)_3]$. Bottom spectrum is taken in a longitudinal external magnetic field of 4 T.

It might be possible to strengthen the interlayer exchange and to achieve the corresponding increase expected in critical temperature (from $T_c = 6$ K) by bringing the layers of metal ions closer together, by (for example) reducing the length of the organic "tail" of the cation by replacing three butyl groups by shorter groups, C_3H_7 or C_2H_5.

Measurements of the magnetization as a function of the external magnetic field, M(H), were carried out on an identical single crystals at 4.5 K for two orientations of the external field: along the *c* axis of the crystal and perpendicular to it (not shown here). It turns out that in the parallel orientation saturation is reached in fields as low as 0.05 T, while in the perpendicular orientation the M(H) curve is still far from saturation in a field H=1 T. According to the data of Ref.1, the saturation field in a polycrystalline sample is ~ 7 T. The magnetic moments of Mn and Cr are probably aligned along the *c* axis of the crystal (it is an Ising ferromagnet), but this conclusion requires further testing.

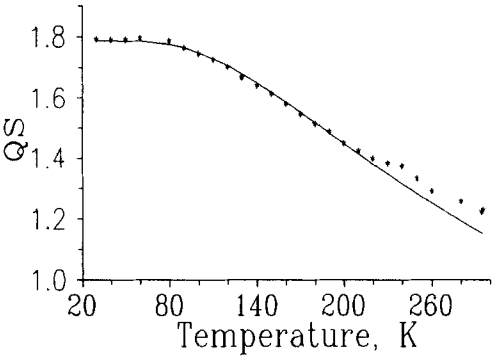

FIGURE 3 Temperature variation of the quadrupole splitting.

To get more insight into the electronic stucture and lattice dynamics of this new family of quasi-2D ferromagnets, Mössbauer experiments on powdered samples of the $NBu_4[FeCr(ox)_3]$ composition have been performed. Measurements were made from 4.2 K to 296 K without and with applied magnetic fields up to 7 T. The spectra obtained in the paramagnetic state showed the narrow line quadrupole doublet (Fig. 2a) with parameters typical for high-spin Fe^{2+} (isomer shift, IS = 1.18(1) mm/s, quadrupole splitting, QS = 1.23(1) mm/s). At 4.2 K (Fig. 2b), below the ferromagnetic transition temperature (T_c = 12.5 K), calculated hyperfine parameter values H_{hf} = 4.5 T, QS = -1.78 mm/s, $\eta = 0$, $\theta = 90^o$, imply that the internal spin direction is in the crystal basal plane and the electronic ground state of the Fe^{2+} ion in a trigonal field is an orbital singlet. However, a positive sign of the magnetic hyperfine field, H_{hf}, determined by in-field Mössbauer experiments (Fig. 2c) indicates a large positive orbital contribution comparable with the negative Fermi-contact field. The non-zero orbital momentum and strong spin-orbit coupling within the Fe^{2+} ion (contrary to the Mn^{2+} $^6A_1$ ion) is thought to be the main source of the magnetic anisotropy field which confines magnetic moments to the basal plane of the crystal.

The existence of low-lying orbital doublet state relative to the singlet ground state within the T_{2g} space of Fe^{2+} responsible for strong spin-orbit coupling is also corroborated by the temperature dependence of quadrupole splitting (Fig. 3). The axial field splitting parameter, Δ_1, calculated from QS(T) curve was found to be equal to 330 cm^{-1}. To fit the experimental points, highly reduced covalency parameter, $\alpha = 0.62$, should be taken into account.[3]

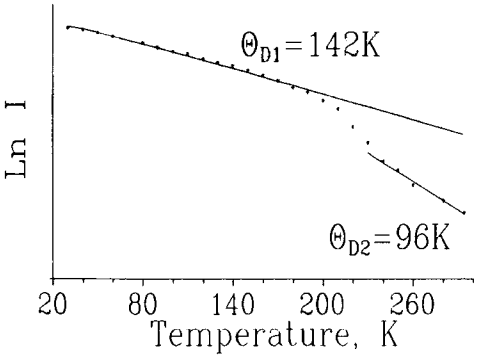

FIGURE 4 Temperature variation of absorption intensity, Ln(I).

The temperature dependence of the intensity of Mössbauer absorption proportional to the mean-square displacement of Fe^{2+} ions indicates a broad phase transition in the range 200 - 240K (Fig.4). Low values of Debye temperatures in low-temperature (below 200 K) and high-temperature (above 240 K) phases, $\Theta_{D1} = 142$ K and $\Theta_{D2} = 96$ K respectively, are characteristic of layered compounds with weak interlayer coupling. An anomalous fall in intensity above 200 K accompanied by an increase in asymmetry of the doublet lines (Goldanskii-Karyagin effect) leads us to the conclusion that the mean square displacement of the iron atoms increases drastically along the crystal *c*-axis. This effect is thought to be related to the orientational disorder of the butyl groups above 200 K. The preliminary low-temperature X-ray diffraction data are consistent with this assumption.

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