Molecular-based Mixed Valency Ferrimagnets $(XR_4)Fe^{II}Fe^{III}(C_2O_4)_3$ (X = N, P; R = *n*-propyl, *n*-butyl, phenyl): Anomalous Negative Magnetisation in the Tetra-*n*-butylammonium Derivative

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The phases $AFe^{II}Fe^{III}(C_2O_4)_3$ (A = NPr^{n}_{4}; NBu^{n}_{4}; PPh_4) have been synthesised and characterised chemically, structurally and magnetically; they behave as ferrimagnets, but the tetrabutylammonium salt shows a highly unusual negative magnetisation at low temperature.

The oxalate ion has been used widely to construct transition metal-containing clusters and arrays in the search for new molecular-based magnets.[1] Only recently, however, have simple ternary and quaternary salts been prepared that contain only oxalate as a coordinating ligand.[2] Lattices based on tris-oxalato-chromium(III) are only poorly crystalline,[2] but we find that the corresponding Fe^{III} compounds are highly crystalline. In particular, the phases $AFe^{II}Fe^{III}(C_2O_4)_3$ (A = quaternary ammonium or phosphonium) are especially interesting because of their mixed valency character. In this communication we report the synthesis and crystallographic unit cell parameters of three such compounds, with the cation A = NPr^{n}_{4}, NBu^{n}_{4} and PPh_4. All three behave as ferrimagnets, but the NBu^{n}_{4} salt alone shows unprecedented magnetic behaviour at low temperature, the magnetisation in field-cooled specimens becoming strongly negative.

The compounds were prepared as green microcrystals by adding an aqueous solution of $K_3Fe(C_2O_4)_3{\cdot}7H_2O$ to one of $FeSO_4{\cdot}7H_2O$ and filtering after 0.5 h. To the filtrate was added a methanol solution of respectively $NBu^{n}_{4}I$, $NPr^{n}_{4}Br$ and PPh_4I to precipitate the products $AFe^{II}Fe^{III}(C_2O_4)_3$. Analyses for C, H, N were in excellent agreement with this formula though the Fe content was slightly low in each case. To interpret the magnetic behaviour, special attention must be paid to phase purity. Some samples of all three compounds showed traces of $Fe(C_2O_4){\cdot}2H_2O$ in their X-ray powder diffraction patterns, eliminated in the samples used for magnetic study by optimising the preparative conditions. The X-ray powder diffracton profiles were recorded on a Siemens D500 diffractometer using Cu-Kα radiation. A recent publication[3] gives unit cell parameters for the related $NBu^{n}_{4}MnCr(C_2O_4)_3$ compound as a = 9.414(5) Å and c = 53.662(6) Å in the hexagonal system, so the diffraction profiles were indexed on a hexagonal cell, as in Table 1.

The peak widths in the NBu^{n}_{4} compound were greater than in the other two, suggesting greater disorder. That a remains almost constant while c varies with the organic cation suggests that all three compounds have the same basic layer structure in which a two-dimensional bimetallic honeycomb lattice consisting of coordinated oxalato-anions is interleaved with A^+, as hypothesised in refs. 2 and 3.

The magnetic behaviour of polycrystalline samples of the three compounds was examined using a Quantum Design MPMS 7 SQUID magnetometer over the temperature range 300–4.2 K. From 300 to 100 K their susceptibilities obey the Curie–Weiss law, with Weiss constants as follows: NPr^{n}_{4}, −114; NBu^{n}_{4}, −119; PPh_4, −113 K (Fig. 1). The large negative values indicate that the near-neighbour Fe^{II}–Fe^{III} magnetic exchange interaction is antiferromagnetic. Below 50 K the behaviour of the compounds depends strongly on the measurement protocol. For A = NPr^{n}_{4} and PPh_4, on cooling in zero field there is a sharp increase in magnetisation at respectively 35 and 37 K followed by a drop consistent with formation of magnetic domains. When these samples are cooled in a field of 100 G (1 G = 10^{-4} T), sharp increases in magnetisation occur at the same temperatures, followed by a further monotonic increase down to 4.2 K as conventionally found in materials with finite spontaneous magnetisation when the applied field is sufficient to align the magnetic domains (Fig. 2). In contrast, when the A = NBu^{n}_{4} sample is cooled in a 100 G field, a sharp increase in magnetisation is found at 45 K, further increasing up to a maximum at 39 K, below which the magnetisation decreases monotonically down to 6 K, becoming strongly negative below 30 K (Fig. 2). To our knowledge, in the whole of condensed matter, only one precedent exists for such negative magnetisation. When the canted antiferromagnetic perovskite $LaVO_3$ is cooled below

Table 1 Unit cell parameters

A	a/Å	c/Å
NPr^{n}_{4}	9.334(2)	49.37(3)
NBu^{n}_{4}	9.402(3)	53.88(5)
PPh_4	9.375(4)	57.45(5)

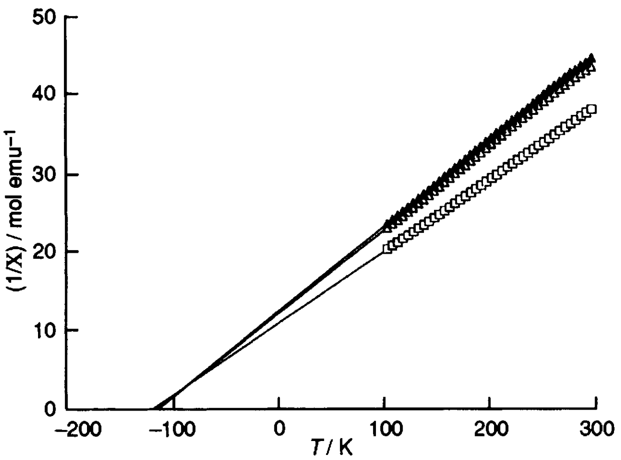

Fig. 1 Inverse susceptibility *vs.* temperature of $AFe^{II}Fe^{III}(C_2O_4)_3$ [A = NPr^{n}_{4} (△); PPh_4 (▲); NBu^{n}_{4} (□)]

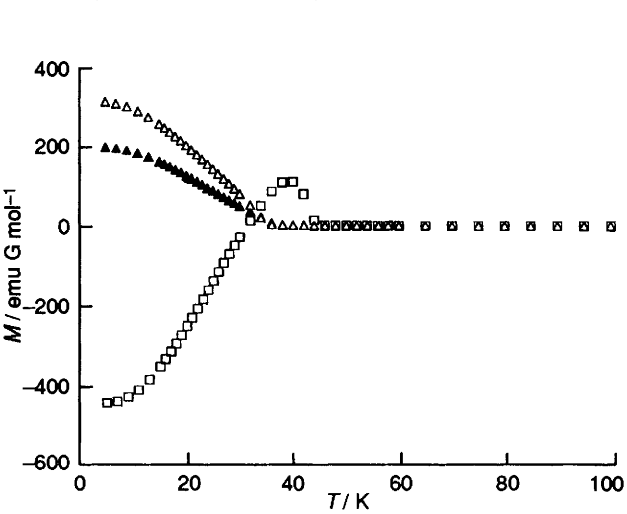

Fig. 2 Magnetisation *vs.* temperature of $AFe^{II}Fe^{III}(C_2O_4)_3$ [A = NPr^{n}_{4} (△); PPh_4 (▲); NBu^{n}_{4} (□)], cooled in a field of 100 G

its Neel temperature of 142 K in magnetic fields up to 1000 G a large apparent diamagnetism develops, *i.e.* the moments appear to align antiparallel to the applied field.[4] To date, no explanation has been given for the extraordinary behaviour of $LaVO_3$, but in the present instance we note the following points: (*i*) both $LaVO_3$ and $NBu^n{}_4Fe^{II}Fe^{III}(C_2O_4)_3$, which are non-metallic, exhibit finite spontaneous magnetisation at low temperature, the former due to spin canting in the antiferromagnetic structure, the latter because it is ferrimagnetic; (*ii*) of the three $AFe^{II}Fe^{III}(C_2O_4)_3$ compounds we have examined, only the $NBu^n{}_4$ one shows such behaviour; (*iii*) in this compound no minor phases are detectable in the powder X-ray diffraction pattern. Magnetisation alternating between positive and negative has been observed in ferrites and garnets, where the magnetisation of two magnetic sublattices varies differently with temperature.[5] Nevertheless, the oxalate series provides the first instance where such a phenomenon has been observed in a molecular-based magnet. Neutron diffraction studies are in progress to clarify this unusual behaviour.

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