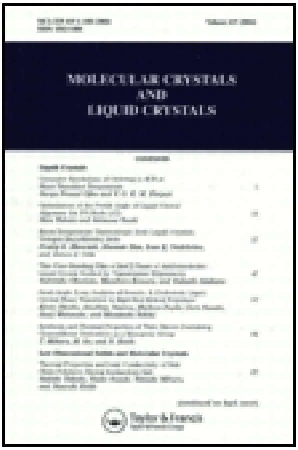

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Metal-Organic Layers in Molecular Magnets and Superconductors

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METAL-ORGANIC LAYERS IN MOLECULAR MAGNETS AND SUPERCONDUCTORS

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Abstract Examples are given of recent work from the Royal Institution on organic-inorganic hybrid layer compounds that behave as canted antiferromagnets, ferrimagnets and superconductors containing paramagnetic metal ions.

INTRODUCTION

It is some years since we coined the phrases 'organic-inorganic molecular composite'[1] and 'chemically constructed multilayer'[2] to describe compounds containing alternating sheets of organic molecular cations and inorganic anions. Such a spatial arrangement in the crystal lattice is found in a very wide variety of examples. In some, the organic cations are electronically inactive, and form flexible spacers between the inorganic layers, which therefore behave as low-dimensional magnets. In others the frontier orbitals of the organic cations overlap so that low-dimensional conductivity ranging from semiconductivity to superconductivity results. In this brief review some examples of each of these categories are summarised, based on work carried out by the group at the Royal Institution.

Physical mechanisms of ferromagnetic exchange coupling between localised moments are based on the notion of 'orthogonal magnetic orbitals',[3] a situation that is very difficult to achieve in a three-dimensionally continuous lattice. We showed some time ago[4] that in two dimensions a cooperative Jahn-Teller lattice distortion provided a suitable means of creating 'orbital ordering', such that singly occupied 3d orbitals on a given metal ion were rendered orthogonal to the corresponding ones on all the nearest neighbour ions. The resulting series A_2CrX_4 (A representing a wide range of monopositive organic and inorganic cations and X an halide ion) are ferromagnets with Curie temperatures between 30 and 60K.[5]

Given the difficulty of engineering near-neighbour ferromagnetic exchange in the absence of conduction electrons, it is appropriate to seek alternative strategies for inducing finite zero-field magnetisation. One route lies in exploiting ferrimagnetism, and we discuss some molecular-based examples below, while a third strategy, less exploited than the other two, consists in synthesising lattices containing only one kind of magnetic ion, and in which, because of competition with single-ion anisotropy induced by a low-symmetry ligand field and second-order spin-orbit coupling, the moments on neighbouring ions are not precisely antiparallel. This is called canted antiferromagnetism or (because the resultant of two vectors that are nearly, but not quite, antiparallel is a small vector at right angles) weak ferromagnetism. This article surveys some of our work in all three of these fields.

CANTED ANTIFERROMAGNETS: ALKYLPHOSPHONATES

Some time ago we implemented a strategy of exploiting canted antiferromagnetism to prepare organic-inorganic layer compounds having a spontaneous magnetisation. Our aim was to discover how the canted moment varies with the length of the alkyl sidechain and the metal ion. For example in Mn^{II} alkylphosphonates the spin canting proves to be surprisingly sensitive to the nature of the organic substituent.[6] Although the precise atomic coordinates of these materials are not yet known, the unit cell parameters show that the inorganic layers are almost identical to those in the ammonium and potassium salts,[7] and there is no evidence of variation with alkyl chain length (Figure 1).

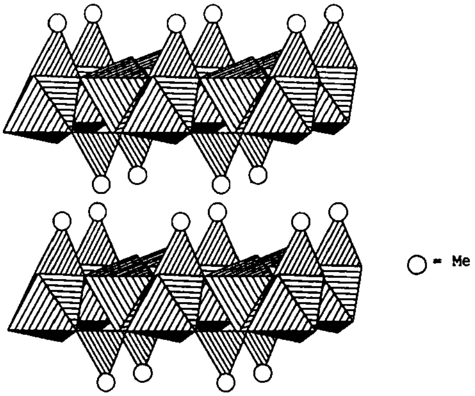

Figure 1 Schematic Structure of $CH_3PO_3Mn.H_2O$ [6]

The marked variation in canting with increasing chain length must therefore be due to a very subtle change in structure. In the phosphate compounds, the P–O bond not involved in coordinating manganese lies in the *bc* plane at a slight angle to the *b* axis. The most probably structure for the phosphonate compounds would replace this P–O bond with a P–C bond, and it is therefore possible that the packing of the longer chains exerts a torque on the phosphonate group, leading to a change in the distortion of the MO_6 octahedron. The apparent alternation of T_N with odd and even chain lengths supports this hypothesis, since successive C–C bonds will alternate in angle to the stacking axis as a consequence of the *trans* nature of the alkyl chains.

The symmetry of space group $Pmn2_1$ is sufficiently low that the antisymmetric exchange proposed by Moriya[8] to account for weak ferromagnetism can occur. A measure of the canting angle, α, of the Mn^{2+} spins can be obtained by comparing the ferromagnetic moments with the paramagnetic moments extracted from fitting the high temperature susceptibilities to the Curie-Weiss law:

$$\alpha = \sin^{-1}\left(\frac{\mu_{ferro}}{\mu_{eff}}\right)$$

Varying the chain length of the alkyl group leads to wide variation in the interlayer spacing. For example in $MnCH_3PO_3 \cdot H_2O$ it is 8.82 Å and in $MnC_4H_9PO_3 \cdot H_2O$ 14.71 Å. We studied the critical behaviour of the magnetisation of $NH_4MnPO_4 \cdot H_2O$ and its deuterated analogue by a combination of neutron diffraction and bulk magnetometry, finding that the critical exponent β of the magnetisation below T_N underwent a crossover from a value of 0.20 when the reduced temperature $\in = (T_N - T)/T_N$ was >0.03-0.07 to a much higher value (0.39-0.40) on approaching T_N.[9] Then we examined the alkylphosphonates to see whether there is a corresponding crossover and if so, how it varies with interlayer spacing.[10]

Data more remote from T_N obey the relationship $M_\in = M_0 \in^\beta$ with β_1 in the region of 0.20 for all three $C_nH_{2n+1}PO_3Mn \cdot H_2O$ ($n = 2$-4). However, as T_N is approached from below the exponential relationship changes and a much higher exponent β_2 becomes evident. The value of β_1 is close to that found in $M^IMnPO_4 \cdot H_2O$ (M^I = NH_4, ND_4, K) and is far from any of the estimates of [2d] or [3d] magnetic models. Thus in [3d] the Ising, XY and Heisenberg models predict respectively 0.31, 0.33 and 0.35 while the [2d] Ising model predicts 0.125. The related compound $Mn(HCOO)_2 \cdot 2D_2O$, also a quadratic layer Heisenberg antiferromagnet, gives β_1 = 0.22(1), with a crossover to $\beta_2 = 0.312$ at $\in \sim 0.02$. Recently, Bramwell and Holdsworth[11] have shown how β values in the region of 0.23 can arise from a [2d] model. Whilst the measured β_2 are larger than predicted for any of the [3d] models it seems safe to say that the crossover is a consequence of an evolution from [2d] to [3d] behaviour.

The reduced temperatures $\in_{X0}$ at which the crossovers occur also vary significantly from one compound to another within the Mn phosphate (phosphonate) hydrate series. Among the M^I compounds $\in_{X0}$ is a little larger in $KMnPO_4 \cdot H_2O$ (0.09(1)) than in the NH_4 compound (0.07(1)), no doubt to be correlated with the smaller interlayer separation in the former. In the alkyl phosphonates, $\in_{X0}$ decreases as the interlayer separation increases, corresponding to a decrease in the ratio of in-plane to out-of-plane exchange constants. We believe this was the first systematic study of the critical exponents and crossover temperatures for a series of two-dimensional weak ferromagnets.

FERRIMAGNETISM: BIMETALLIC TRIS-OXALATO-SALTS

A second strategy for achieving finite zero-field magnetisation in a molecular-based array, without the need for ferromagnetic near neighbour exchange, is to exploit ferrimagnetism. The examples chosen here are bimetallic tris-oxalato-salts with general formula $AM^{II}M^{III}(C_2O_4)_3$, which constitute a very extensive series, being formed by a wide range of organic cations A^+, as well as divalent and trivalent M both from transition metal and B-subgroup ions.[12]

Connection between $M^{III}(C_2O_4)_3{}^{3-}$ by M^{II} in two dimensions produces a honeycomb structure in which both metal ions occupy sites of trigonally distorted octahedral geometry, with all near neighbour M^{II}, M^{III} pairs bridged by oxalate ions (Figure 2).

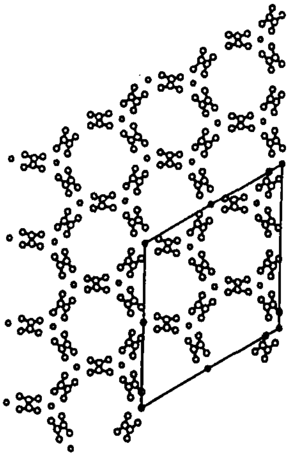

Figure 2 Two- dimensional honeycomb lattice of $AM^{II}M^{III}(C_2O_4)_3$

Many compounds in this series therefore have crystal structures that are approximately hexagonal, with basal plane unit cell constants that vary only slightly with A^+, though with strongly varying interlayer separation: a factor of 2 in interlayer separation is easily achievable.

The $AM^{II}Fe(C_2O_4)_3$ compounds with M^{II} = Mn are unusual ferrimagnets in that the electronic ground states of the two metal ions are the same, $^6A_1$ in D_3 symmetry.[13] The near neighbour exchange interaction is strongly antiferromagnetic, as indicated by the large negative Weiss constants, which do not vary much with A since the exchange pathway is only slightly affected by changing the organic group. The short range magnetic order therefore mimics that of a two-dimensional antiferromagnet. However, with the onset of long range order, which takes place around 27K (again nearly independent of A), the susceptibility increases abruptly, to reach a value which varies strongly with A, being smallest for $N(n\text{-}C_4H_9)_4$ and largest for $(C_6H_5)_3PNP(C_6H_5)_3$. Such an effect is reminiscent of the Mn alkylphosphonates, and is also attributed to spin canting. Again, the magnitude of the uncompensated moment is determined by an organic group which is not only not implicated in the exchange mechanism, but is spatially remote from the site of the magnetic moment.

When M^{II} = Fe in the bimetallic tris-oxalato-Fe(III) series an even more striking magnetic phenomenon is seen. The two magnetic ions being now $S = 2$ and $S = {}^5/_2$, the resulting behaviour is that of a conventional ferrimagnet. However, depending on the nature of the organic cation A one either has a conventional magnetisation at low temperature, increasing monotonically from zero at T_c to a limiting value at $T \rightarrow 0$, or a magnetisation that increases at first from zero below T_c but then reaches a maximum. At lower temperatures, the magnetisation then falls again, passing through zero and becoming strongly negative (Figure 3).[14]

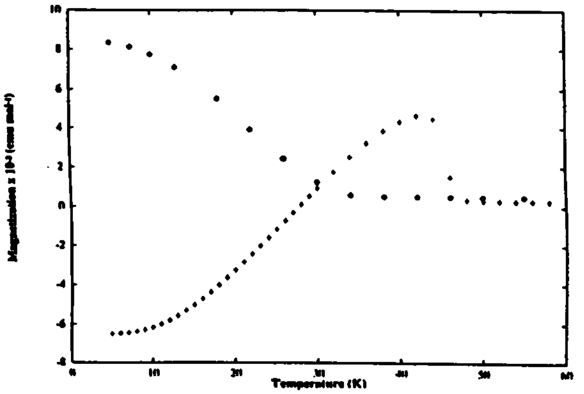

Figure 3 Magnetisation of $AFe^{II}Fe^{III}(C_2O_4)_3$: A= $(C_6H_5)_3PNP(C_6H_5)_3$,crosses; $As(C_6H_5)_3$, dots [13]

The latter behaviour is unprecedented among molecular-based magnetic materials but finds a precedent among continuous lattice oxides.

To explain the phenomenon we note that in a ferrimagnet the net magnetisation at a given temperature is the vector sum of the magnetisations of each sublattice. Should the temperature dependence of the magnetisations of each sublattice be similar the resultant will be a monotonic increase from T_c to absolute zero as shown in Figure 3 for $As(C_6H_5)_4Fe^{II}Fe^{III}(C_2O_4)_3$. On the other hand if the temperature derivatives of sublattice magnetisation $dM_{Fe(II)}/dT$ and $dM_{Fe(III)}/dT$ have a different dependence on temperature, then the temperature derivative of the resultant $d(M_{Fe(II)} - M_{Fe(III)})/dT$ can change sign. The magnetisations of the two sublattices cancel at some temperature called the compensation temperature. However, the feature distinguishing the bimetallic tris-oxalato compounds from the oxides is that the drastically varying magnetic behaviour comes about by changing organic groups far away in the lattice from the magnetic centres.

BEDT-TTF TRIS-OXALATOFERRATE (III): MAGNETIC SUPERCONDUCTOR

A feature of the superconducting charge transfer salts based on the donor molecule bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) is the spatial segregation of the organic cations and inorganic anions into alternating layers. Because of this separation into well-defined organic and inorganic components the BEDT-TTF charge transfer salts are attractive synthetic targets for combining superconductivity in a molecular lattice with properties more characteristic of the inorganic solid state like cooperative magnetism. The electrons close to the Fermi surface are largely confined to frontier orbitals of the BEDT-TTF while magnetic moments localised on the anions can be built in if the latter are transition metal complexes. Of the small number of BEDT-TTF salts containing 3d complex anions, several are semiconductors[15] but we reported one example, $(BEDT\text{-}TTF)_3CuCl_4 \cdot H_2O$, which remains metallic down to 400 mK though without becoming superconducting, and in which magnetic resonance from the conduction electrons and the localised 3d electrons can be resolved.[16]

The previous section of this review described some two-dimensional bimetallic layers containing uni- or dipositive cations and $M^{III}(C_2O_4)_3^{3-}$ in which the oxalato-ion acts a bridging ligand, leading to infinite sheets of approximately hexagonal symmetry, separated by bulky organic cations[12, 13]. In parallel with our studies of their magnetic properties we have therefore begun to explore the synthesis of compounds containing anion lattices of similar type, but interleaved with BEDT-TTF molecules. In the series $(BEDT\text{-}TTF)_4AFe(C_2O_4)_3 \cdot C_6H_5CN$, ($A = H_2O$, K, NH_4), while the stoichiometric ratio of BEDT-TTF to Fe is the same, as is the basic topology of the anion layer, the presence of absence of a monopositive cation not only changes the electron count (and hence the band filling) in the organic layer, but drastically alters the packing motif of the BEDT-TTF. Thus, the compounds with A = K, NH_4 are semiconductors with the organic molecules present as $(BEDT\text{-}TTF)_2^{2+}$ and $(BEDT\text{-}TTF)^0$.[17] In contrast the compound with $A = H_2O$ has BEDT-TTF packed in the β" arrangement and is the first example of a molecular superconductor containing magnetic ions.[18]

The crystal structures of all three compounds consist of alternating layers containing only BEDT-TTF and only $AFe(C_2O_4)_3 \cdot C_6H_5CN$. Whilst the molecular packing in the latter is quite similar in all three cases the molecular packing arrangement within the BEDT-TTF layers differs markedly from the other two when A = H_2O. When projected on to the mean plane of the A and Fe, the anion layers have a clear honeycomb arrangement, with alternate A and Fe forming an approximately hexagonal network (Figure 4).

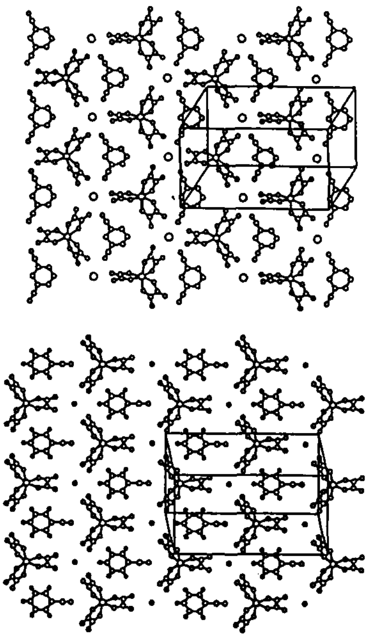

Figure 4 Anion and Solvent Layers in $(BEDT\text{-}TTF)_4\ AFe(C_2O_4)_3\ C_6H_5CN$ A=K, top; A=H_2O, bottom [22]

The Fe are octahedrally coordinated by three bidentate oxalate ions, giving rise to a trigonal component of the crystal field.

In contrast to the closely similar anion layers, the molecular arrangements in the BEDT-TTF layers are quite different in the K and NH_4 salts from that found in the H_2O one. In the former the asymmetric unit consists of two independent BEDT-TTF. Comparison with corresponding bond lengths in other BEDT-TTF salts with established levels of oxidation[10] indicates charges of 0 and +1. The unipositive ions occur as face to face dimers, surrounded by monomeric neutral molecules (Figure 5).

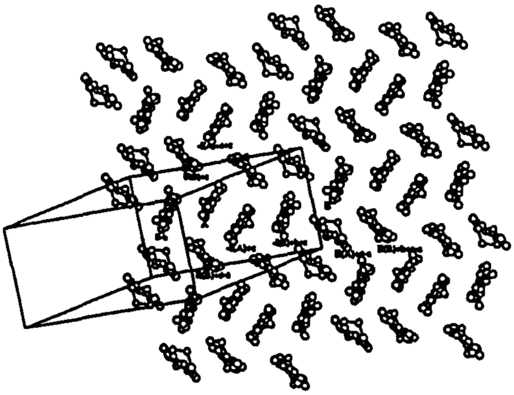

Figure 5 BEDT-TTF Layer in $(BEDT\text{-}TTF)_4\ KFe(C_2O_4)_3\ C_6H_5CN$ [22]

Molecular planes of neighbouring dimers along [011] are oriented nearly orthogonal to one another, but the planes of the dimers along [100] are parallel. Packing of the BEDT-TTF molecules in the H_2O salt is quite different from that in the K and NH_4 salts: there are no discrete dimers. Instead stacks are formed, with short S...S distances between them. Overall the packing closely resembles that of the β''-structure found in metallic $(BEDT\text{-}TTF)_2AuBr_2$[20] and the pressure-induced superconductor $(BEDT\text{-}TTF)_3Cl_2{\cdot}2H_2O$.[21]

An important structural factor in the dimensionality of the conduction in the family of molecular charge transfer salts is the 'thickness' of the anion layer separating the conducting planes of BEDT-TTF. A convenient measure of the thickness is the distance between the terminal C atoms of BEDT-TTF molecules on either side of the anion layer. Following that measure, a salt with a linear anion such as $Cu(NCS)_2^-$ has an effective thickness of 5.32 Å while ones with double anion layers like $[KHg(SCN)_4]^-$ are distinctly thicker (7.42 Å). In the present compound the mean thickness is 5.47 Å. At least in these three cases T_c correlates with the thickness of the anion layer since they have T_c 10.4, 1.1 and 8.5 K respectively.

Clearly the oxalato-bridged network of A and M^{III} provides an elegant means of introducing transition metal ions carrying localised magnetic moments into the lattice of a molecular charge transfer salt. In the case of the A = H_2O compound it has enabled us to prepare the first molecular superconductor containing localised magnetic moments within its structure, while the A = K, NH_4 compounds are semiconducting.[22] The packing of the BEDT-TTF in the A = K, NH_4 phases is of a type not previously observed, with spin-paired $(BEDT\text{-}TTF)_2^{2+}$ separated by closed shell $(BEDT\text{-}TTF)^0$, while that in the

This brief review has tried to illustrate the potential of combining layers containing metal ions with ones consisting of organic molecules to create lattices having unusual conjunctions of physical properties. Such organic-inorganic hybrid compounds clearly have much to offer as we search for novel behaviour in the solid state.

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