

New molecular superconductor containing paramagnetic chromium(III) ions

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The molecular charge-transfer salt β'' -(bedt-ttf)₄(H₂O)Cr(C₂O₄)₃·PhCN [bedt-ttf = bis(ethylenedithio)tetrathiafulvalene], containing paramagnetic Cr^{III} ions ($S = 3/2$), is a superconductor with $T_c = 6.0(5)$ K.

Superconductivity can be destroyed by magnetic fields, through break up of $S = 0$ Cooper pair charge carriers. This is true whether the field is applied externally by a magnet, or arises internally from magnetic moments within the lattice.¹ However there is evidence to suggest that $S = 1$ Cooper pairs can coexist with strong magnetic fields. To explore this antagonism between magnetism and superconductivity we have been systematically preparing molecular charge-transfer salts in which layers consisting of stacks of the organic donor molecule bedt-ttf [bis(ethylenedithio)tetrathiafulvalene] are interleaved by layers containing anionic transition-metal complexes which are paramagnetic. Among many bedt-ttf charge-transfer salts we found one containing paramagnetic high-spin Fe^{III} ions which was a superconductor below 8.5(3) K.² The compound in question, β'' -(bedt-ttf)₄[(H₂O)Fe(C₂O₄)₃]·PhCN **1**, contains the trigonally distorted-octahedral [Fe(C₂O₄)₃]³⁻ with $S = 5/2$, which is one of numerous known oxalate complexes of d-block elements. It is therefore pertinent to seek other examples with different magnetic moments to compare the effect of such a change on the superconducting critical temperature. Here we report that the corresponding Cr^{III} compound, with a lower magnetic moment ($S = 3/2$) is indeed a superconductor, but with a slightly lower T_c than the Fe^{III} compound.

Crystals of (bedt-ttf)₄(H₂O)Cr(C₂O₄)₃·PhCN **2** were grown from solutions generated electrochemically in H-shaped cells at a constant current of 1 μ A using wet PhCN as solvent and [NH₄]₃[Cr(C₂O₄)₃]·3H₂O as supporting electrolyte. The solvent was saturated with bedt-ttf, excess solid being placed at the base of the anode arm of the H-cell. Black needle shaped crystals grew on the Pt anode. The structure of this new charge-transfer salt³ is isostructural to that of **1**, featuring alternate layers of bedt-ttf cations, and layers containing [Cr(C₂O₄)₃]³⁻, H₂O and PhCN. The cation layers adopt the β'' packing arrangement, with stacks of bedt-ttf having numerous short intermolecular S...S distances. The anion layers have a honeycomb arrangement of [Cr(C₂O₄)₃]³⁻ with their outer oxygens hydrogen-bonded to the water molecules. Within each layer there is exclusively one chiral form of [Cr(C₂O₄)₃]³⁻ and successive layers contain alternating Δ and Λ enantiomers. The PhCN molecules occupy hexagonal cavities with the CN groups parallel, causing an elongation of the hexagonal network along the b -axis.

Susceptibility measurements were performed on a Quantum Design MPMS7 SQUID magnetometer on randomly oriented polycrystalline samples within a gelatin capsule, and the data was collected on a Hewlett-Packard 486/33N PC. In fields > 0.01 T the susceptibility from 300 to 4 K is well fitted by the Curie–Weiss law together with a temperature-independent Pauli contribution to give a Curie constant of 1.956(2) emu K mol⁻¹ (1.875 is expected for Cr³⁺, $S = 3/2$). The fitted Weiss constant of $-0.21(1)$ K indicates a very weak antiferromagnetic interaction between Cr centres. The Pauli contribution is 0.0016(3). In a plot of χ^{-1} vs. T there is a distinct change of

slope near 150 K, probably indicative of a minor structural phase transition. In contrast, upon cooling the sample in zero applied field and measuring the susceptibility in a field of 5×10^{-4} T whilst warming, the response is diamagnetic from 1.75 to 6.0 K indicating the presence of superconductivity. Type II superconducting behaviour is observed upon recooling as flux is trapped inside the sample and the susceptibility is less negative (Fig. 1). As the applied field is increased, the diamagnetism decreases, until at 0.002 T a Curie tail begins to develop as the high susceptibility of the Cr³⁺ obscures the superconducting transition. The superconducting transition is completely suppressed by fields greater than 0.01 T, when the susceptibility obeys the Curie–Weiss law from 1.75 K to room temperature.

Polarised optical reflectivity of single crystals was recorded at room temp. using a Perkin Elmer 1710 spectrometer fitted with a Spectra Tech microscope and a KRS5 polariser. When the electric vector is both parallel and perpendicular to the needles axis of the crystal, the spectrum of **2** shows a high metallic reflectivity at frequencies below *ca.* 3800 cm⁻¹ with weak sharp vibrational features superimposed (Fig. 2). Several of the latter are assigned⁴ to the [Cr(C₂O₄)₃]³⁻: an O–C–O stretching vibration as 1270 and 1320 cm⁻¹, an O–C–O symmetric stretching vibration at 1390 cm⁻¹ and an O–C–O asymmetric stretching vibration at 1645 cm⁻¹. The other weak vibrational modes due to bedt-ttf and PhCN can be assigned by comparison with published data.⁵ The metallic reflectivity has been fitted to a Drude expression⁶ for free electrons with a damping term for the charge carrier motion. A value of 3570 cm⁻¹ is calculated for the plasma frequency.

The EPR spectra of a polycrystalline sample were recorded at X- and K-band from 4 to 300 K on a Bruker ESP300E spectrometer. Cooling was achieved *via* a BVT2000 variable-temperature unit (300–100 K) or an Oxford Instruments ESR910 cryostat (< 100 K). Spectrum simulations were achieved *via* in-house software.⁷ At each temperature the spectrum consisted of separate resonances attributable to the localised Cr³⁺ and to the conduction electrons. The relative

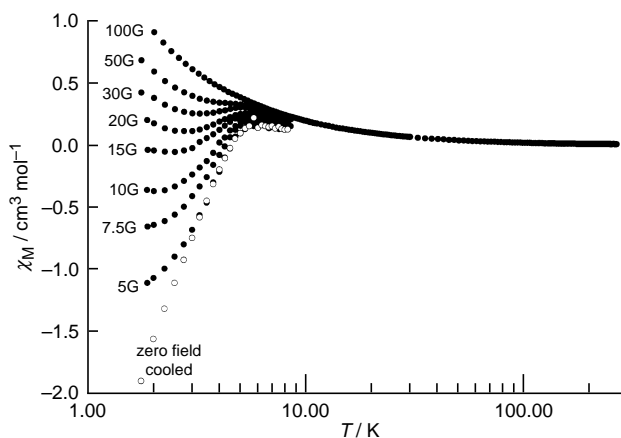


Fig. 1 Temperature variation of the magnetic susceptibility of **2** in fields from 0 to 0.01 T. Open circles are zero-field cooled data and filled circles are field-cooled data.

intensities of the resonances arising from each of these vary with temperature, see Fig. 3. Those for the conduction electrons decrease with decreasing temperature, in contrast to those due to the chromium centres which increase. The observation of spectra from the two different centres indicates that interaction between them remains weak over the whole temperature range. The resonance due to the conduction electrons consists of a single line at $g = 2.006(1)$ comparable with the free-electron g value, whereas the spectrum relating to Cr^{3+} is complex. Simulations of the Cr^{3+} resonances at both X- and K-band resulted in acceptable fits only if the presence of two different Cr centres in a 1 : 1 ratio was assumed. These two centres have the same g values (2.00) but significantly different zero-field splitting parameters; $|D| = 0.52 \text{ cm}^{-1}$, $|E/D| = 0.07 \text{ cm}^{-1}$ and $|D| = 0.70 \text{ cm}^{-1}$, $|E/D| = 0.16 \text{ cm}^{-1}$. Since $|D|$ is more sensitive to changes in the electronic environment about

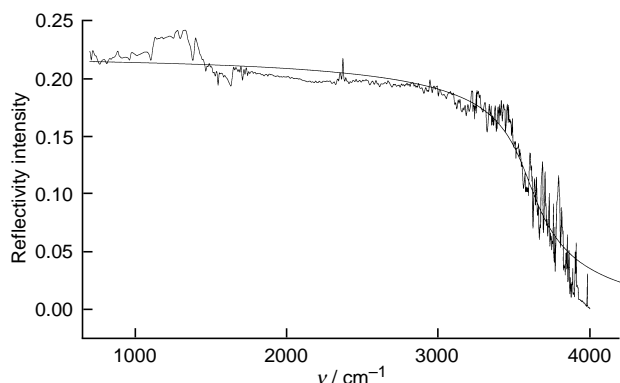


Fig. 2 Reflectivity of a crystal of **2** with the electric vector of the incident light parallel and perpendicular to the needle axis. The line is a fit to a damped Drude expression.

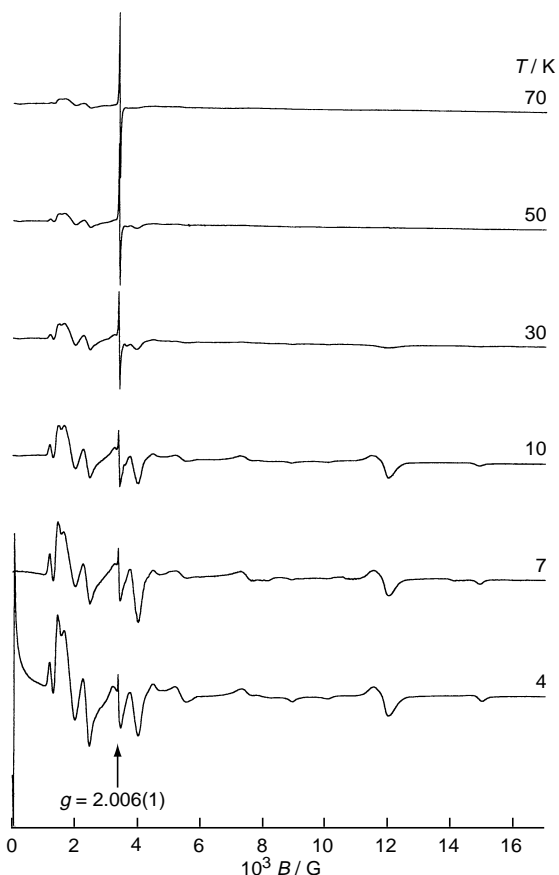


Fig. 3 X-Band EPR spectra of a polycrystalline sample of **2** in the temperature range 70–4 K

Cr than g , there are two types of coordinated chromium differentiated by very small structural changes, probably in the O–Cr–O angles rather than bond distances. This is apparently in contradiction to the crystal structure. However the latter was refined from room-temperature data and it is likely that there is a structural phase transition to a lower symmetry on cooling, as already indicated by the bulk susceptibility data. The fact that the ratio of the two metal centres is 1 : 1 points to the possibility that the origin of this effect may be the interaction of each chiral form with the bedt-ttf layers.

An interesting feature of the EPR at X-band is a line with inverted phase compared to the rest of the spectrum near to zero frequency at the lowest temperatures. The origin of this feature is unknown and is the subject of further investigations. However, similar features have been observed in the EPR of high-temperature cuprate⁸ superconductors as well as bedt-ttf⁹ and C_{60} ¹⁰ based superconductors. It has been suggested to be due to the formation of weak links and closed superconducting loops between grains and is considered to be a marker for the onset of superconductivity.¹¹ Detailed investigations of the EPR spectra of **1** and similar materials will be reported in subsequent articles.

In conclusion we have found that replacing Fe by Cr in the paramagnetic molecular superconductor **1** brings about a small decrease in T_c and H_c despite the smaller magnitude of the paramagnetic moment embedded in the lattice. Thus, given that the unit-cell constants of **1** and **2** are essentially identical, there is no simple relationship between the strength of the local magnetic binding energy of the Cooper pairs. We are continuing to explore this intriguing family of superconductors, including synthesis of examples containing only closed-shell metal ions.

We are grateful to Professor W. Hayes of the Clarendon Laboratory, Oxford, for access to IR reflectivity equipment. We thank Professor M. B. Hursthouse and Dr S. J. Coles of the EPSRC X-ray Crystallography Service, Cardiff, for communication of results. One of us (S. S. T.) thanks Dr P. Harper for discussions on Drude theory. The work is supported by the EPSRC.

Footnote

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Received in Cambridge, UK, 15th May 1997; 7/03352D