

## Correlation of Magnetic and Optical Properties in the Organic-intercalated Two-dimensional Ionic Ferromagnet Bis(monomethylammonium) Tetrachlorochromate(II)

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**Summary** A simple correlation exists between the intensity of a quintet-to-triplet transition in the visible absorption spectrum of  $(\text{MeNH}_3)_2\text{CrCl}_4$  ( $T_c$  58 K) and the magnetic order; from 6 to 50 K the oscillator strength of the optical transition is proportional to  $T^2$  and from 70 to 125 K it is nearly constant.

COMPOUNDS with the general formulae  $(\text{RNH}_3)_2\text{MX}_4$ , where R is an alkyl or aryl group, M a  $3d$  ion, and X a halide ion, have excited interest in the last few years because, although their lattices contain layers of ferromagnetically (M = Cu) or antiferromagnetically (M = Mn, Fe) coupled metal ions, separated by as much as 25 Å from one another by organic material, they nevertheless undergo transitions to three-dimensional magnetic order at finite temperatures.<sup>1</sup> The Cu members of the series have had the added interest of belonging to the very small group of ionic transition metal salts which order as three-dimensional ferromagnets.<sup>2</sup> We recently showed<sup>3</sup> that the previously unknown Cr salts with similar formulae also contain layers of ferromagnetically coupled spins and furthermore, that their Curie temperatures are much higher than those of the Cu salts containing the same R groups (50–60 K compared with 7–10 K). Like their alkali-metal analogues,<sup>4</sup> the bis(monoalkylammonium)tetrachlorochromates have two particularly sharp absorption bands in the visible region, assigned as spin-forbidden ligand field transitions. Indeed, the tetrachlorochromates are unique even among the small number of three-dimensional ionic ferromagnets in showing

such well resolved optical transitions. In this note we report that the temperature dependence of one of these transitions in the first member of the series,  $(\text{MeNH}_3)_2\text{CrCl}_4$ , correlates with the onset of three-dimensional ferromagnetic order. Thus the optical spectrum measured without an applied magnetic field is an excellent probe of the magnetic order in this important class of organic-intercalated ionic ferromagnets.

Complex  $(\text{MeNH}_3)_2\text{CrCl}_4$  was prepared as described previously<sup>3</sup> and crystals were grown by slowly cooling an ethanolic solution. Both the crystals themselves and the  $\text{Cr}^{\text{II}}$  solutions are extremely sensitive to air oxidation and all manipulations including crystal mounting were carried out exclusively under nitrogen. The crystals which are orthorhombic at room temperature<sup>2,5</sup> grow as thin flat plates and the spectra were measured with the light propagating along the  $c$ -axis.

In the visible region of the spectrum  $(\text{MeNH}_3)_2\text{CrCl}_4$  has two prominent absorption bands at 533 and 626 nm with halfwidths at 120 K of only 3 and 7 nm respectively. This compares with 535 and 629 nm for the wavelengths of the corresponding bands in  $\text{K}_2\text{CrCl}_4$ .<sup>4</sup> The  $d^4$  Tanabe–Sugano diagram indicates that from 700 to 400 nm in octahedrally co-ordinated metal ions quintet-to-triplet transitions are to be expected and because the wavelengths of the two bands observed vary so little from one  $\text{Cr}^{\text{II}}$  salt to another we attribute them to pure 'spin-flip' transitions. Our earlier assignment<sup>4</sup> of the  $\text{K}_2\text{CrCl}_4$  bands [ ${}^3B_{1g}(D_{4h})$  of  ${}^3E_g(O_h)$ ( ${}^3H$ ) and  ${}^3B_{1g}(D_{4h})$  of  ${}^3A_{2g}(O_h)$ ( $a^3F$ )] would therefore still stand in the monomethylammonium salt.

The most striking feature of the spectrum of  $(\text{MeNH}_3)_2\text{-CrCl}_4$  is that below *ca.* 70 K the two visible absorption bands lose their intensity very rapidly. In the Figure we plot the integrated area of the 533 nm band as a function of temperature. From 6 to 50 K the variation is described by a simple power law  $T^x$  with  $x = 2.1 \pm 0.1$ . In the same Figure is plotted the reduced magnetisation  $1 - [M(T)/M(O)]$ , measured by the Faraday method for a powdered sample at 0.3 T. The latter also obeys a power law up to at least  $0.9 T_c$ , with an exponent of  $1.5 \pm 0.1$ . From magnetization measurements the Curie temperature of  $(\text{MeNH}_3)_2\text{-CrCl}_4$  has been estimated<sup>3</sup> as  $58 \pm 2$  K, which is within 2 K of the temperature extrapolated from the high temperature and low temperature behaviour of the intensity of the 533 nm absorption band, as shown in the Figure.

We demonstrated previously that both in the metamagnetic transition metal dihalides and in compounds like  $\text{K}_2\text{CrCl}_4$  which, though they have layer structures, order as three-dimensional ferromagnets, the temperature dependence of the intensity of spin-forbidden ligand field transition can be thought of as arising solely from coupling between excitons and magnons propagating within the layers. In other words, as far as the limiting optical properties at low temperatures are concerned, those interactions between the layers which determine the nature of the three dimensional ordering are unimportant. For example, using the calculated magnon dispersion relation for a two-dimensional easy-plane ferromagnet we derived a  $T^2$  law for the intensity of the exciton-magnon combination bands in ferromagnetic  $\text{K}_2\text{CrCl}_4$ <sup>6</sup> and metamagnetic  $\text{NiBr}_2$ ,<sup>7</sup> in both cases in excellent agreement with observation at lower temperatures compared to  $T_c$ . The result reported in this note is important because, having extended the intensity data on an exciton-magnon band in a layer ferromagnet to temperatures well above  $T_c$  one can see, first that the  $T^2$  law appropriate to a two-dimensional easy-plane ferromagnet remains valid almost up to  $T_c$  and, second, that it rapidly becomes invalid above  $T_c$ , although in an essentially two-dimensional magnetic system one would expect substantial intra-layer correlations to persist above the three-dimensional ordering temperature. It is clear that the uniquely well resolved optical transitions in this new class of organic-intercalated layer ferromagnets will provide the

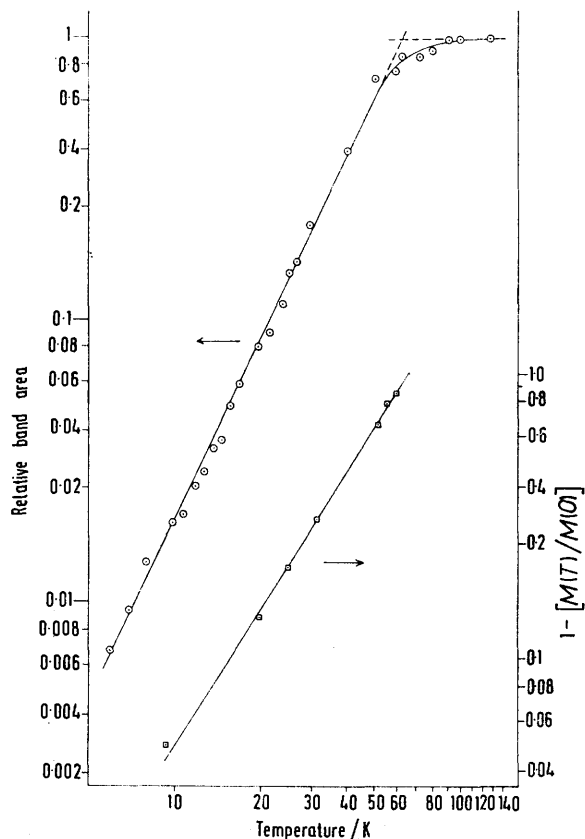


FIGURE. Intensity of the 533 nm absorption band and magnetization of  $(\text{MeNH}_3)_2\text{CrCl}_4$  vs. temperature.

basis for a variety of experiments on the onset of the ordering process.

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