

Magnetic Susceptibility and Optical Study of the Organic-intercalated Two-dimensional Ionic Ferromagnet Bis(benzylammonium) Tetrachlorochromate(II) †

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The powder a.c. magnetic susceptibility of bis(benzylammonium) tetrachlorochromate(II) has been measured from 4.2 to 150 K and a transition to three-dimensional ferromagnetic order observed at 37.0 K. From 80 to 150 K the susceptibility follows the Curie–Weiss law with the Curie and Weiss constants respectively 4.80 and 58 K. The susceptibility from 40 to 150 K is fitted to a high-temperature series expansion for a square two-dimensional lattice to give the near neighbour exchange constant $J/k = 10.6(2)$ K ($\mathcal{H} = JS_1 \cdot S_2$) and $g = 2.10(5)$. The divergence of the 'energetic' initial susceptibility $\chi_0 T/C$ as T_c is approached from above is fitted to a power law in $(T - T_c)/T$ to yield an exponent γ varying from 2.2 (far from T_c) to 1.87 (within 4 K of T_c). The ligand-field band system near 626 nm shows more structure than in corresponding Group 1A or n-alkylammonium salts. Temperature dependence of the intensity from 1.5 to 15 K shows that the zone centre magnon gap is smaller than in any of the other salts since the intensity closely follows a T^2 law down to 1.5 K. Minor differences in the intensity behaviour of the components of the 621 nm band system suggest that the ground state consists of three closely spaced levels. Comparison with other tetrachlorochromate(II) salts shows no clear correlation of either kT_c/θ or kT_c/J with interlayer separation.

Tetrahalogenochromate(II) salts have been of interest not only as rare examples of ionic transition-metal compounds that order ferromagnetically, but also because it has proved possible to probe their magnetic properties by optical, as well as conventional magnetic measurements.¹ Their visible absorption is dominated by spin-forbidden ligand-field transitions which gain their intensity by coupling to thermally populated spin waves. Thus the striking temperature dependence of the intensity of these bands is a measure of the spin wave density-of-states. The structures of the salts are based on the $K_2[NiF_4]$ structure and if organic cations are used in place of the Group 1A cations, the layers of magnetic ions become sufficiently separated that the magnetic properties should approximate to two-dimensional. As well as extensive optical,² magnetic,³ and neutron scattering⁴ measurements on the prototype compound $Rb_2[CrCl_4]$, we have reported optical and magnetic susceptibility studies on the compounds $[NH_3(C_nH_{2n+1})]_2[CrCl_4]$ with $n = 1, 2, 3, 5,$ or 12 which permit a variation in interlayer separation from 9.5 to 31 Å.⁵ In the present paper we extend these measurements to the benzylammonium salt, to observe the effect of placing conjugated aromatic sidechains between the layers. Because interlayer exchange is weak in all the tetrachlorochromate(II) salts, magnetic susceptibilities determined in moderately high fields by the Faraday method⁵ do not yield precise values for the transition temperatures as the ordering is influenced by the field. For the benzylammonium salt we therefore report the a.c. susceptibility measured in zero external field. This also enables us to determine the critical exponent γ of the divergent susceptibility above T_c . Optical absorption measurements between 1.5 and 10 K are also used to put an upper limit on the zone-centre spin wave gap while the fine structure of the 621 nm band gives information on the zero-field splitting in the ground state.

Experimental

Preparation.—Bis(benzylammonium) tetrachlorochromate(II) was prepared by the same method as the alkylammonium salts⁵ and crystals were grown by cooling a solution in a sealed tube as described previously.⁶ The compound is air-sensitive and all the manipulations were done under an inert atmosphere.

Magnetic Susceptibility.—For the a.c. susceptibility measurements⁷ a powdered sample was placed in a Teflon cylinder (diameter 3 mm and 6 mm long) and mounted inside a coil system consisting of a primary and two secondary coils. The two secondary coils are equal but oppositely wound on top of the primary coil and are connected in series. An a.c. current is fed to the primary coil *via* a current-stabilized low-frequency amplifier. Moving a magnetic sample from the centre of one of the secondary coils to the centre of the other causes a change in the voltage across the secondary coils, proportional to the mutual inductance M and the resistance R can be opposed. At balance, M is proportional to the real part of the susceptibility of the sample. The in-phase susceptibility χ^1 was recorded at a fixed frequency of 198 Hz and an absolute calibration of the susceptibility was made by reference to a standard sample of $Hg[Co(NCS)_4]$.

To perform measurements as a function of temperature, sample and coil systems were placed in an Oxford Instruments static cryostat consisting of two concentric Dewars, where the vacuum space can be evacuated to *ca.* 10^{-6} Torr. The sample holder is placed in the inner Dewar. Temperatures above 4.2 K were obtained by adjusting the pressure of the helium exchange gas in the inner Dewar and in the sample holder tube and regulating the current through the heater.

Optical Spectroscopy.—Visible absorption spectra were measured on a McPherson RS10 spectrophotometer with a Thor Cryogenics superconducting magnet cryostat. Below 4.2 K the crystal was immersed in liquid helium and the temperature varied by pumping on the liquid. The temperature was

† *Non-S.I. units employed:* Torr = (101 325)/760 Pa, Oe = $1\ 000/4\pi$ A m^{-1} , B.M. = 9.27×10^{-24} J T⁻¹.

measured by a calibrated carbon resistor. The crystal was *ca.* 2 mm² and 1 mm thick, and the light was propagated along the *c* axis perpendicular to the layers of metal ions. Output from the spectrophotometer was fed *via* a Hewlett-Packard digital voltmeter to a Research Machines 380Z microcomputer and stored on disc. Band areas were obtained from an integration program which subtracts a background calculated by linear interpolation between the average of two points each on either side of the band.

Results

X-Ray Diffraction.—Powder X-ray diffraction data were indexed in the orthorhombic *Cmca* space group with the unit-cell parameters $a_0 = 7.6(0)$, $b_0 = 7.4(4)$, and $c_0 = 31.4(5)$ Å.

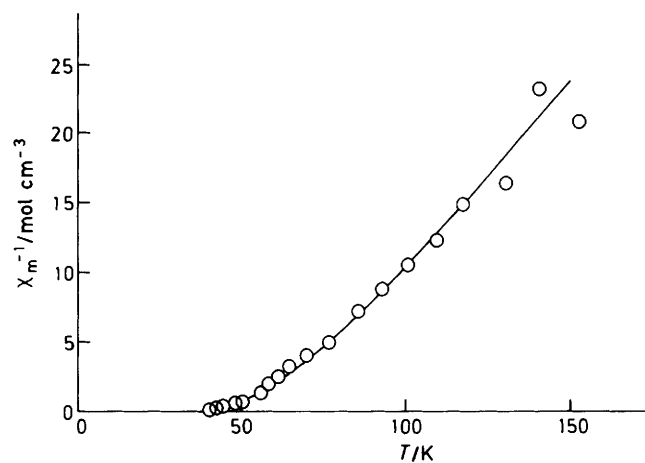


Figure 1. Inverse molar susceptibility of $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$. The full line is equation (1) with $J/k = 10.6$ K and $g = 2.10$

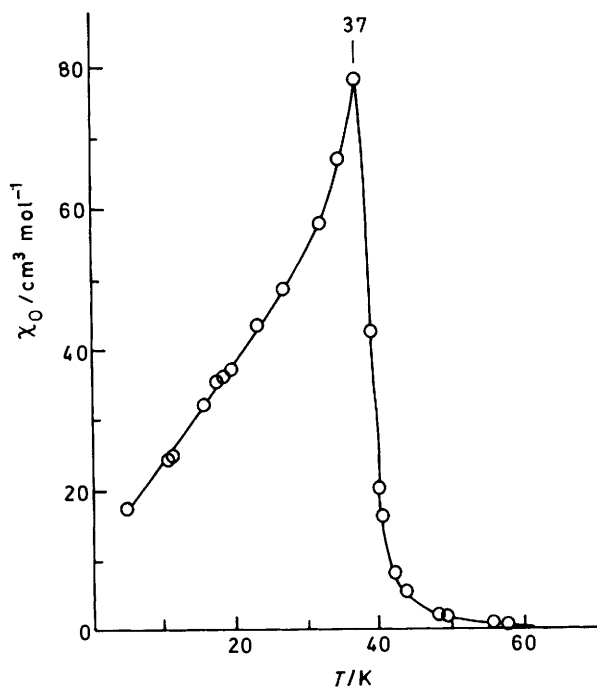


Figure 2. Initial susceptibility of $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$ from 5 to 60 K

Attempts to determine the structure by single-crystal X-ray diffraction failed as the crystal decomposed in the X-ray beam.

Magnetic Susceptibility.—From *ca.* 80 to 150 K the magnetic susceptibility follows the Curie-Weiss law $\chi = C/(T + \theta)$. A linear least-squares fit gives the Curie and Weiss constants C and θ as respectively 4.80 and 58 K. The effective moment $\mu_{\text{eff.}} = 2.828\sqrt{C}$ is 5.7 B.M., which is well above the spin-only value of 4.90 B.M. and increases as the temperature is lowered.

The experimental data above 50 K were fitted to the high-temperature series expansion for an $S = 2$ two-dimensional square Heisenberg ferromagnet⁸ as modified by Lines⁹ with the exchange Hamiltonian $\mathcal{H} = -JS_1 \cdot S_2$, equation (1), where $x =$

$$Ng^2\mu_B^2/\chi = \frac{1}{2}kT + J(-4 + 9x - 9.072x^2 + 55.728x^3 - 160.704x^4 + 116.640x^5) \quad (1)$$

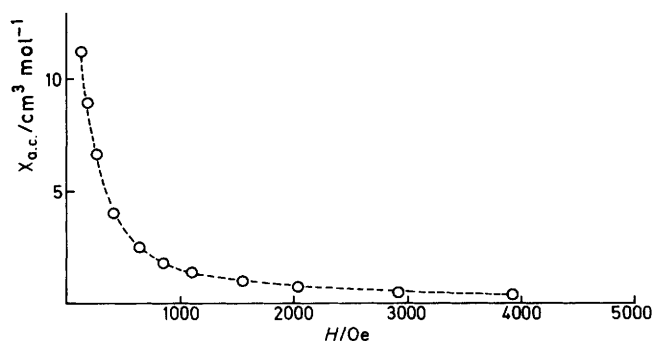


Figure 3. Field dependence of a.c. susceptibility of $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$ at 4 K

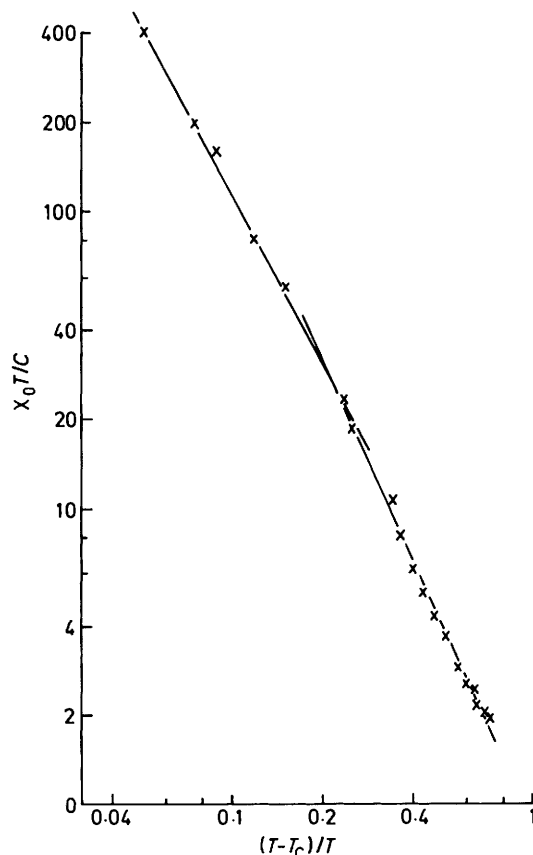


Figure 4. Energetic zero-field susceptibility $\chi_0 T/C$ versus $(T - T_c)/T$ for $T > T_c$

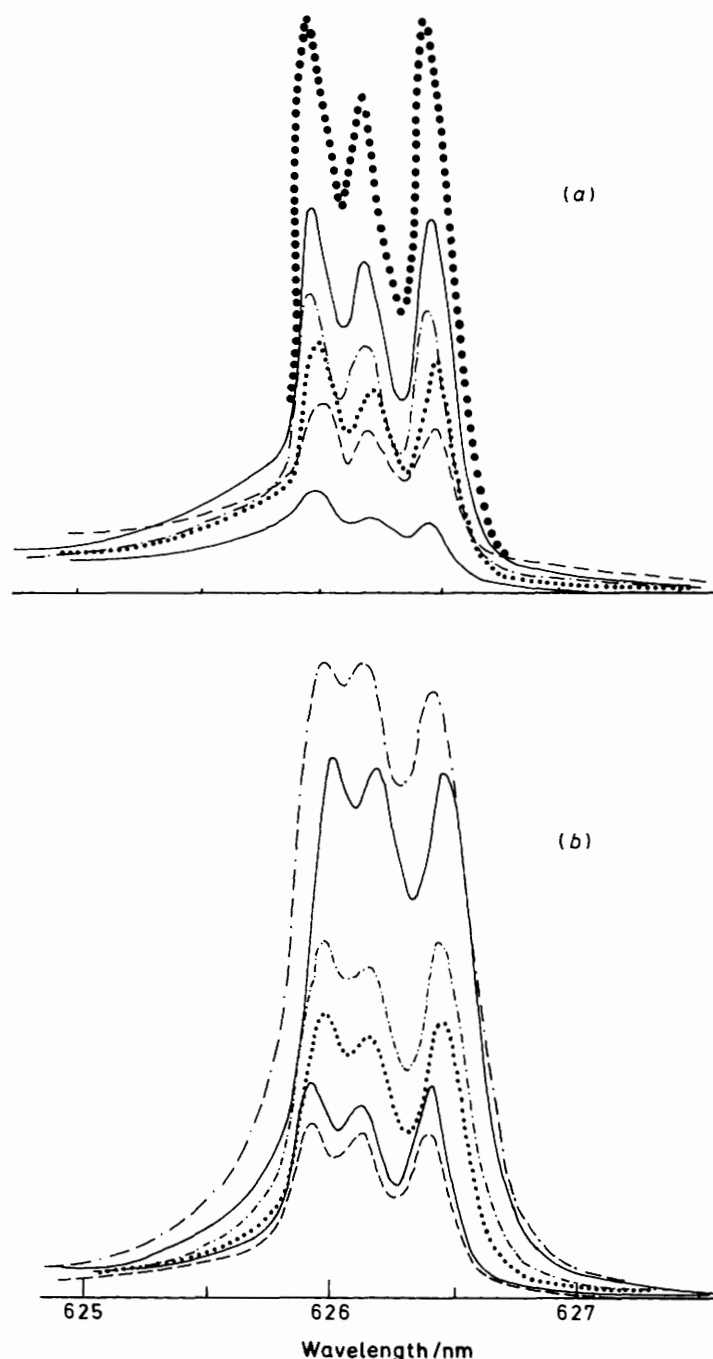


Figure 5. Exciton-magnon absorption bands of $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$ near 626 nm: (a) from top to bottom 4.22, 3.35, 3.00, 2.65, 2.19, 1.53 K, (b) from top to bottom 11.3, 10.4, 9.0, 7.4, 6.4, 5.4 K

J/kT and g is the Lande factor. Figure 1 shows the fit. Best values of J/k and g were found to be 10.6(2) K and 2.10(5) respectively, similar in value to those found in analogous bis(monoalkylammonium) tetrachlorochromates.^{5,10} The sign of J indicates that the near neighbour exchange is ferromagnetic.

Below 50 K the initial susceptibility χ_0 increases sharply to a maximum at 37 K and then decreases more slowly down to 4.2 K (Figure 2). The maximum at 37 K is due to the onset of three-dimensional ferromagnetic ordering brought about by intra- and inter-layer exchange interactions and weak anisotropy while the decrease at lower temperature is due to the formation

of magnetic domains. No evidence was found for the presence of any additional maxima at higher temperatures. An applied field of a few thousand oersteds is sufficient to saturate the ferromagnetic domains as shown by the vanishingly small a.c. susceptibility at 3 kOe (see Figure 3), at 4.2 K (well below T_c).

To follow the divergence of the initial susceptibility as the transition to long range order is approached from high temperature the data were fitted to a power law following the method of Kouvel and Fisher.¹¹ It has been suggested¹² that the correct thermodynamic function to monitor is the 'energetic' zero-field susceptibility $\chi_0 T/C$, so in Figure 4 this quantity is plotted against the reduced temperature $(T - T_c)/T$ on a

Table. Magnetic parameters and interlayer spacings of organic-intercalated tetrachlorochromate(II) salts

Compound	T_c /K	J/k (K)	θ /K	T_c/θ	kT/J	Interlayer separation/Å
$\text{Rb}_2[\text{CrCl}_4]$	52.1 ^a	14.4 ^a	92 ^b	0.57	3.6	7.88 ^c
$[\text{NH}_3\text{Me}]_2[\text{CrCl}_4]$	42.0 ^d	13.0 ^e	59 ^e	0.69	3.2	9.44 ^e
$[\text{NH}_3\text{Et}]_2[\text{CrCl}_4]$	41.0 ^d	10.1 ^e	58 ^e	0.71	4.1	10.71 ^e
$[\text{NH}_3(\text{C}_3\text{H}_7)]_2[\text{CrCl}_4]$	39.5 ^d	9.3 ^e	57 ^e	0.72	4.2	12.35 ^e
$[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$	37.0 ^f	10.6 ^f	58 ^f	0.64	3.5	15.71 ^f
$[\text{NH}_3(\text{C}_5\text{H}_{11})]_2[\text{CrCl}_4]$		9.3 ^e	57 ^e			17.81 ^e

^a Ref. 4. ^b Ref. 3. ^c Ref. 14. ^d Ref. 17. ^e Ref. 5. ^f This work.

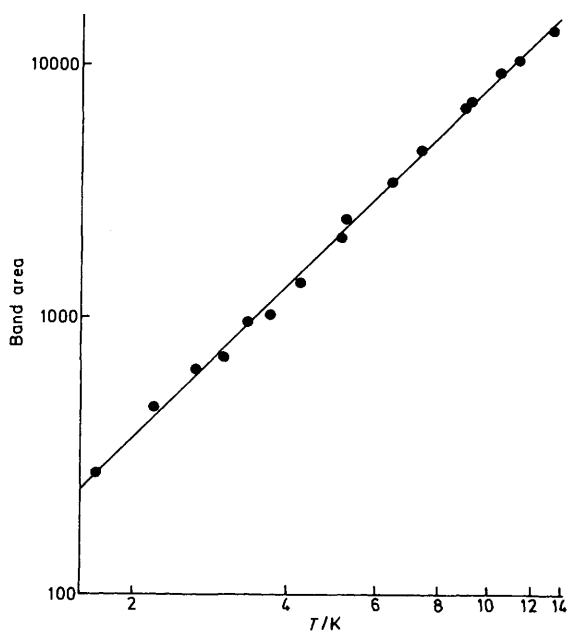


Figure 6. Temperature dependence of the integrated intensity of the 626 nm band system from 1.5 to 14 K. The full line is a least-squares fit with slope 2.02

logarithmic scale. A gradual diminution in the gradient of the curve leads to limiting values of the critical exponent γ of 2.2 and 1.87 at temperatures far away, and close to, T_c respectively.

Optical Spectra.—As in other tetrachlorochromate(II) salts,^{2,5} the visible absorption is concentrated in two regions around 530 and 630 nm. The former consists of at least three components but as they are unresolved we make no further comment on them. The latter consists of a broad asymmetric but unstructured band at 621.2 nm and a group of three closely spaced bands near 626.0 nm whose temperature variation from 1.5 to 4.2 K is shown in Figure 5(a), and from 5.4 to 11.3 K in Figure 5(b). All the band systems show a striking increase in intensity with increasing temperature, of the kind found in all the ferromagnetic Cr^{II} salts.^{2,5} The integrated area of the three 626 nm bands is shown in Figure 6 from which it is clear that the intensity follows a simple power law quite closely over the entire range from 1.5 to 14 K. A least-squares fit yields a slope of 2.02(1), i.e. T^2 .

Similar plots for the other band systems show positive deviations from a T^2 dependence at the lowest temperatures, indicating a temperature independent contribution to the intensity which, however, cannot be deconvoluted since the 'cold' and 'hot' bands overlap.

Discussion

Although we have no complete structure for $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$ the orthorhombic unit cell, and in particular the basal plane cell parameters, show that its structure is closely similar to other layer perovskite halide salts $[\text{NH}_3\text{R}]_2[\text{MX}_4]$ (R = alkyl, X = halide, M = Mn, Fe, Cu or Cd) in which layers of corner-sharing MX_6 octahedra form a square array in the basal plane.¹³ These layers are separated by NH_3R^+ , which are joined to them by weak H-bonding. The *c*-axis parameter suggests that the phenyl groups attached to opposite sides of adjacent layers are not interleaved between one another but form an extended array as in the alkylammonium compounds. This interaction between the layers occurs only through C-H...H-C van der Waals contacts. Since the near neighbour exchange constant in $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{CrCl}_4]$ is ferromagnetic it can safely be assumed that there is a co-operative Jahn-Teller distortion within the $[\text{CrCl}_4]_{\infty}^{2-}$ layers of the kind found in the Rb^+ ¹⁴ and NH_3Me^+ ¹⁵ salts.

The values of J/k and θ are compared with those of other tetrachlorochromate(II) salts in the Table. In $\text{Rb}_2[\text{CrCl}_4]$, whose structure has been determined in detail,¹⁴ the coordination around the chromium(II) is tetragonally elongated with principal axes alternately along $[011]$ and $[0\bar{1}\bar{1}]$ of the *Cmca* unit cell. This leads to the ferromagnetic exchange because the Jahn-Teller distortion constrains the single $e_g(O_h)$ electron of each Cr^{2+} to the d_{z^2} orbital and permits superexchange *via* bridging chloride anions between a half-filled d_{z^2} orbital on one chromium ion and the empty $d_{x^2-y^2}$ orbital of its neighbours. The exchange constant of 10.6 K derived from the high-temperature series expansion for the benzylammonium salt is lower than the values found for the Rb^+ ⁴ and methylammonium salts⁵ and comparable with those found in the higher alkylammonium derivatives. In the Rb salt the Cr-Cl...Cr bond angles within the basal plane are all 180° so the half-filled z^2 and empty x^2-y^2 orbitals are orthogonal.¹⁴ On the other hand in the NH_3Me^+ salt¹⁵ this angle is reduced to 166°, thus permitting a small contribution from a 90° antiferromagnetic superexchange pathway. It appears likely that this is a feature of all the organic-intercalated salts since comparable distortions due to the steric requirements of the H-bonding are found in other $[\text{NH}_3\text{R}]_2[\text{MCl}_4]$ salts.¹⁶

The Curie temperature (37 K) of the benzylammonium compound is comparable with those measured in similar organic-intercalated Cr^{II} derivatives by SQUID magnetometry¹⁷ (see Table). On the other hand the values obtained for the methyl- and ethyl-ammonium salts by the Faraday method are systematically higher than those listed in the Table. This is due to the applied magnetic field used, which increases the short-range correlations in the magnetic phase transition region and therefore the onset in the magnetization *versus* temperature plot is broadened. From the Table the first observation to be made is that on increasing the interlayer distance there is only a small decrease in the three-dimensional magnetic ordering temperature, part of which may in any case be due to the small decrease

in J . This behaviour has been previously observed in the corresponding tetrachlorocuprates(II).¹² It was shown rigorously by Mermin and Wagner¹⁸ that two-dimensional lattices with purely Heisenberg or XY -like exchange would not possess long range order at non-zero temperatures. However, Stanley and Kaplan¹⁹ found evidence from high-temperature series expansions that, at least for $S > \frac{1}{2}$, a transition occurred at a finite temperature $T_c(2)$ to a two-dimensional state in which the susceptibility diverged but there was no truly long range order. If the system has a small Ising-like anisotropy or a small interplanar interaction three-dimensional long range order could occur, the three-dimensional transition temperature T_c being close to $T_c(2)$. The Stanley–Kaplan formula for $T_c(2)$ is¹⁹ given by equation (2) which, for a number of nearest neighbours

$$T_c(2) \sim \frac{1}{10}(z-1)[2S(S+1)-1]J/k \quad (2)$$

$z = 4$ and $S = 2$ predicts $kT_c(2)/J \sim 3.3$. The experimental values of kT_c/J for the tetrachlorochromates, listed in the Table, are quite close to this prediction.

As noted above, the transition to three-dimensional long range order at T_c is brought about by anisotropy within the layers, or interlayer exchange. Given the separation between the layers in these salts we neglect the latter, but estimates of the anisotropy are available from the temperature dependence of the ligand-field absorption band intensity at very low temperatures. We have shown² that when kT becomes comparable to the energy of the anisotropy gap in the spin wave dispersion at the Brillouin zone centre the intensity deviates from the T^2 law predicted²⁰ for a two-dimensional Heisenberg ferromagnet, and found in $\text{Rb}_2[\text{CrCl}_4]$ ² and the corresponding NH_3Me^+ and NH_3Et^+ salts⁵ at higher temperatures. The intensity now becomes proportional to $T^2 \exp[-E(0)/kT]$, where $E(0)$ is the zone centre anisotropy gap. In $\text{Rb}_2[\text{CrCl}_4]$ the gap estimated in this way² is 1.1 K, in good agreement with the inelastic neutron scattering result,⁴ while in $[\text{NH}_3\text{Me}]_2[\text{CrCl}_4]$ it is 1.9 K.²¹ However, Figure 6 demonstrates that there is no measurable deviation from the T^2 law in the benzylammonium salt, even at 1.5 K. Thus an upper limit of $E(0)$ in this case is no more than 1 K.

If there is anisotropy within the basal plane in the benzylammonium salt, however small, the critical behaviour close to T_c is expected to cross over from two-dimensional isotropic to two-dimensional Ising-like.¹² The values of γ found from Figure 4 bear out this prediction since the exponent decreases towards 1.87 as T_c is approached. The theoretical value for a two-dimensional Ising model is 1.75. De Jongh and Miedema¹² found similar behaviour in the series of ferromagnetic $[\text{NH}_3(\text{C}_n\text{H}_{2n+1})]_2[\text{CuCl}_4]$ salts.

Further evidence for a small energy splitting in the ground state comes from the fine structure in the 626 nm region, shown in Figure 5. Because the bands are exciton–magnon combinations they are not Gaussian, so it is not possible to resolve the 626 nm band system into components. However, plotting the maximum intensity of each *versus* temperature shows that the lowest in energy of the three bands ($15\,964\text{ cm}^{-1}$) falls in intensity noticeably more rapidly with decreasing temperature than the second ($15\,971\text{ cm}^{-1}$), which falls more rapidly than the third ($15\,976\text{ cm}^{-1}$). This indicates that the bands arise from different ground-state components. One possibility is that these are the $M_S = 0, \pm 1, \pm 2$ levels of 5A_g , separated by second-

order spin-orbit coupling. Such splitting is the origin of the single ion anisotropy, but it cannot be determined quantitatively from the data in Figure 5 as the bands overlap too strongly.

Finally it is worth noting that a similar triplet of absorption bands occurs in the $^6A_{1g} \rightarrow ^4T_{2g}$ transition of the two-dimensional antiferromagnet $[\text{NH}_3(\text{CH}_2\text{Ph})]_2[\text{MnCl}_4]$, in contrast to the NH_3Me^+ salt, which only shows a single exciton–magnon band in this region.²² In the Mn salt the fine structure was ascribed to singularities in the combined exciton–magnon densities-of-states at X and M high symmetry points of the two-dimensional Brillouin zone, of the type first pointed out by Kojima *et al.*²³ It seems probable that a similar effect is operating in the benzylammonium Cr salt, where the energy separations of the three peaks are of similar magnitude (7 and 5 cm^{-1} , compared with 4 and 9 cm^{-1} in the Mn case).

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