Magnetic Susceptibility and Optical Spectra of the Organic-intercalated Two-dimensional Ferromagnets Bis(monomethylammonium)- and Bis(monoethylammonium) Tetrachlorochromate(II)

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The title compounds have been prepared and characterised by chemical analysis and *X*-ray diffraction. By magnetic-susceptibility and magnetisation measurements they are shown to order ferromagnetically at $T_c = 58 \pm 2$ and 55 ± 2 K respectively. Up to *ca.* 0.7 T_c the magnetisation $M(T)$ obeys the equation $1 - [M(T)/M(0)] = CT^\gamma$ where $\gamma = 1.5 \pm 0.1$. The optical spectra of both compounds contain sharp absorption bands at 533 and 626 nm, assigned as quintet–triplet ligand-field transitions. Up to 0.9 T_c their intensities vary with temperature as T^2, as predicted for ' hot ' exciton–magnon combination bands in a two-dimensional easy-plane ferromagnet.

IN the last few years there has been much interest, both among chemists and physicists, in the magnetic properties of compounds containing layers or chains of metal ions.[1] This activity has been motivated in part by a search for model systems on which to test the predictions of statistical thermodynamic theories of collective magnetic behaviour which take their simplest form where only one- or two-dimensional interactions have to be considered. In part, too, it has stemmed from a desire to probe the three-dimensional ordering mechanism in compounds in which the interactions are essentially low-dimensional. Thus, for example, Mermin and Wagner [2] showed theoretically that a two-dimensional array of spins, with near-neighbour interactions described by an isotropic Heisenberg Hamiltonian, does not undergo a phase transition to a ferromagnetic or antiferromagnetic state above absolute zero. On the other hand, introducing anisotropy into the Hamiltonian raises T_c to a finite level.

From the experimental point of view one of the most attractive groups of low-dimensional magnetic compounds are the layer perovskites $[NRH_3]_2[MX_4]$ (R = an alkyl or aryl group, M = a 3*d* ion, X = halide). Varying R permits variation of the distance between the MX_2 layers. In all these compounds, even when the interlayer distance is as great as 25 Å, spontaneous magnetic order in three dimensions is established between 10 and 90 K. The manganese [3] and iron [4] members have antiferromagnetic near-neighbour coupling, the copper has ferromagnetic.[5] The purpose of the present paper is to report the synthesis, characterisation, and magnetic properties of the corresponding chromium salts. Not only are they ferromagnetic, and hence an addition to the very small group of ionic insulators which order ferromagnetically,[6] but they are unique among optically transparent ferromagnets in showing well resolved spin-forbidden ligand-field transitions, whose intensity variation with temperature provides a direct probe of the magnetic order.

A preliminary communication of these results has appeared.[7]

EXPERIMENTAL

B.D.H. Monoalkylammonium chlorides were dried *in vacuo* over P_4O_{10} for several hours. Since the tetrachlorochromates(II) are hygroscopic and very easily oxidised, all the preparations and sample handling were carried out under oxygen-free nitrogen. To a hot solution of Cr^{II} in dry ethanol, prepared by passing dry HCl gas through a suspension of finely divided Cr metal, was slowly added a stoicheiometric quantity of monoalkylammonium chloride in dry ethanol solution. On cooling, pale green plates of the bis(monoalkylammonium) tetrachlorochromate(II) crystallised. Larger crystals could be grown by slow recrystallisation (Found: C, 9.70; H, 4.70; Cl, 54.1; Cr, 20.8; N, 10.9. Calc. for $C_2H_{12}Cl_4CrN_2$: C, 9.30; H, 4.65; Cl, 55.0; Cr, 20.15; N, 10.85. Found: C, 16.8; H, 5.80; Cl, 49.7; Cr, 18.25; N, 9.65. Calc. for $C_4H_{16}Cl_4CrN_2$: C, 16.8; H, 5.60; Cl, 49.6; Cr, 18.2; N, 9.80%).

X-Ray powder photographs were obtained using a Philips W 1024 camera (nickel-filtered Cu-K_α radiation), the samples being sealed in Lindemann tubes. Single-crystal transmission spectra were recorded either by a Cary 14R spectrophotometer equipped with an Oxford Instruments CF 100 continuous-flow helium cryostat and Harwell temperature controller, or a McPherson RS 10 high-resolution double-beam spectrophotometer together with a Thor Cryogenics cryostat containing a 5-T split-coil superconducting solenoid. The latter is equipped with a Thor Cryogenics temperature controller and carbon resistance thermometer, providing temperatures from 1.5 to 150 K controllable to ±0.1 K.

Magnetic-susceptibility measurements were made from 150 to 80 K using a Faraday balance at the Materials Physics Division, A.E.R.E., Harwell, and from 80 to 4.2 K using Oxford Instruments Faraday balances at the Inorganic Chemistry Laboratory, Oxford, and the Laboratorio di Teoria e Struttura Elettronica dei Composti di Coordinazione, Rome. The powdered samples were contained in ' Rislan ' spheres and suspended by quartz fibres from a Sartorius microbalance. Temperatures were measured with a Au (0.03 atom % Fe) *vs.* chromel thermocouple with its

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[1] For an excellent review, see L. J. de Jongh and R. A. Miedema, *Adv. Phys.*, 1974, **23**, 1.

[2] N. D. Mermin and H. Wagner, *Phys. Rev. Letters*, 1966, **17**, 1133.

[3] W. D. Van Amstel and L. J. de Jongh, *Solid State Comm.*, 1972, **11**, 1423.

[4] F. M. Mostafa and R. D. Willett, *Phys. Rev.*, 1971, **B3**, 2213.

[5] L. J. de Jongh and W. D. Van Amstel, *J. Phys.* (*Paris*), *Colloq.*, 1971, **1**, C1–880.

[6] For a brief review see P. Day, *Colloques Int. C.N.R.S.*, 1977, No. 255, 237.

[7] C. Bellitto and P. Day, *J.C.S. Chem. Comm.*, 1976, 870.

reference junction in a liquid-helium bath. The balances were calibrated with Pt.

RESULTS

Crystal Structure.—The *X*-ray powder photographs could be indexed in the space group *Cmca* (D_{2h}^{18}), the same as that of the corresponding compounds of Mn [8] and Cd [9] at room temperature. The results are given in Table 1 and least-squares values of the unit-cell dimensions below:

TABLE 1

Powder *X*-ray diffraction data (unit-cell parameters are given in the text)

			$[NMeH_3]_2[CrCl_4]$			$[NEtH_3]_2[CrCl_4]$		
h	*k*	*l*	$\sin^2\theta$(obs.)	Intensity	$\sin^2\theta$(calc.)	$\sin^2\theta$(obs.)	Intensity	$\sin^2\theta$(calc.)
0	0	2	0.006 07	vs	0.006 67	0.004 68	vs	0.005 19
			0.007 05	vs		0.005 36	vs	
1	1	1	0.022 68	vs	0.023 69	0.022 87	s	0.022 60
0	0	4	0.024 40	vs	0.026 67	0.022 23	s	0.020 76
1	1	3	0.035 98	m		0.032 74	s	0.032 97
			0.037 95	m	0.037 03	0.033 36	s	
2	0	0	0.042 22	m	0.043 09	0.041 64	m	0.041 29
0	2	0	0.044 89	m	0.045 00	0.044 29	m	0.043 91
2	0	2	0.048 94	w	0.049 76	0.046 66	w	0.046 48
			0.051 42	w				
0	2	2	0.053 95	w	0.051 67			0.049 10
			0.056 74	w				
0	0	6	0.058 98	m	0.060 00	0.046 66	w	0.046 69
1	1	5	0.060 21	m	0.063 70	0.053 70	w	0.053 73
2	0	4	0.068 77	s	0.069 76	0.062 05	m	0.062 04
0	2	4	0.071 67	s	0.071 67	0.064 60	m	0.064 66
2	2	0	0.085 98	vs	0.088 10	0.084 75	vs	0.085 20
			0.088 44	vs				
2	2	2	0.093 45	m	0.094 76	0.090 67	s	0.090 39
			0.095 49	m				
2	0	6	0.103 84	m	0.103 10	0.086 70	s	0.087 98
0	2	6			0.105 01	0.099 63	w	0.090 60
0	0	8	0.106 78	m	0.106 69	0.080 66	w	0.083 08
3	1	1	0.110 30	w	0.109 87	0.106 80	w	0.105 18
1	3	1	0.112 50	w	0.113 70	0.110 05	w	0.110 42
3	1	3	0.122 89	w	0.123 20			0.115 56
1	3	3			0.127 03	0.124 08	w	0.120 79
2	2	6	0.147 91	m	0.148 48			
3	1	5	0.149 77	w	0.149 70	0.132 24	w	0.133 10
1	1	9	0.156 67	m	0.157 05	0.126 39	w	0.126 36
4	0	0	0.172 50	w	0.172 35	0.168 38	m	0.156 16
0	4	0	0.178 14	m	0.180 01			
4	0	4	0.199 62	w	0.199 19			
2	4	0	0.221 64	m	0.223 10	0.213 90	m	0.216 94

Compound	a_0	b_0	c_0
		Å	
$[NMeH_3]_2[CrCl_4]$	7.27	7.43	18.89
$[NEtH_3]_2[CrCl_4]$	7.59	7.35	21.41

The full crystal and magnetic structures at 300 K and low temperatures are currently under investigation.[10] However, preliminary powder neutron-diffraction scans obtained at 87 and 4.2 K, using the Curran diffractometer at A.E.R.E., Harwell, indicate that, like its cadmium analogue, $[NMeH_3]_2[CrCl_4]$ undergoes a transition to a monoclinic phase, $P2_1/c$ (C_{2h}), between 300 and 87 K. The low-temperature unit-cell dimensions of $[NMeH_3]_2[CrCl_4]$ are as follows:

T/K	a_0	b_0	c_0	β/°
		Å		
87	7.19	7.43	18.80	90.0
4.2	7.16	7.42	18.82	90.9

High-temperature Susceptibility.—Figure 1 shows the inverse susceptibilities of $[NMeH_3]_2[CrCl_4]$ and $[NEtH_3]_2[CrCl_4]$ as a function of temperature from 150 K down to the ordering temperature. At *ca.* >90 K the Curie–Weiss law is obeyed, with values of the Weiss constant θ of 61 and 58 K respectively. The observed susceptibilities were corrected for the diamagnetism of the constituent atoms and for temperature-independent paramagnetism (t.i.p.). For the ^5E cubic-field ground state of a high-spin d^4 ion the t.i.p. correction is $4N\mu_B^2/10Dq$, where *Dq* is the ligand-field splitting parameter. Taking 10*Dq* as 10 000 cm^{-1}, the t.i.p. correction is 10^{-4} cm^3 mol^{-1}. With these corrections, the room-temperature susceptibilities of the methyl- and ethyl-ammonium salts are respectively 5.62 and 4.98 μ_B, values which are to be compared with 4.89 μ_B at 300 K in a magnetically dilute chromium(II) compound such as $Rb_2[CrCl_4(OH_2)_2]$,[11] very close to the spin-only value of 4.90 μ_B.

To analyse the temperature dependence of the susceptibility at temperatures well above T_c we use the series-expansion method of Rushbrooke and Wood,[12] as refined by Lines [13] specifically for the quadratic-layer Heisenberg magnet. Writing the exchange Hamiltonian as (1) where

$$H = \sum_{n,m} JS_iS_j \qquad (1)$$

the summation *n,m* covers all pairs of near-neighbour ions *i,j*, the susceptibility is given by a power series (2). In equation (2) $\phi = kT/JS(S+1)$ and the coefficients C_n

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[8] H. Arend, R. Hofmann, and F. Waldner, *Solid State Comm.*, 1973, **9**, 1629.

[9] G. Chapuis, H. Arend, and R. Kind, *Phys. Stat. Sol.*, 1975, **31**, 449.

[10] P. Battle, C. Daul, and P. Day, unpublished work.

[11] L. F. Larkworthy and J. K. Trigg, *Chem. Comm.*, 1970, 1221.

[12] G. S. Rushbrooke and P. J. Wood, *Mol. Phys.*, 1958, **1**, 257.

[13] M. E. Lines, *J. Phys. Chem. Solids*, 1970, **31**, 101.

depend on the value of the spin S. When the exchange is ferromagnetic the C_n are multiplied by $(-1)^n$, so for $S = 2$ equation (2) becomes (3) where $x = J/kT$. Equation (3)

$$\frac{Ng^2\mu_B{}^2}{\chi J} = 3\phi + \sum_{n=1}^{\infty} \frac{C_n}{\phi^{n-1}} \qquad (2)$$

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

is the same as the one we used earlier to analyse the high-temperature susceptibility of the ferromagnets $A_2[CrCl_4]$ (A = K, Rb, or Cs).[14]

Figure 1 shows the susceptibilities of the two salts, plotted as $1/\chi$ against temperature, together with the best-fit curves calculated according to equation (3). For the methylammonium salt the best agreement between theory and experiment is obtained for a value of $J = 9$ cm^{-1} and $g = 2.00$, while for the ethylammonium salt a slightly lower J (7 cm^{-1}) and a g value reduced to 1.95 give an excellent account of the data from 60 to 150 K. An average g value slightly below 2.00 is quite typical of chromium(II) salts, *e.g.* $Cr[SO_4]\cdot 5H_2O$.[15] Further evidence of a higher exchange constant in the monomethylammonium salt is provided by the apparently larger magnitude of the high-temperature magnetic moment (see above).

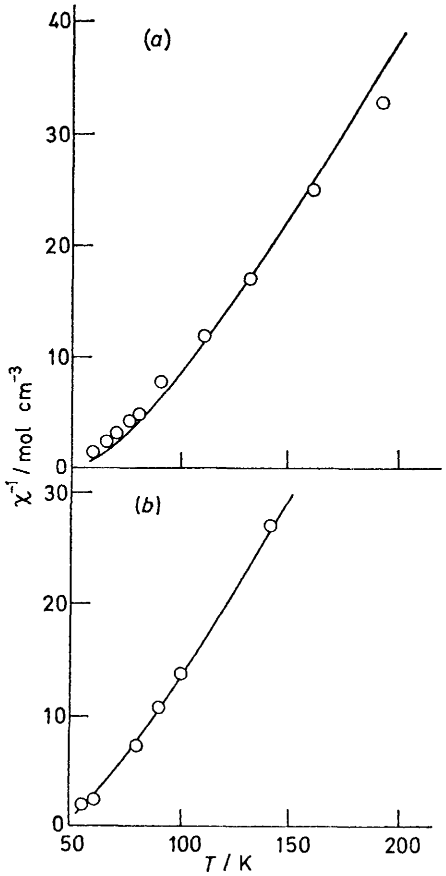

FIGURE 1 Plots of inverse susceptibility against temperature for (*a*) $[NMeH_3]_2[CrCl_4]$ and (*b*) $[NEtH_3]_2[CrCl_4]$. The lines are fits to equation (3) for (*a*) $J = 9$ cm^{-1}, $g = 2.00$ and (*b*) $J = 7$ cm^{-1}, $g = 1.95$

Low-temperature Magnetisation.—At 4.2 K polycrystalline samples of both salts were already essentially saturated by the lowest field (0.1 T) which could be applied conveniently with the superconducting solenoid using the available power supplies. The variation of the magnetisation with temperature for the two salts, measured at 0.3 T, is shown in Figure 2. In both cases the curves show appreciable rounding in the vicinity of T_c, reflecting the field-induced ordering above the spontaneous-ordering temperature characteristic of low-dimensional magnets. It is therefore difficult to be very precise about T_c, although a reasonable estimate would be 58 ± 2 and 55 ± 2 K for the methyl- and ethyl-ammonium salts respectively. We shall see below that this value agrees quite closely with that obtained from the optical spectrum, which is of course a zero-field measurement.

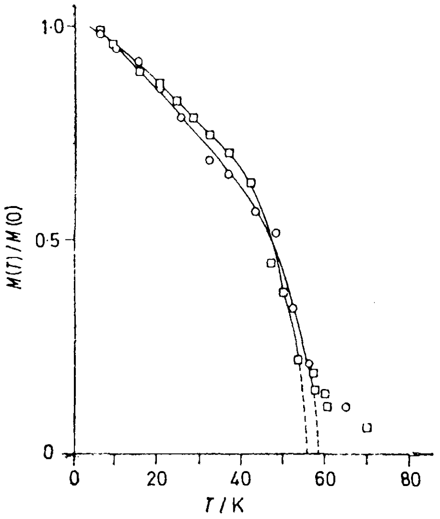

FIGURE 2 Plots of reduced magnetisation against temperature for $[NMeH_3]_2[CrCl_4]$ (○) and $[NEtH_3]_2[CrCl_4]$ (□)

An alternative way to express the variation of magnetisation with temperature is through equation (4). In

$$1 - [M(T)/M(0)] = CT^{\gamma} \qquad (4)$$

Figure 3 magnetisation data for both compounds in terms of equation (4) are plotted on a logarithmic scale. Equation (4) is obeyed almost up to T_c. Least-squares fits to the two straight lines yield values of C and γ as follows: $[NMeH_3]_2[CrCl_4]$, $C = 0.001\,55$, $\gamma = 1.50 \pm 0.10$; $[NEtH_3]_2[CrCl_4]$, $C = 0.000\,86$, $\gamma = 1.64 \pm 0.15$. To a reasonable approximation, therefore, the exponent is $\frac{3}{2}$. Only in a low-dimensional magnet would one expect such a simple power law to apply up to a high fraction of T_c, since the high density of low-lying magnon modes near the centre of the Brillouin zone (*i.e.* with long wavelengths) means that magnon–magnon interaction effects are less important than they would be in a three-dimensional ferromagnet. In the latter, the Bloch $T^{\frac{3}{2}}$ law[16] applies only to *ca.* 0.1—0.2 T_c.[17] Again, one may note that analogous behaviour is found in

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[14] A. K. Gregson, P. Day, D. H. Leech, M. J. Fair, and W. E. Gardner, *J.C.S. Dalton*, 1975, 1306.

[15] K. Ono, S. Koide, H. Sekiyama, and H. Abe, *Phys. Rev.*, 1964, **96**, 38.

[16] F. Bloch, *Z. Physik*, 1931, **61**, 206.

[17] C. Kittel, ' Introduction to Solid State Physics,' 4th edn., Wiley, New York, 1971, p. 535.

the two-dimensional ferromagnets $K_2[CuF_4]$ [18] and $Rb_2[CrCl_4]$.[14,19]

Optical Spectra.—Both monoalkylammonium salts grow as thin flat plates, so optical spectra can only be recorded with the incident light parallel to the *c* axis, *i.e.* perpendicular to the sheets of exchanged-coupled metal ions. Figure 4 shows the spectra of the two salts in the visible region. For the methylammonium example we also show spectra measured at two different temperatures. The major spectral features are a pair of sharp well resolved bands at 15 800 and 18 760 cm^{-1}, almost at the same frequency as the bands in the alkali-metal analogues.[6,20] Otherwise the whole visible region is remarkably featureless. Also in common with the alkali-metal tetrachlorochromates(II), the intensities of the two visible bands in the present compounds vary very strongly with temperature. Figure 5 demonstrates that for temperatures nearly up to T_c the integrated area of the band at 18 760 cm^{-1} is quite accurately described by a simple power law T^{β} with $\beta = 2.0 \pm 0.1$. Qualitatively, the consequence of this variation is that at <10 K the compounds are all but colourless, while at higher temperatures they become olive-green. It can also be seen from Figure 5 that above T_c the intensities of the two visible bands become constant.

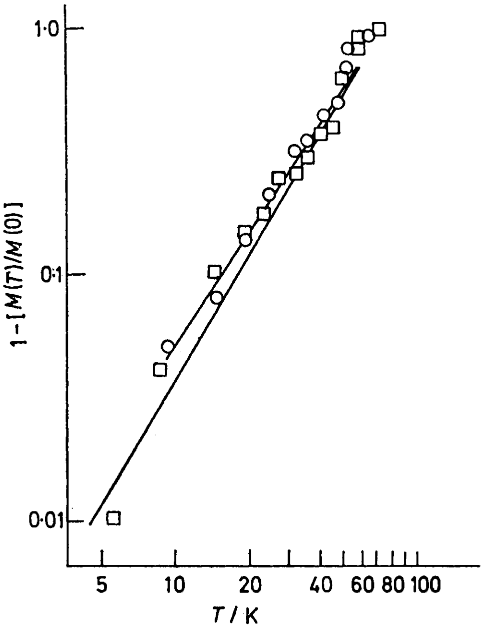

FIGURE 3 Magnetisation of $[NMeH_3]_2[CrCl_4]$ (○) and $[NEtH_3]_2[CrCl_4]$ (□)

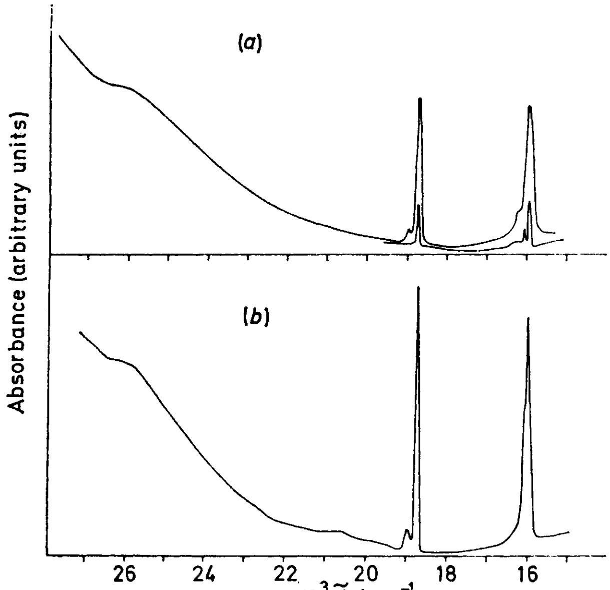

FIGURE 4 Visible absorption spectra of (*a*) $[NMeH_3]_2[CrCl_4]$ at 130 and 20 K and (*b*) $[NEtH_3]_2[CrCl_4]$ at 38 K

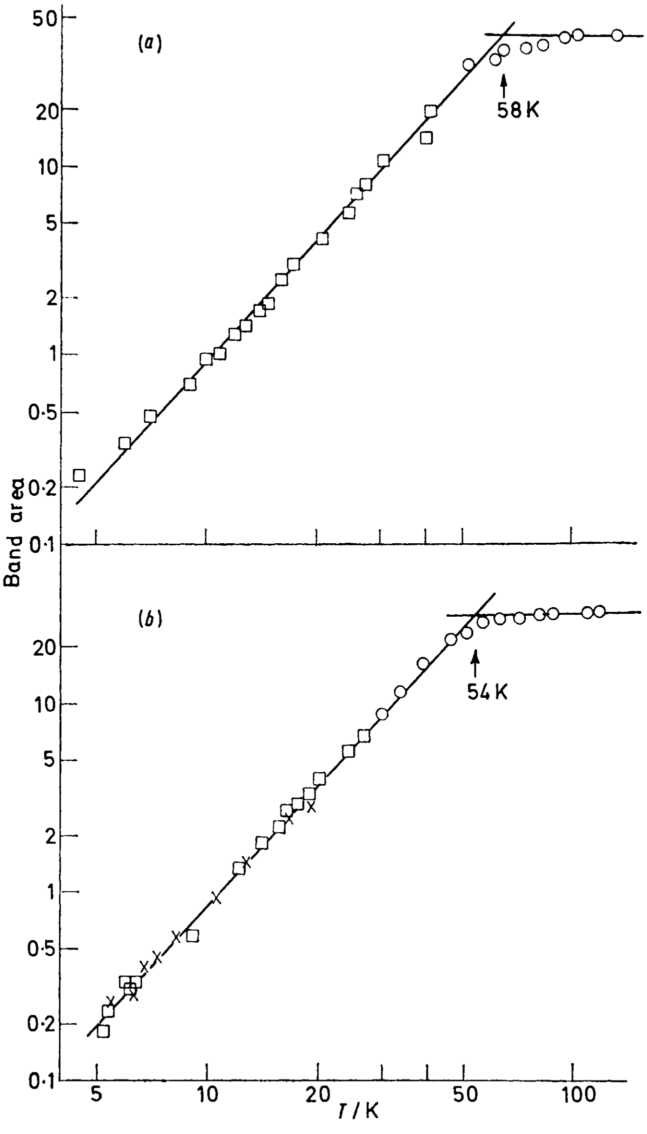

FIGURE 5 Temperature variation of the area of the band at 18 600 cm^{-1} for (*a*) $[NMeH_3]_2[CrCl_4]$ and (*b*) $[NEtH_3]_2[CrCl_4]$

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[18] K. Hirakawa and H. Ikeda, *J. Phys. Soc. Japan*, 1973, **35**, 1328.

[19] M. J. Fair, A. K. Gregson, P. Day, and M. T. Hutchings, *Physica*, 1977, **B86—88**, 657.

[20] P. Day, A. K. Gregson, and D. H. Leech, *Phys. Rev. Letters*, 1973, **30**, 19.

DISCUSSION

The space group and unit-cell parameters of the bis(monoalkylammonium) tetrachlorochromates(II) are very similar to those of their Mn, Fe, Cu, and Cd analogues, whose structures have been determined in detail. Thus one may safely assume that they too contain layers of metal ions bridged by chloride ions, separated from one another by the organic groups, in a manner approximating to the $K_2[NiF_4]$ structure. A potentially complicating feature of the chromium salts is the Jahn–Teller effect, which is assumed to be operative in these high-spin $3d^4$ ions. Although the detailed structures of the tetrachlorochromates(II) are still under investigation,[10] it seems likely that the co-ordination around the chromium(II) ions will be similar to that found in the corresponding copper(II) salts,[21] *i.e.* a tetragonally distorted octahedron of chloride ions with its long axis within the plane of the metal ions. Such an arrangement would account for the ferromagnetic sign of the near-neighbour magnetic interaction by superexchange between a half-filled z^2 and an empty $x^2 - y^2$ orbital at right angles to each other.[22] A similar explanation has been given for the ferromagnetism of $K_2[CuF_4]$ [23] and the bis(monoalkylammonium) tetrachlorocuprates(II). It is also worth noting that in $Rb_2[CrCl_4]$ the same kind of tetragonal distortion has been inferred from the angular variation of the ^{53}Cr n.m.r. frequency within the *ab* plane.[24]

TABLE 2

Magnetic and structural parameters of tetrachlorochromates(II)

Compound	Interplanar Cr–Cr (Å)	J/cm^{-1}	T_c(obs.)/K	T_c/calc.)/K Molecular field	Ref. 26	Ref. 27	Ref. 29
$K_2[CrCl_4]$	9.07	7	60—75	80	33	22	36
$Rb_2[CrCl_4]$	9.41	10.7	63	123	51	34	55
$Cs_2[CrCl_4]$	9.73	6.5	61	75	31	21	33
$[NMeH_3]_2[CrCl_4]$	10.78	9	58	103	43	29	45
$[NEtH_3]_2[CrCl_4]$	11.93	7	55	80	33	22	36

That the near-neighbour exchange is indeed ferromagnetic is confirmed by the high-temperature series-expansion fits to the susceptibility of both compounds from 80 to 150 K. The exchange constants which give the best fit to the high-temperature susceptibility data are similar in magnitude to those derived in a similar fashion for the alkali-metal tetrachlorochromates(II) (J 7, 8.5, and 6.5 cm^{-1} for K, Rb, and Cs salts respectively).[14] A more accurate value of J for $Rb_2[CrCl_4]$ obtained by fitting the spin-wave dispersion curve determined by inelastic neutron scattering was 10.7 ± 0.1 cm^{-1}.[25]

Likewise the Curie temperatures of the two organic-intercalated salts are quite close to those of their alkali-metal analogues, thus demonstrating that the temperature for three-dimensional magnetic ordering is not very sensitive to the distance separating the layers of ferromagnetically coupled ions. On the assumption (the validity of which was discussed above) that the structures of the bis(monoalkylammonium) tetrachlorochromates(II) are very similar to those of the corresponding cuprates(II), we find the correlation given in Table 2, *i.e.* for a 35% increase in interplanar spacing T_c decreases by *ca.* 14%. Nevertheless, it is interesting to notice that the T_c values of the tetrachlorocuprates(II) are even less sensitive to interplanar separation. Thus on passing from the $[NMeH_3]^+$ to the $[N(C_5H_{11})H_3]^+$ salt the interplanar spacing increases by almost 80% while T_c diminishes from 8.9 to 7.3 K, *i.e.* by 18%.[5]

As mentioned at the outset, there exists [2] a rigorous proof that two-dimensional lattices with purely Heisenberg or XY-like interactions cannot possess long-range order above absolute zero. On the other hand, Stanley and Kaplan [26] found evidence from high-temperature series expansions that, at least for $S > \frac{1}{2}$, some kind of transition might be possible at a temperature $T_c^{(2)}$ to a state in which the susceptibility diverged, but there was no truly long-range order. Further arguments for [27] and against [28] Stanley and Kaplan's proposal have been given, but what does seem clear [29] is that a small Ising-like anisotropy or, of course, a small interplanar interaction [30] is sufficient to bring about three-dimensional ordering in a layer compound at a finite temperature. However, in such cases the predicted three-dimensional T_c is very close to $T_c^{(2)}$. Consequently, it is of interest to correlate the values of T_c and J in the tetrachlorochromates(II) according to the various theories available. The relevant equations are as follows:

Molecular field $T_c = \frac{1}{3}zJS(S + 1)$
Ref. 26 $T_c^{(2)} = \frac{1}{10}J(z - 1)[2S(S + 1) - 1]$
Ref. 27 $T_c^{(2)} \sim 0.55JS^2$
Ref. 29 $T_c^{(2)} = 0.595JS(S + 1)$

Clearly none of the theories gives particularly good agreement between J and T_c, although as expected the mean-field theory prediction is too high (Table 2). Of

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[21] J. P. Steadman and R. D. Willett, *Inorg. Chim. Acta*, 1970, **4**, 367.

[22] J. B. Goodenough, 'Magnetism and the Chemical Bond,' Interscience, New York, 1966, p. 222.

[23] D. I. Khomskii and K. I. Kugel, *Solid State Comm.*, 1973, **13**, 763.

[24] K. Le Dang, P. Veillet, and P. J. Walker, *J. Phys.* (*C*), 1977, **10**, 4593.

[25] M. T. Hutchings, M. J. Fair, P. Day, and P. J. Walker, *J. Phys.* (*C*), 1976, **9**, L55.

[26] H. E. Stanley and T. A. Kaplan, *Phys. Rev. Letters*, 1966, **17**, 913.

[27] J. Villain, *J. Phys.* (*Paris*), 1975, **36**, 581.

[28] K. Yamaji and J. Kondo, *J. Phys. Soc. Japan*, 1973, **35**, 25.

[29] M. E. Lines, *Phys. Rev.*, 1971, **B3**, 1749.

[30] L. J. de Jongh, *Physica*, 1976, **B82**, 247.

the experimental values of J, that for $Rb_2[CrCl_4]$, obtained by fitting the spin-wave spectrum, is much the most precise while the others, obtained from high-temperature series expansions, may be in error by as much as ± 1 cm^{-1}. Nevertheless, all the other equations predict $T_c^{(2)}$ distinctly lower than the observed T_c in all cases. It should also be pointed out that the values of T_c listed in Table 2 were measured in an applied field of 0.3 T which, in a weakly coupled layer magnet, might easily be sufficient to change the ordering temperature. Some measure of the initial (zero-field) magnetisation is therefore needed. We contend that the optical spectrum provides such a measure.

In earlier papers [6,31,32] we have demonstrated that in a wide variety of low-dimensional ionic ferromagnets exciton–magnon combination bands associated with spin-forbidden ligand-field transitions gain their intensity primarily through the annihilation of a thermally created ' spin-down ' magnon simultaneous with creation of the exciton. The oscillator strength of such a band at a particular temperature is therefore related directly to the initial magnetisation at that temperature. We also showed [32] that by taking into account explicitly the magnon dispersion, and hence the density of magnon states as a function of energy, one could calculate simple analytic expressions for the variation of oscillator strength with temperature. For instance, for a two-dimensional easy-plane ferromagnet with negligible anisotropy one finds that the oscillator strength should be proportional to T^2, precisely as found for $Rb_2[CrCl_4]$ [6] and the monoalkylammonium salts described in this paper. From Figure 5 we see that the T^2 law is obeyed by the band at 18 650 cm^{-1} of the monoalkylammonium salts up to *ca.* 0.9 T_c, but that from *ca.* 1.1 T_c upwards the oscillator strength of the band becomes constant. A simple linear interpolation therefore gives quite a good estimate of T_c in zero applied field. In fact, from Figure 5, T_c values estimated in this way are 58 ± 1 and 54 ± 1 K for the monomethyl- and monoethylammonium salts respectively. These values agree closely with those obtained from the magnetisation measurements, suggesting that the applied field in the latter experiment does not influence the magnitude of T_c noticeably. To our knowledge, the tetrahalogenochromates(II) are the only ferromagnetic substances in which spin-forbidden ligand-field transitions are fully resolved, and in which the ' hot-band ' exciton–magnon combination mechanism can be tested. Consequently, they provide a unique opportunity to use a combination of optical and magnetic methods to probe the ordering mechanism in a low-dimensional magnet. Further experiments on these and other members of the same series will be reported in due course.

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