Magnetic Susceptibility and Magnetization of the Ionic Ferromagnets Dipotassium, Dirubidium, and Dicaesium Tetrachlorochromate(II)

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High-temperature (300—80 K) susceptibility data are reported for polycrystalline samples of the ionic ferromagnets M_2CrCl_4 (M = K, Rb, or Cs) and interpreted using the high-temperature series-expansion method for the quadratic-layer Heisenberg $S = 2$ ferromagnet to yield estimates of 7·0, 8·5, and 6·5 cm^{-1} for the nearest-neighbour exchange integrals. Low-temperature (80—4·2 K) magnetization measurements are also reported for polycrystalline Rb_2CrCl_4 and Cs_2CrCl_4. In both compounds the magnetization obeys the equation $\{1 - [M(T)/M(0)]\} = CT^{\gamma}$ with $\gamma = 1{\cdot}54$ up to 60 K, *i.e. ca.* 0·9 T_c. Saturation magnetizations are *ca.* 0·4 B.M. lower than expected for $S = 2$ ions.

THREE-DIMENSIONAL ferromagnetism in ionic compounds is extremely rare, and the small number of examples available up till now have been intensively studied, both for their intrinsic interest, and for technological reasons.[1] The first ionic ferromagnet to be discovered was $Y_3Fe_5O_{12}$(YIG),[2] followed by EuO [3] and $CrBr_3$ [4] and more recently by K_2CuF_4 [5] and [Fe(phen)$_2$Cl$_2$] (phen = 1,10-phenanthroline).[6] Recent magnetic-susceptibility measurements [7-9] on the series M_2CrCl_4 (M = K, Rb, or Cs) suggested that they too ordered ferromagnetically, with Curie temperatures in the region of 65 K. We therefore decided to examine their physical properties in more detail, particularly the relation between the magnetic ordering and the optical properties in the visible region of the spectrum.

Neutron diffraction from powdered Cs_2CrCl_4 [10] and single-crystal Rb_2CrCl_4 [9] confirms the ferromagnetic ordering in these two compounds. In the latter,[9,11] as also in K_2CrCl_4,[12] the onset of ferromagnetic ordering is accompanied by some very startling changes in the visible absorption spectrum. At 300 K several of the spin-forbidden ligand-field transitions are quite intense, but below the Curie temperature their intensity falls rapidly. Thus at 4·2 K the entire visible region from 14 000 to 25 000 cm^{-1} is very nearly transparent. Qualitatively, this effect may be explained by an exchange-coupled electric-dipole-intensity mechanism since in a ferromagnet electronic transitions which lead to a decrease in the spin projection of the crystal (*e.g.* quintet-to-triplet ligand-field excitations) can only become electric-dipole allowed if thermally excited magnons which also decrease the spin projection are simultaneously annihilated. To understand such effects in detail, a more complete analysis of the magnetic susceptibility is clearly needed. On the other hand there are also good reasons why the magnetic properties of the M_2CrCl_4 series are interesting and important in their own right.

The compounds have the K_2NiF_4 structure [10,13] so that in Cs_2CrCl_4, for example, there is a two-dimensional network of Cr and Cl atoms, each Cr being surrounded by four others, with 180° Cr–Cl–Cr bonds. Each layer is separated from the next by two layers with the stoicheiometry CsCl, each Cl completing the octahedral coordination about a Cr ion (Figure 1). The resulting anisotropy in the exchange interaction is evident in the high-temperature ($T > T_c$) susceptibility and low-temperature ($T < T_c$) magnetization data. The properties of these compounds may also be relevant to the

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[1] See, for example, D. F. Nelson, *Sci. Amer.*, 1968, **218**, 17.

[2] R. Pauthenet, *Ann. Physique*, 1958, **3**, 424.

[3] B. T. Mathias, R. M. Bozorth, and J. H. Van Vleck, *Phys. Rev. Letters*, 1961, **7**, 160.

[4] For example, see H. L. Davis and A. Narath, *Phys. Rev.*, 1964, **A134**, 433.

[5] I. Yamada, *J. Phys. Soc. Japan*, 1972, **33**, 979.

[6] W. M. Reiff and S. Foner, *J. Amer. Chem. Soc.*, 1973, **95**, 260.

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

[8] D. H. Leech, Ph.D. Thesis, Victoria University of Manchester, 1971.

[9] M. J. Fair, Chemistry Part II Thesis, Oxford, 1973.

[10] M. T. Hutchings, A. K. Gregson, P. Day, and D. H. Leech, *Solid-State Comm.*, 1974, **15**, 313.

[11] A. K. Gregson, P. Day, and M. J. Fair, Autumn Meeting, The Chemical Society (Dalton Division), University of East Anglia, September 1973.

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

[13] H. J. Seifert and K. Klatyk, *Z. anorg. Chem.*, 1964, **334**, 113.

current controversy [14] about the existence or otherwise of phase transitions in two-dimensional lattices.

In the present paper we report susceptibility measurements on powdered samples of M_2CrCl_4 (M = K, Rb, or Cs) from 300 to 80 K, which we analyse by high-temperature series-expansion methods, and also magnetization measurements at 4·2 K. Single-crystal neutron-diffraction, including polarized, measurements, and an extended description of the optical properties will be published separately. A brief preliminary account of the high-temperature (300—80 K) powder-susceptibility data on K_2CrCl_4 and Cs_2CrCl_4 has recently appeared.[15]

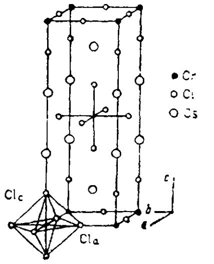

FIGURE 1 Crystal structure of Cs_2CrCl_4. The Cr^{2+} ion is surrounded by a tetragonally compressed octahedron of chlorine atoms. Bond distances are Cr–Cl_a 2·609 and Cr–Cl_c 2·399 Å where Cl_a and Cl_c are the chlorine atoms on the *a* and *c* axes respectively [10]

EXPERIMENTAL

Samples used for the susceptibility measurements were prepared by two different methods: K_2CrCl_4 and Rb_2CrCl_4 were obtained by melting $CrCl_2$ and the appropriate alkali-metal halide together in the correct stoicheiometric ratio; [8] in the second method, which was employed for K_2CrCl_4 and Cs_2CrCl_4, molten $CrCl_3$ was treated with the alkali-metal halide in the presence of excess of chromium metal, the excess of unchanged metal being removed by high-temperature filtration.[8] Crystalline samples of the congruently melting salts K_2CrCl_4 and Rb_2CrCl_4 were grown from the melt in a Bridgeman furnace and then finely ground.

The magnetic-susceptibility measurements on K_2CrCl_4 and Cs_2CrCl_4 from 300 to 77 K were made using a Gouy balance, at field strengths in the range 1·5—6·5 kOe.[*] All measurements on Rb_2CrCl_4, and those on K_2CrCl_4 and Cs_2CrCl_4 below 77 K, were made on a Faraday balance at the Materials Physics Division, A.E.R.E., Harwell.[16] For the latter, the samples were placed inside a Perspex sphere and suspended by a fine silica wire from a Sartorious vacuum microbalance. The magnetic field was furnished by a superconducting solenoid. The crystallites were free to orientate themselves inside the Perspex sphere, and it is therefore anticipated that the direction of easy magnetization lies parallel to the magnetic field. The Faraday measurements were made down to 4·2 K and at field strengths up to 41 kOe.

RESULTS

High-temperature Susceptibility.—The Table records the effective magnetic moments of K_2CrCl_4, Rb_2CrCl_4, and Cs_2CrCl_4 at 300 and 90 K. The small differences between our results and Larkworthy's [7] are most likely due to preparative difficulties and impurities. To investigate the detailed temperature dependence using the high-temperature series-expansion method, we therefore used the average values of the magnetic moments of the three compounds. Corrections for both the diamagnetism of the constituent atoms and temperature-independent paramagnetism (t.i.p.) were made. For the formal ^5E ground state of the high-spin d^4 configuration, the t.i.p. contribution is $4N\beta^2/10Dq$ [17] (usual symbols) and with $10Dq$ *ca.* 10 000 cm^{-1} [15] we take this to be 100×10^{-6} cm^{-3} mol^{-1}. Apart from the t.i.p. contributions, any departures from Curie behaviour should only be due to the effect of the exchange interaction because even in formal octahedral symmetry the ground ^5E state behaves magnetically as an orbital singlet, any orbital contributions being absorbed into the variation of the *g* value from 2·0023. Room-temperature magnetic-moment values of 5·8 B.M. of, for example, Rb_2CrCl_4 are to be compared with magnetic moments of 4·89 B.M. at 300 K for the magnetically dilute $Rb_2[CrCl_4(H_2O)_2]$,[7] quite close to the spin-only value of 4·90 B.M. Even more striking are the moments at 90 K, which for $Rb_2[CrCl_4(H_2O)_2]$ is 4·91 B.M. whereas for the ferromagnetic anhydrous compound it is 11·3 B.M.[7]

Magnetic-moment data

	μ(300 K)/ B.M.	μ(90 K)/ B.M.	θ [a]/K	Ref.
K_2CrCl_4	5·34	8·90		7
	5·54	8·93	67·5	8 [b]
	5·61	9·32	64·5	8 [c]
Rb_2CrCl_4	5·80	11·30		7
	5·80	11·65	82	*d*
Cs_2CrCl_4	5·78	11·60		7
	5·53	10·05	77	8

[a] Curie–Weiss θ in $\chi = C/(T - \theta)$. [b,c] Two different preparations. [d] This work; normalized to data at 300 K in ref. 1.

To examine the temperature variation of the susceptibility above T_c we made use of series expansions. Assuming a Heisenberg-exchange Hamiltonian, and confining the exchange to nearest neighbours, Rushbrooke and Wood calculated exact series-expansion formulae for the paramagnetic susceptibility in powers of reciprocal temperature up to six for arbitrary spin and wide range of lattice structures.[18] More recently, Lines [19] re-examined the series for the quadratic-layer Heisenberg antiferromagnet using the

$$H = \sum_{n,m} JS_i.S_j \qquad (1)$$

exchange Hamiltonian (1) where *n,m* covers all pairs of nearest-neighbour spins *i* and *j*. The power series in reciprocal susceptibility is then given by (2) where $\theta = kT/JS(S+1)$ and the coefficients C_n depend on the value

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

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[*] 1Oe = $(10^{-5}\mathrm{N})^{\frac{1}{2}}$ cm^{-1}, 1 B.M. ≈ 9·27 × 10^{-24} A m^2.

[14] For example, recent evidence for and against is presented respectively in (*a*) H. K. Charles and R. I. Joseph, *Phys. Rev.*, 1973, **B7**, 2046; (*b*) K. Yamaji and J. Kondo, *J. Phys. Soc. Japan*, 1973, **35**, 25.

[15] D. H. Leech and D. J. Machin, *J.C.S. Chem. Comm.*, 1974, 866.

[16] W. E. Gardner and A. K. Gregson, *Proc. Vac. Microbalance Techniques*, 1973, **2**, 183.

[17] B. N. Figgis, 'Introduction to Ligand Fields,' Interscience, 1968, p. 266.

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

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

of the spin S, other symbols having their usual meanings. Remembering that for the ferromagnetic interaction the coefficients C_n are to be multiplied by $(-1)^n$, the series for

$$Ng^2\beta^2/\chi = \tfrac{1}{2}\boldsymbol{k}T + J(-4 + 9x - 9{\cdot}0720x^2 + 55{\cdot}7280x^3 - 160{\cdot}7040x^4 + 116{\cdot}64x^5) \quad (3)$$

$S = 2$ becomes (3) where $x = J/\boldsymbol{k}T$. Choosing $g = 1{\cdot}98$ (appropriate to the average g value of a typical Cr^{II} compound such as $CrSO_4{\cdot}5H_2O$)[20] equation (3) gave an excellent fit to the high-temperature susceptibility data on K_2CrCl_4 with $J = 7$ cm^{-1} (Figure 2). The non-linearity of the reciprocal susceptibility against temperature plot below *ca.* 115 K is characteristic of ferromagnetic interactions with the presence of short-range order.

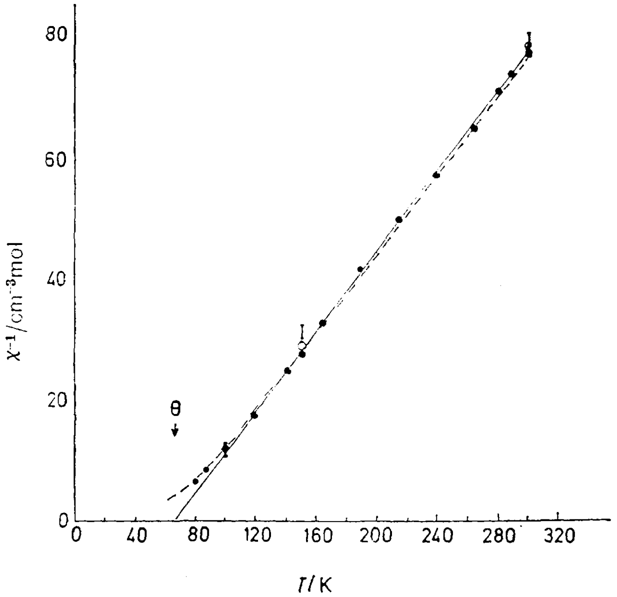

FIGURE 2 Plot of reciprocal susceptibility against temperature for K_2CrCl_4: (●), Gouy data;[8] (I), Faraday data; (——), Curie–Weiss plot; and (— — —), equation (3) with $g = 1{\cdot}98$ and $J = 7{\cdot}0$ cm^{-1}

Equation (3) gave only a fair fit to the high-temperature susceptibility data on Rb_2CrCl_4 and Cs_2CrCl_4 (Figures 3 and 4), the optimum values of J being 8·5 and 6·5 cm^{-1} respectively. To improve the gradient of the plot of χ^{-1} against T for Cs_2CrCl_4 a g value of 1·90 and $J = 8$ cm^{-1} was sufficient for acceptable agreement down to *ca.* 115 K, but 1·90 is rather low for normal paramagnetic Cr^{II} compounds. Other possible reasons for the poorer fit to the Rb_2CrCl_4 and Cs_2CrCl_4 data are that the interaction may have some three-dimensional character or, alternatively, that the Heisenberg interaction may have a small XY-like anisotropy. However, the magnetic properties of K_2CuF_4, another ferromagnet with the K_2NiF_4 structure,[5] were accurately described by the series expansion for the strictly two-dimensional plane-square lattice with $S = \frac{1}{2}$, and furthermore the interaction had only *ca.* 1% XY-like anisotropy. Thus we conclude that these two factors are probably not responsible for the difference in gradient between the calculated and experimental χ^{-1} against T plots. The difference in gradient might also be caused by a slight error in the mass of the very small amount of sample used. However, we do not think this likely as the limiting saturation magnetizations of the three polycrystalline compounds at 4·2 K (see below) are very similar.

The saturation magnetizations are reduced from the normal value of 4·0 B.M. for the $S = 2$ Cr^{II} ion to *ca.* 3·6 B.M., another fact which may be responsible for the departures from the ideal isotropic Heisenberg interaction in the two-dimensional lattice. However, rather than speculate further, at this point we merely conclude that the high-temperature susceptibility data on K_2CrCl_4 appears to be well described by the isotropic Heisenberg series expansion appropriate to the square lattice with J *ca* 7·0 cm^{-1} whereas in Rb_2CrCl_4 and Cs_2CrCl_4 $J = 8{\cdot}5$ and 6·5 cm^{-1}, respectively, although the agreement is not as good. These values of J may be compared with that of *ca.* 7 cm^{-1} obtained by Okiji[21] from the temperature variation about T_c of the oscillator strengths of the two quintet–triplet ligand-field transitions,

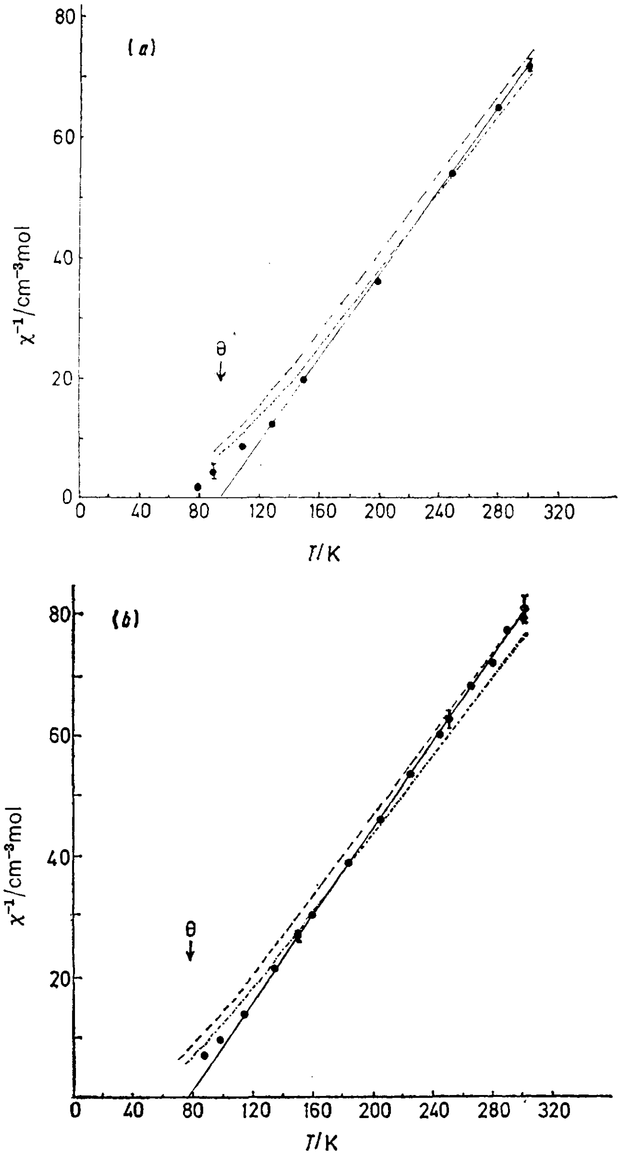

FIGURE 3 Plots of reciprocal susceptibility against temperature for Rb_2CrCl_4 (*a*) and Cs_2CrCl_4 (*b*): (●), Gouy data;[8] (I), Faraday data; (——), Curie–Weiss plot; (— — —), and (· · · ·), equation (3) with $g = 1{\cdot}98$ and $J = 8{\cdot}0$ and 9·0 cm^{-1} respectively [J 6·0 and 7·0 cm^{-1} for (*b*)]

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[20] K. Ono, S. Koide, H. Sekiyama, and H. Abe, *Phys. Rev.*, **1954**, **96**, 38.

[21] A. Okiji, personal communication and unpublished work.

using the simple pairwise approximation. A value of J of similar magnitude also gives a good account of the complicated temperature-dependent intensities of the same transitions between 4 and 10 K.[21]

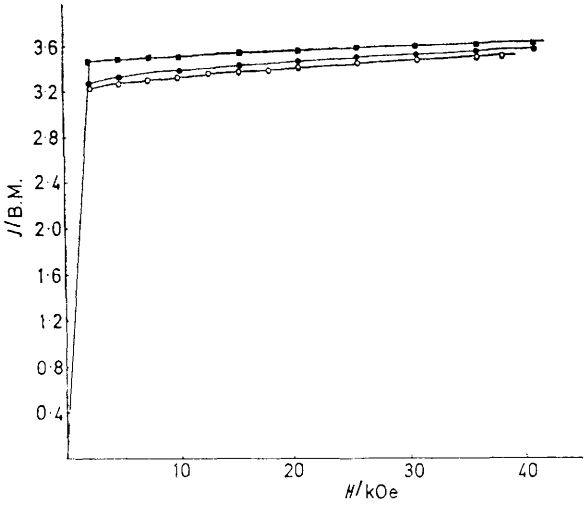

FIGURE 4 Plot of magnetization against applied magnetic field for polycrystalline samples of K_2CrCl_4 (●), Rb_2CrCl_4 (○), and Cs_2CrCl_4 (■), at 4·2 K

Low-temperature Magnetization.—At 4·2 K polycrystalline samples of all three compounds saturated in applied fields greater than 2 kOe in a manner characteristic of simple ferromagnets. The saturated magnetic moments of 3·5—3·6 B.M. (Figure 4) are rather lower than the value of 4·0 expected for the $S = 2$ Cr^{II} ion. Both the very small amounts of metal-halide impurity detected in the powder neutron-diffraction pattern [10] and experimental error in the measurements would tend to reduce the observed magnetic moment. However, the major factor responsible for reducing the saturated magnetization below 4·0 B.M. is probably covalency, as discussed later.

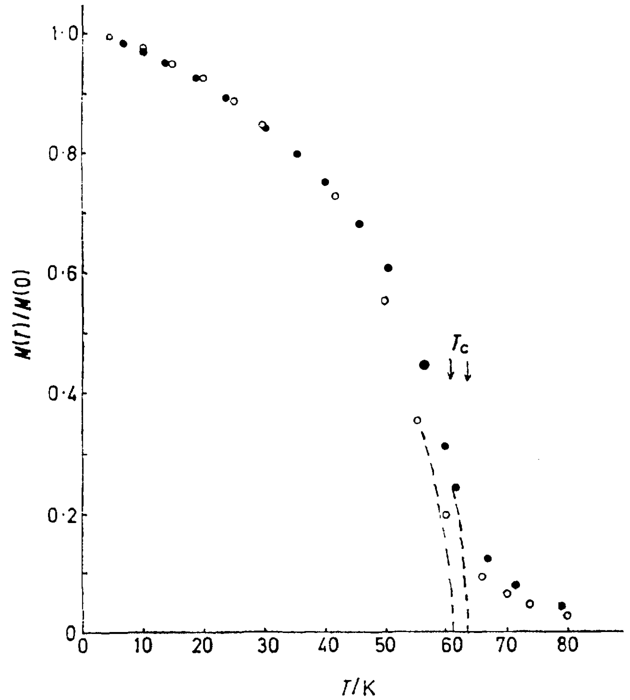

FIGURE 5 Plot of reduced magnetization against temperature for polycrystalline samples of Rb_2CsCl_4 (●) and Cs_2CrCl_4 (○), measured in 2·31 kOe

Temperature Variation of the Magnetization.—A sensitive test of the effect of dimensionality on the magnetic properties of a ferromagnet is the temperature variation of the magnetization from zero to *ca.* 0·5 T_c and then, to test theories concerning critical phenomena, around T_c itself. The reduced magnetizations $M(T)/M(0)$ for Rb_2CrCl_4 and Cs_2CrCl_4 are plotted in Figure 5, $M(0)$ being the magnetization between 4·2 and 10 K extrapolated to 0 K and $M(T)$ the magnetization between 4·2 and 80 K. The data on these two compounds are very similar except near T_c where the larger value of J deduced from the high-temperature series expansion for Rb_2CrCl_4 reflects the higher T_c. The large 'tails' in the magnetizations for both compounds between 60 and 80 K make it difficult to obtain precise values for T_c. No data on K_2CrCl_4 have been included in Figure 5 since we could not obtain consistent results for this compound.

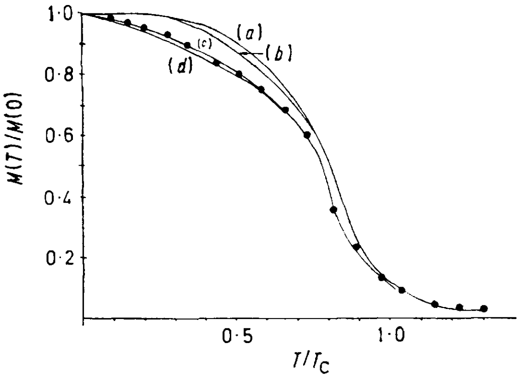

FIGURE 6 Plot of reduced magnetization against temperature for Rb_2CrCl_4: (——), calculated using Weiss molecular-field theory and the Brillouin function, after Smart;[23] $S = \infty$ (*a*), 1 (*b*), 2 (*c*), and 20 (*d*)

For both Rb_2CrCl_4 and Cs_2CrCl_4 the reduced magnetization may be expressed empirically as a function of temperature by (4). With $C = 0{\cdot}0091$ and $\gamma = 1{\cdot}54$ this expression represents the reduced magnetization quite well up to

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

nearly 60 K, *i.e. ca.* 0·9 T_c. That equation (4) fits the reduced magnetization up to such a high fraction of T_c is quite remarkable because in most magnetic compounds the reduced magnetization against temperature curves depart from such a simple expression by at most 0·5 T_c and often at much lower temperatures. An exception relevant to the present example is K_2CuF_4,[22] the reduced magnetization

$$\{1 - [M(T)/M(0)]\} = 0{\cdot}0299\, T^{3/2} \tag{5}$$

of which could be expressed as in (5) up to *ca.* 0·64 T_c (T_c 6·25 K).

The simplest method of relating reduced magnetization to temperature is through the Weiss molecular-field model, using a Brillouin function, as described, for example, by Smart.[23] Curves calculated using the experimental values of $M(T)/M(0)$ are illustrated for Rb_2CrCl_4 in Figure 6. At

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

[23] J. S. Smart, 'Effective Field Theories of Magnetism,' W. B. Saunders Company, 1966, p. 25.

temperatures well below T_c the experimental reduced magnetization is much smaller than expected for an $S = 2$ system; in fact the best fit is for $S = 20$! Clearly no physical significance can be attached to this value of S, which simply illustrates the inadequacy of the molecular-field approximation for the present series of compounds. For temperatures well below T_c, particularly near zero, a spin-wave description of the magnetization behaviour is much more appropriate. In the spin-wave description of three-dimensional magnetic behaviour the magnetization decreases much more rapidly at temperatures just above zero than predicted by molecular-field theory. Bloch's

$$\frac{M(T)}{M(0)} = 1 - \frac{T^{3/2}}{T_{\mathrm{B}}} -, \textit{etc.} \qquad (6)$$

equation, (6), where $T_{\mathrm{B}} = 21\ S^{5/3}\ J/\boldsymbol{k}$ for the body-centred cubic lattice, agrees well with experiment at temperatures much less than $0{\cdot}5\ T_c$. At higher temperatures, and especially in three-dimensional systems, spin-wave interactions lead to higher terms in equation (6), which can be derived by considering spin-wave renormalization.

DISCUSSION

In all three M_2CrCl_4 compounds we have examined the strongly rising magnetic moments with decreasing temperature provide clear evidence of ferromagnetic interactions, amply confirmed by the magnetization measurements at 4·2 K and up to T_c. The existence of magnetic order at finite temperatures in predominantly two-dimensional materials such as those with K_2NiF_4 structures has in the past posed several theoretical problems. The original prediction for two-dimensional spin arrays with isotropic Heisenberg interactions was that no long-range order could be established above absolute zero [24] so there would be no phase transition. However, numerical evidence from high-temperature series-expansion techniques supports the existence of a phase transition in the two-dimensional Heisenberg model.[14a,25] The formula (7) reproduces these latest

$$\boldsymbol{k}T_c^{(2)}/J = (12/5)[z - (5/z)](4S + 3)^{-1} \qquad (7)$$

numerical results [14a] and hence, for the square lattice ($z = 4$) and $S = 2$, we would anticipate that $\boldsymbol{k}T_c^{(2)}/J = 0{\cdot}33$, a result which clearly does not hold for Rb_2CrCl_4 and Cs_2CrCl_4. On the other hand it must be recognized that in real systems there is often an anisotropy in the exchange interaction which will normally induce a magnetic ordering, even when the superexchange is dominated by a one- or two-dimensional path.

Of course any interlayer exchange automatically gives the system three-dimensional character and so the question of a two-dimensional phase transition does not arise. On the other hand, using a Green's function approach with wave-vector-dependent magnon renormalization, Lines [26] showed that, in a two-dimensional system and for any spin, $\boldsymbol{k}T_c^{(2)}$ is *ca.* $1{\cdot}19JS(S + 1)$ which in the present case would predict T_c to be 87 or 67 K for Rb_2CrCl_4 and Cs_2CrCl_4 respectively, close to the observed critical temperatures. It is interesting to compare the predicted two-dimensional ordering temperatures with those predicted for three-dimensional body-centred cubic lattices. In the latter [18] equation (8) is applicable and so $T_c^{(3)}$ would be 62 and 47 K for Rb_2CrCl_4 and Cs_2CrCl_4.

$$\boldsymbol{k}T_c^{(3)}/J = (5/192)(z - 1)[11S(S + 1) - 1] \qquad (8)$$

These theoretical relations between T_c and J do not lead to estimates of T_c which are very sensitive to the dimensionality of the exchange. For example, the anisotropy energy, which is difficult to predict, probably provides the reason for the stability of the long-range order. Nevertheless, the effect of the dimensionality of the exchange is brought out clearly by several other experimental observables. The first is the temperature dependence of the magnetization above 4·2 K. As Figure 6 shows, the Weiss molecular-field theory, which assumes an isotropic Heisenberg interaction in three dimensions, is by no means an adequate description of the magnetization of Rb_2CrCl_4 and Cs_2CrCl_4. This is because two-dimensional systems have a much larger proportion of low-energy magnons than three-dimensional ones so the magnetization decreases much more rapidly as the temperature is raised. At higher temperatures no simple theory is likely to be really adequate, even with renormalization modifications, because excitation processes near the transition or critical region become important. In two-dimensional lattices such processes extend over a much wider temperature range, both above and below the transition temperature, than in three-dimensional lattices, and are responsible for the pronounced short-range-order effects observed, for example, in Figures 2, 3, and 5. In Figures 2 and 3 the reciprocal susceptibility diverges from the Curie–Weiss behaviour well above the predicted T_c; in Figure 5 the magnetization does not continue to fall towards zero but retains a sizeable value well past the temperature at which $M(T)$ goes to zero by simple extrapolation of the low-temperature magnetization. Both types of behaviour are quite characteristic of two-dimensional systems. Finally, the reduction in the moments of the M_2CrCl_4 compounds is most plausibly attributed to covalency. Thus, for example, a moment reduction of 4·1% due to covalency alone has been found in MnO [27] while the total reduction of 13% in the moment of K_2CuF_4 [22] has been ascribed to covalency, as demonstrated by paramagnetic diffuse neutron scattering.[28]

The only other ferromagnetic compound in any way related to those we have described in this paper is K_2CuF_4,[5,22,28] which also has the K_2NiF_4 structure. Both magnetic and neutron-scattering measurements have been made on K_2CuF_4 and, as in the chromium compounds, the magnetization can be represented by a

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

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

[26] M. E. Lines, *Phys. Rev.*, 1971, **3**, 1749.

[27] A. J. Jacobson in 'Chemical Applications of Thermal Neutron Scattering,' ed. B. T. M. Willis, Oxford University Press, 1973, ch. 12.

[28] K. Hirakawa and H. Ikeda, *J. Phys. Soc. Japan*, 1973, **35**, 1608.

simple $T^{3/2}$ dependence up to 0·86 T_c (T_c 6·25 K). Again this is a result of the low dimensionality of the system so that magnon interactions, and hence renormalization effects, are small. In Figure 7 the magnetization curves for K_2CuF_4, K_2NiF_4, and K_2MnF_4 are plotted for comparison with data for Rb_2CrCl_4. The similarity between the two ferromagnets is very noticeable, at least in the low-temperature region. In K_2CuF_4 the three-dimensional ordering is apparently due to interlayer coupling because the single-ion anisotropy is zero and dipole–dipole interactions are very small. Because the contributions to the anisotropy energy are either zero or small, the spins in K_2CuF_4 are aligned perpendicular to the *c* axis. However, it should be noted that in the M_2CrCl_4 compounds an analysis of the unpolarized neutron-diffraction data on powders and single crystals shows that the magnetic moment lies at an angle of 34° to the *c* plane,[10] presumably because of the various competing contributions to the anisotropy field.

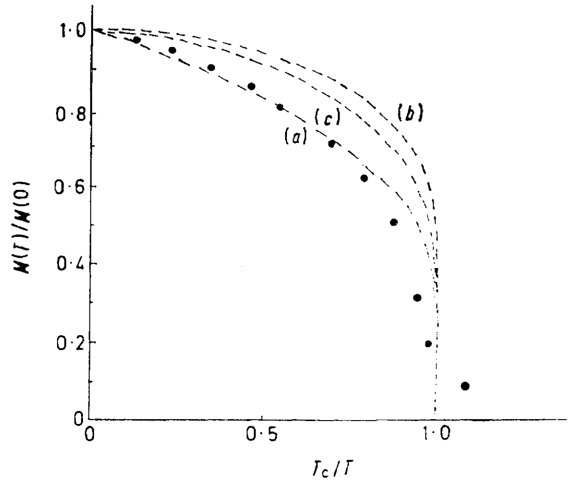

FIGURE 7 Comparison of the reduced magnetizations for K_2CuF_4 (*a*), K_2NiF_4 (*b*), and K_2MnF_4 (*c*) with Rb_2CrCl_4 (●)

The actual mechanism of the intralayer ferromagnetism in M_2CrCl_4 must lie in the 180° $3d^4$–anion–$3d^4$ interaction, corresponding to half-filled e_g–empty e_g cation–anion–cation superexchange. According to Goodenough's description the ferromagnetic interaction arises from Jahn–Teller effects, approximating to his 'quasistatic' limit,[29] a situation which has been re-examined recently by Khomskii and Kugel.[30]

In summary, the compounds K_2CrCl_4, Rb_2CrCl_4, and Cs_2CrCl_4 appear to be typical two-dimensional ferromagnets. Although the actual critical temperatures may not reflect their dimensionality very precisely, the magnitude and temperature dependence of the susceptibility can be explained at least qualitatively using relatively simple theory appropriate to the two-dimensional lattice. In contrast, both in the M_2CrCl_4 series and in K_2CuF_4, the $T^{3/2}$ dependence of the magnetization is more in line with a three-dimensional isotropic Heisenberg-interaction model although the significance of the proportionality constant C remains unclear. However, in the three-dimensional Heisenberg ferromagnet the description of the magnetization in terms of a single temperature exponent is in any case expected to hold only up to a small fraction of T_c whereas in the present compounds and K_2CuF_4 the simple $T^{3/2}$ dependence holds nearly up to T_c. Experiments now in progress on the spin-wave dispersion in Rb_2CrCl_4 may throw further light on this question.

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