The Compounds $ACrCl_3$ and A_2CrCl_4 (A=Cs or K) as One- and Two-dimensional Magnetic Systems

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Summary Paramagnetic susceptibilities for the title compounds have been interpreted with the aid of theoretical expressions for one- and two-dimensional Heisenberg models for interacting magnetic systems.

THERE is considerable interest in optically transparent ferromagnetic systems for applications in communications and data display. The compounds Cs_2CrCl_4 and K_2CrCl_4 are the first ferromagnets which have substantial transmission in the visible region. A number of phase studies[1-3] of alkali-metal chloride $-CrCl_2$ systems show the presence of intermediate phases and some of these have been shown[4-6] to display magnetic interaction between Cr^{II} ions. To date, no attempt has been made to relate magnetic properties to structure in these phases. Representative tri- and tetrachlorochromates have been synthesised as potassium and caesium salts, using fused-salt techniques. Magnetic susceptibility measurements on fine powders have been interpreted on the basis of n-dimensional spin-arrays with nearest-neighbour isotropic Heisenberg coupling. The values of n were deduced from crystallographic data. Magnetic data are given in the Tables.

$CsCrCl_3$. This compound is isostructural[7] with either $CsNiCl_3$ or $CsCuCl_3$. The chromium atoms thus either form chains or helical arrays, held together by the caesium ions. In either case the magnetic behaviour should approximate to that of a one-dimensional array of spins. The broad maximum in the susceptibility near 140 K (see Table) arises from short-range ordering since a purely one-dimensional array cannot support long-range order.

Smith and Friedberg[8] give expression (1) for the zero-field susceptibility of this system,

$$\chi_n(T) = \frac{Ng^2\beta^2S(S+1)}{3kT} \times \frac{1+u(K)}{1-u(K)} \qquad (1)$$

where $u(K) = \coth K - (1/K)$ and $K = 2JS(S+1)/kT$. We define J as being positive for ferromagnetic coupling.

This expression with $S = 2$ and $J = 0$ reproduces the general trend of our results quite well but predicts too high a temperature for the maximum. Better fits are obtained when g is in the range 1·94—1·98, the corresponding range of J values being $-25{\cdot}0$ to $-26{\cdot}5$ cm^{-1}.

$KCrCl_3$. The structure of this compound is not known but the magnetic data can be described by equation (1) for a one-dimensional system, J lying between $-4{\cdot}5$ and $-5{\cdot}5$ cm^{-1} if S and g are fixed at 2. Varying J and g give limits $J = 5{\cdot}0$—$14{\cdot}0$ cm^{-1} when $g = 1{\cdot}98$—$1{\cdot}96$. A maximum in the susceptibility is predicted at *ca.* 25 K.

TABLE 1

Compound and preparative history	μ_{eff}/B.M. at T/K temp in parentheses	θ/K	Temperatures (in K) for which $\chi = C/(T + \theta)$
ACl + $CrCl_3$ + Cr(0) $CsCrCl_3$	3·41 (290·7)	θ large and + ve; χ *vs.* T shows broad max. near 140 K	
Cs_2CrCl_4	5·52 (290·8)	−77·0	120—300
$KCrCl_3$	4·56 (291·8)	45·3	90—300
K_2CrCl_4	5·61 (291·5)	−66·5	110—300
KCl + $CrCl_2$ $KCrCl_3$	4·55 (291·3)	43·2	90—300
K_2CrCl_4	5·55 (291·0)	−68·0	115—300

The uncertainty in the θ values quoted above (which are simply the mean of those found at several field strengths), is estimated to be ± 5 K.

TABLE 2

Magnetic susceptibilities (c.g.s. units) as a function of absolute temperature. Data were obtained by the Guoy method.

$CsCrCl_3$		$KCrCl_3$		Cs_2CrCl_4[a]		K_2CrCl_4[a]	
T/K	$10^6\chi_{Cr}$	T/K	$10^6\chi_{Cr}$	T/K	$10^6\chi_{Cr}$	T/K	$10^6\chi_{Cr}$
300·8	4940	300·8	8660	300·8	12,700	301·3	13,100
289·5	5030	289·3	8960	289·3	13,000	289·5	13,600
280·0	5060	282·0	9180	280·3	14,000	280·8	14,200
265·5	5160	265·0	9590	265·0	14,700	264·8	15,500
236·8	5290	238·8	10,400	245·8	16,700	239·3	17,600
204·8	5410	215·8	11,300	225·8	18,800	215·3	20,300
174·8	5530	190·5	12,500	205·3	21,800	189·5	24,100
155·8	5590	164·8	14,100	185·5	25·800	164·5	30,600
142·5	5590	141·3	16,000	160·8	33,300	140·8	40,100
132·8	5590	120·0	18,100	135·5	46,700	119·0	57,400
122·8	5570	101·0	20,400	115·3	71,700	100·8	82,500
110·0	5530	90·3	21,700	98·8	105,000	87·8	113,000
93·5	5450	79·3	23,400	88·0	144,000	79·3	150,000
80·0	5430						

[a] Data obtained at 1710 and 1910 Oe for Cs_2CrCl_4 and K_2CrCl_4 respectively. These compounds show increasing field dependence of their susceptibilities as the temperature is lowered. There is little difference in behaviour between the two methods of preparation. The trichlorides show no significant field dependence of their susceptibilities.

Cs_2CrCl_4. This compound has the K_2NiF_4 structure.[2] Thus there is a two-dimensional array of chromium atoms. Cs_2CrCl_4 behaves as a typical insulating ferromagnet. The plot of χ^{-1} *vs.* T is linear from 300 to 120 K with $\theta = -77°$ in the Curie–Weiss expression $\chi = C/(T + \theta)$. At lower temperatures the plot shows concave-upward curvature as expected[9] for a relationship $\chi^{-1} \propto (T - T_c^{\gamma})$ where $\gamma = ca.$ 2·67 for a two-dimensional, $S = 2$, Heisenberg ferromagnet as $T \rightarrow T_c$. Lines[10] gives expression (2) for ferromagnets of this type, where $\theta = kT/JS(S + 1)$ and values of C_n

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

are given by Lines.

Since the saturation moment of Cs_2CrCl_4 is only 3·8 B.M.,[5] we scaled g and s by a factor 3·8/4·0 which leads to reproduction of our data with $J = 5{\cdot}25$ and $6{\cdot}00\ cm^{-1}$ for the high- and-low temperature regions respectively.

K_2CrCl_4. This material is structurally and magnetically very similar to Cs_2CrCl_4. A similar treatment of the magnetic data gives J in the range 4·75—5·25 cm^{-1}. Appropriately scaled, Stanley's series expansion[11] of χ for the corresponding classical Heisenberg model gives $J = 4{\cdot}8\ cm^{-1}$. Spectroscopic studies of this compound have also been described.[12]

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