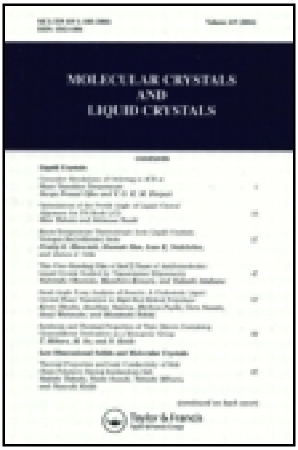

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Synthesis and Characterization of 2d Ferromagnetic $(RNH_3)_2CrX_4$ Containing Mixed-Halides, R = C_nH_{2n+1}, X = Br, C1

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SYNTHESIS AND CHARACTERIZATION OF 2D FERROMAGNETIC $(RNH_3)_2CrX_4$ CONTAINING MIXED-HALIDES, $R = C_nH_{2n+1}$, $X = Br, Cl$.

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Abstract. The bis(benzylammonium)tetrahalogenochromate(II),$(C_6H_5CH_2NH_3)_2CrBr_{3.3}Cl_{0.7}$, has been synthesized and characterized. The crystal structure is related to that of K_2NiF_4 . The compound is ferromagnetic and the Curie temperature T_C (T_C= 49 K) has been measured by a mutual inductance technique. The susceptibility increases sharply at T_C and then shows a drop-off below T_C, typical of a single-domain powder sample. The compound is found to behave as a typical 2D easy plane ferromagnet.

INTRODUCTION

Recently in our Laboratory, several tetrachlorochromates and tetrabromochromates (II) containing monoalkylammonium cations, $(RNH_3)_2CrX_4$, where $R = C_nH_{2n+1}$, X = Cl,Br, have been synthesized and characterized. They have been found to order ferromagnetically[1-3]. Their crystal structure is similar to the K_2NiF_4 structure [4], see figure 1, and consists of layers of CrX_6 octahedra, linked into a square array by sharing equatorial vertices. Two adjacent layers of the $(CrX_4)^{2n-}{}_n$ anions are separated by the diamagnetic alkylammonium cations, RNH_3^+. The 4-fold symmetry of the K_2NiF_4 crystal lattice is destroyed by the 3-fold symmetry of the $-NH_3^+$ group which is attached to the layer by the weak N-H....X bonds. The layers are not perfectly planar

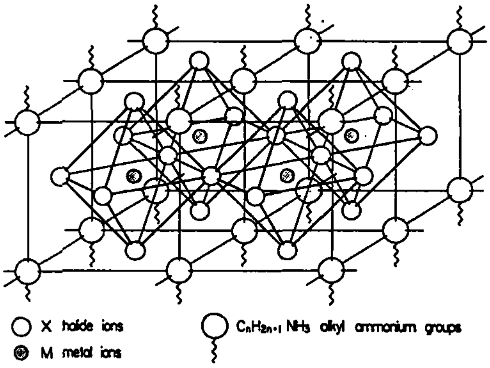

FIGURE 1. Schematic representation of a single layer of monoalkylammonium family salts : $(RNH_3)_2MX_4$.

and therefore the M - X - M superexchange pathway is no longer linear. The aliphatic chain attached to the $-NH_3^+$ group extends away from the inorganic layers of the magnetic ions. Van der Waals contacts are present between the R groups belonging to two adjacent layers. In this respect, they can be considered **molecular-based** ferromagnets.

We have extended the range of this class of compounds and here present the synthesis and the magnetic properties of a new tetrahalogenochromate (II) salt containing mixed halides : **$(C_6H_5CH_2NH_3)_2CrBr_{3.3}Cl_{0.7}$**.

RESULTS

The mixed-halide compound $(C_6H_5CH_2NH_3)_2CrBr_{3.3}Cl_{0.7}$ was prepared under inert atmosphere by a convenient method described previously[5]. To a hot solution of Cr(II) in glacial acetic acid, prepared by passing HBr gas through a suspension of finely divided electrolytic chromium metal, was slowly added a stoichiometric quantity of benzylammonium chloride in the same solvent. On cooling, yellow plates of the title compound were isolated. The compound has been characterized by elemental analysis and x-ray powder diffraction. Anal.calcd. for $C_{14}H_{20}N_2CrBr_{3.3}Cl_{0.7}$: C = 30.20; H = 3.62; N = 5.03; Cr = 9.34; Br = 47.36; Cl = 4.46. Found: C = 29.28; H = 3.45; N = 4.86; Cr = 9.20; Br = 46.03; Cl = 4.36.

The x-ray powder diffraction photograph has been indexed in the space group Cmca (D_{2h}^{18}), similarly to the pure ones[1,3]. The unit-cell parameters, obtained by a least-squares method, are :

$$\underline{a} = 7.6_0 \quad , \underline{b} = 7.8_0 \quad , \underline{c} = 32.2_0 \ \text{Å} \ .$$

The unit-cell parameter $\underline{c}$ is related to the interplanar distance, d by a factor of 1/2. In table 1 is shown the relationship between the interlayer separation, d, and the number of carbon atoms in the aliphatic chain of the RNH_3^+ group.

MAGNETIC PROPERTIES

We have measured the magnetic properties of the title compounds by the a.c. mutual inductance bridge [6], operated at fixed frequency, both on powder and single crystal, at temperatures down to 4.2 K. The mixed-halide compound $(C_6H_5CH_2NH_3)_2CrBr_{3.3}Cl_{0.7}$ shows typical ferromagnetic behaviour.

a. High-temperature region :

Above 60 K, the magnetic susceptibility follows the

Curie-Weiss law :

$$\chi = C / (T - \Theta)$$

with the magnetic moment greater than the spin-only value, i.e. 4.90 B.M., typical of Cr(II) in the high-spin configuration d^4. The large positive value of Θ indicates mainly ferromagnetic exchange interactions. The experimental data above 60 K were analysed in terms of the Rushbrooke-Wood series expansion method, appropriate to an S = 2, quadratic layer Heisenberg ferromagnet [7,8] :

$$N g^2 \mu_B{}^2 / \chi = 1/2\ k_B T + J(-4+9x-9.072x^2+ 55.728x^3-160.704x^4+116.64x^5) \qquad (1)$$

where $x= J/k_BT$, J is nearest-neighbour exchange constant and g is the Landè factor. Figure 2 shows the susceptibility plotted as $1/\chi$ vs T , together with the best fit curve calculated according to the equation (1). The best values of J/k_B and g were found to be :

$J = 12.5$ K ; $g = 2.06$.

b. Zero-field magnetic susceptibility .

The a.c. susceptibility features a sharp peak at T = 49 K, associated with 3D ferromagnetic order, T_C, see figure 3. The susceptibility decreases steeply below T_C. This can be ascribed to a single-domain powder sample[9]. The divergence of the initial susceptibility in the high temperature side of the peak can be fitted to a function of the form [10]:

$$\chi_o = \Gamma (t_+)^{-\tau} \qquad (2)$$

where t_+ is $(T-T_C)/T_C$ and τ is the critical exponent.

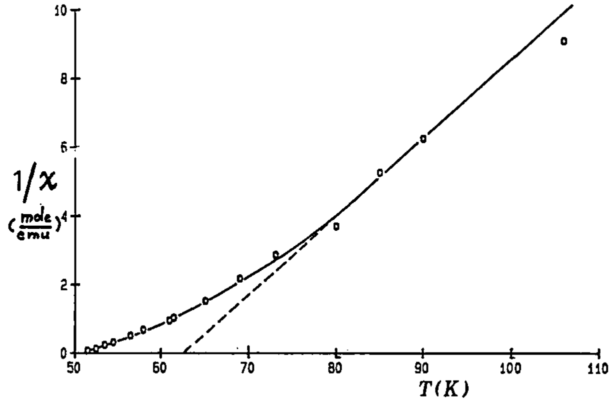

FIGURE 2. Reciprocal molar susceptibility χ^{-1} of the title compound vs temperature T.

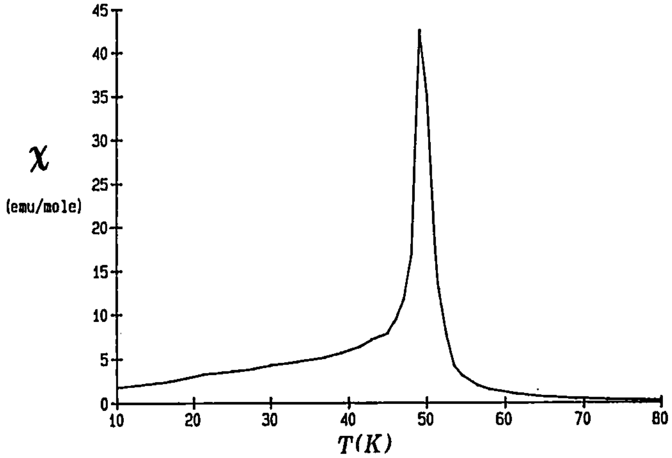

FIGURE 3. The a.c. magnetic susceptibility χ_0 vs temperature T.

The log-log plot of the initial susceptibility vs the reduced temperature t_+ gave the critical exponent 1.43 in the reduced temperature range 0.03 - 0.4 . Preliminary a.c. magnetic susceptibility measurements on a single crystal show the existence of a strong anisotropy between the $\chi_{//}$ and $\chi_{\perp}$ to the c axis, with the $\chi_{//}$ constant and approximately two orders of magnitude smaller than that in the c plane below T_c.

OPTICAL SPECTRUM.

The diffuse reflectance spectrum of the title compound is characterized by two sharp spin-forbidden bands in the visible region, at 18.7 kK (10,000 cm^{-1} = 1 kK) and at 16.2 kK. These bands have been observed previously in the pure compounds[1,3] and they appear at the same frequencies. They are " hot exciton-magnon " combination bands [11]. These pure spin-flip transitions have been assigned, in D_{4h} symmetry, as electronic transitions :

$${}^5B_{1g}\ ({}^5E_g) \longrightarrow {}^3B_{1g}({}^3E_g({}^3H))$$

and

$$\longrightarrow {}^3B_{1g}({}^3A_{2g}({}^3F))$$

on the basis of the exchange intensity mechanism [12]. The small number of spin-forbidden bands in these ferromagnetic A_2CrX_4 is in fact due to the lack of orbital overlap between the magnetic orbitals on nearest-neighbour Cr^{2+} ions [13].

TABLE I . Magnetic parameters and interlayer spacings of $(RNH_3)_2CrX_4$, R=alkyl,X =Cl,Br.

Compound	T_c (K)	J/k (K)	Θ (K)	kT_c/J	d (Å)
$(CH_3NH_3)_2CrCl_4$	42	13.0	59	3.23	9.44
$(C_2H_5NH_3)_2CrCl_4$	41	10.1	58	4.06	10.71
$(C_3H_7NH_3)_2CrCl_4$	39.5	9.3	57	4.25	12.35
$(C_6H_5CH_2NH_3)_2CrCl_4$	37	10.6	58	3.40	15.71
$(C_6H_5CH_2NH_3)_2CrBr_4$	52	13.1	77	3.97	16.24
$(C_6H_5CH_2NH_3)_2CrBr_{3.3}Cl_{0.7}$	49	12.5	62	3.92	16.10

DISCUSSION.

The title compound has been synthesized and characterized. It crystallises as yellow platelets and the X- ray powder diffraction data suggest that the crystal structure is similar to that of the layered perovskite compounds $(RNH_3)_2MX_4$, where R =alkyl group, M= Cd, Mn, Fe, Cu, X = halide, where the full structure has been solved [14]. The other important structural feature is that the Cr(II) is six-coordinated, tetragonally distorted, due to the cooperative Jahn-Teller effect. This antiferrodistortive order has been observed previously in Rb_2CrCl_4 [15] and in $[H_3N-(CH_2)_2NH_3]CrCl_4$ [16]. The $[CrCl_6]$ octahedra are tetragonally elongated, with the long axes alternating at right angles in the basal plane. The compound features a ferromagnetic nearest-neighbour exchange and it orders at T_c= 49 K. The ferromagnetic exchange results from the cooperative Jahn-Teller effect, which constrains the unpaired e_g electron of Cr^{2+} to the d_{z^2} orbital and allows superexchange <u>via</u> bridging halide anions between a half-filled d_{z^2} orbital on one Cr^{2+} ion and the empty $d_{x^2-y^2}$ one of its neighbours[15,17]. The value of the exchange constant, J/k, is closer to the value found in the pure bromide derivative and definitively bigger than that of the pure chloride derivative (see table I). From the unit-cell parameter $\underline{c}$ we can reasonably assume that only bromide anions lie in axial position and that the chloride anions should be coordinated in the plane. In agreement with this situation, we observe a slightly lower value of J/k and T_c. The other remarkable result is that the substitution of chloride by bromide strongly increases the extent of the ferromagnetic exchange and the value of the ordering temperature T_C. A similar trend has been observed in the copper analogues [18]. The interplanar distance along the chloride series does not influence the value of T_C. Finally, the single-crystal susceptibility data suggest that the spins lie in the (001) plane.

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