

excitation should therefore lead to a weakening of the metal-nitrogen bond and ultimate dinitrogen dissociation. In the W(0) complex the  $^1B_{1u}$  and  $^3B_{1u}$  MLCT terms lie lower in energy than the LF terms. Excitation of MLCT states is not expected to lead to dissociative photochemistry; however,  $\sim 200\text{ cm}^{-1}$  higher than the  $^3B_{1u}$  term lies the  $^3B_{2g}$  LF term. This potentially dissociative state can be populated thermally even at low temperatures. One would therefore expect a temperature dependence of  $N_2$  dissociation for the W(0) complex. No such dependence is predicted for the Mo(0) compound. Even at room temperature, the greater

population of the  $^3B_{2g}$  term in *trans*-( $N_2$ ) $_2$ Mo(dppe) $_2$  as opposed to *trans*-( $N_2$ ) $_2$ W(dppe) $_2$  should lead to a greater photoreactivity for the former complex. This inference, derived entirely from spectroscopic evidence, agrees with the known relative photoreactivities of the two molecules.<sup>4</sup>

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**Registry No.** *trans*-( $N_2$ ) $_2$ W(dppe) $_2$ , 28915-54-0; *trans*-( $N_2$ ) $_2$ Mo(dppe) $_2$ , 25145-64-6.

Contribution from the Istituto Teoria, Struttura Elettronica Composti di Coordinazione del CNR, Area di Ricerca di Roma, Rome, Italy, and Inorganic Chemistry Laboratory, Oxford University, Oxford OX1 3QR, England

## Low-Temperature Optical and Magneto-Optical Study of the Organic-Intercalated Two-Dimensional Ferromagnet ( $CH_3NH_3$ ) $_2$ CrCl $_4$

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Optical absorption spectra have been measured of single crystals of the two-dimensional ferromagnet ( $CH_3NH_3$ ) $_2$ CrCl $_4$  in the region of the quintet-to-triplet ligand field transitions at 5330 and 6270 Å at temperatures from 1.6 to 9 K and magnetic fields up to 5 T applied parallel to [010] of the *Aba2* unit cell. Above 2 K the absorption is dominated by "hot" exciton-magnon combinations, but at the lowest temperatures there is evidence for cold-band intensity arising from a small amount of spin canting, as in Rb $_2$ CrCl $_4$ . Quantitative analysis of the temperature and field dependence of the intensity and line shape of the bands gives an estimate of the anisotropy gap in the magnon spectrum at the Brillouin zone center as 1.9 (3) K and  $g = 1.93$  (1).

### Introduction

Very few ionic transition-metal compounds order ferromagnetically, and among this small group even fewer have resolved ligand field transitions that permit quantitative studies of the optical and magneto-optical properties. In this respect the tetrahalogenochromate(II) salts are probably unique because they have two groups of sharp bands arising from quintet-to-triplet transitions, which constitute the only visible absorption.<sup>1</sup> The behavior of these bands as a function of temperature and applied field has been studied in detail in Rb $_2$ CrCl $_4$ ,<sup>2</sup> which has a structure related to the K $_2$ NiF $_4$  structure, but with a cooperative Jahn-Teller distortion around the high-spin  $3d^4$  cations within the basal plane.<sup>3</sup>

As well as the group 1 $^{24}$  tetrachlorochromates(II), there also exists a series of organic-intercalated salts (RNH $_3$ ) $_2$ CrCl $_4$ <sup>4</sup> (R = C $_n$ H $_{2n+1}$ ;  $n = 1-12$ ) that are quite similar to the layer perovskite halide salts of Mn(II), Fe(II), Cu(II), and Cd(II), whose magnetic properties and structural phase transitions have been widely studied.<sup>5,6</sup> We reported susceptibility and magnetization data on  $n = 1, 2, 3, 5$ , and 12 examples<sup>7,8</sup> and the variation of the visible absorption bands in the C $_1$  and C $_2$  compounds from about 10 to 150 K.<sup>7</sup> In these ferromagnets, as in the prototype Rb $_2$ CrCl $_4$ , the electric dipole intensity of the formally spin-forbidden transitions arises from combining the creation of an exciton,  $\epsilon(k)$ , which lowers the total spin projection of the crystal, with annihilation of a thermally populated spin fluctuation (magnon)  $m(-k)$ . The combined process  $\epsilon(k) - m(-k)$  conserves momentum and is thus brought about by photon absorption for all values of  $k$ , i.e. across the whole Brillouin zone. The band shape is therefore determined by convoluting the exciton and magnon densities of states and the intensity at a given temperature by the Bose population of magnons. For a square-planar two-dimensional Heisenberg ferromagnet with negligible anisotropy, an intensity proportional to  $T^2$  was predicted<sup>9</sup> and found above 10 K in the Rb $_2$  C $_1$  and C $_2$  salts.<sup>7</sup> However, since the ground state has  $S = 2$ , anisotropy cannot be neglected, and at temperatures where  $kT$  becomes comparable to the anisotropy energy, the  $T^2$  law should fail. In Rb $_2$ CrCl $_4$  this occurs below 4 K $^{11}$  so in the present paper we

report absorption spectra of ( $CH_3NH_3$ ) $_2$ CrCl $_4$  from 1.6 to 9 K and extract an estimate of the zone-center anisotropy gap in the magnon density of states for comparison with that of the Rb salt. The zone-center gap can also be varied by applying a field,<sup>11</sup> and the variation in absorption band intensities from 0 to 5 T is also reported. Finally, if there is any canting of the moments from collinearity, it is predicted<sup>12</sup> that the small antiferromagnetic component should lead to a cold-band contribution to the intensity which, however, may be masked by the greater hot-band intensity, except at very low temperatures.

### Experimental Section

( $CH_3NH_3$ ) $_2$ CrCl $_4$  crystals used for this work were prepared as reported previously.<sup>7</sup> They are extremely air-sensitive, and all solvents etc. must be rigorously oxygen free. All manipulations were carried out by Schlenk techniques under O $_2$ -free nitrogen. Methylammonium chloride was from BDH, and the starting solution of Cr(II) in ethanol was obtained by dissolving electrolytic Cr metal with HCl gas. Good crystals for optical measurements were obtained by a slow cooling of a saturated ethanolic solution of the title compound sealed in a heavily walled ampule. Typically, for 0.5 g of the compound 15 mL of absolute ethanol is needed for solution. Crystal faces were identified easily because the compound crystallizes as platelets, the main face being [010] of the orthorhombic space group *Aba2*.

Absorption spectra were recorded on either a Cary 14 spectrophotometer or a McPherson double-beam spectrophotometer. Temperatures between room temperature and 77 K were recorded with an Oxford Instrument CF 100 cryostat. Spectra below liquid-nitrogen temperature

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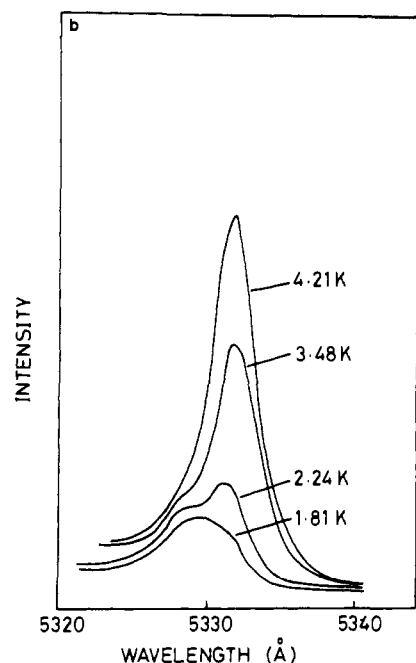
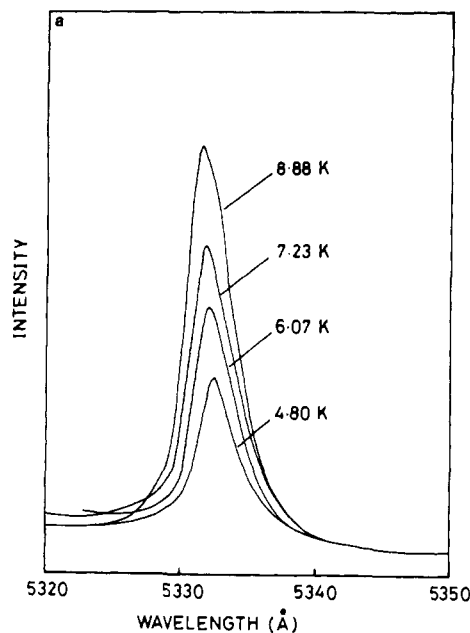


Figure 1. Absorption spectrum of  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  in the 5330-Å region: (a) 8.88–4.80 K; (b) 3.48–1.81 K.

were measured with a Thor Cryogenics cryostat and a McPherson 1-m grating monochromator having a spectral band-pass of approximately 0.15 Å. The crystals were approximately 2 mm  $\times$  0.5 mm, the light being propagated parallel to the [010] direction, i.e. perpendicular to the main face. The absorption spectra of the title compound is concentrated into two well-defined regions, near 530 and 630 nm, each of which contains fine structure. The intensity of the absorption bands at 627 and 533 nm as a function of temperature in the range 1.8–4.2 K was measured by pumping on the liquid helium in the inner vessel of the Thor cryostat. The temperature was measured by a calibrated carbon resistor, and the crystals were immersed in the liquid helium. The effect of applied field parallel and perpendicular to [010] was determined by using a split-coil superconducting magnet contained in the Thor cryostat. Measurements were made on the 533-, 627-, and 622-nm bands in fields up to 5 T over the range 42–1.8 K. The areas of the bands were determined by cutting and weighing several photocopies of each peak and averaging the results. The vertical lines in Figures 3 and 4 represent the standard deviations of these determinations.

### Results

Survey spectra of the whole visible region in  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  measured at 20 and 130 K were given earlier.<sup>4,7</sup> In this paper

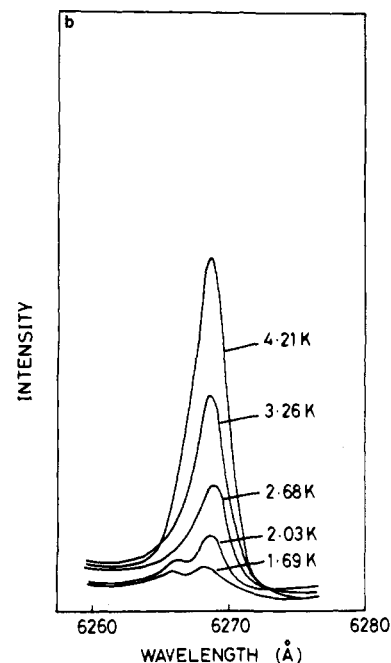
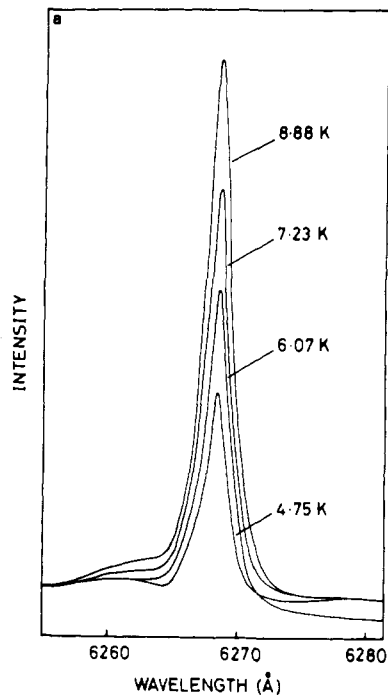
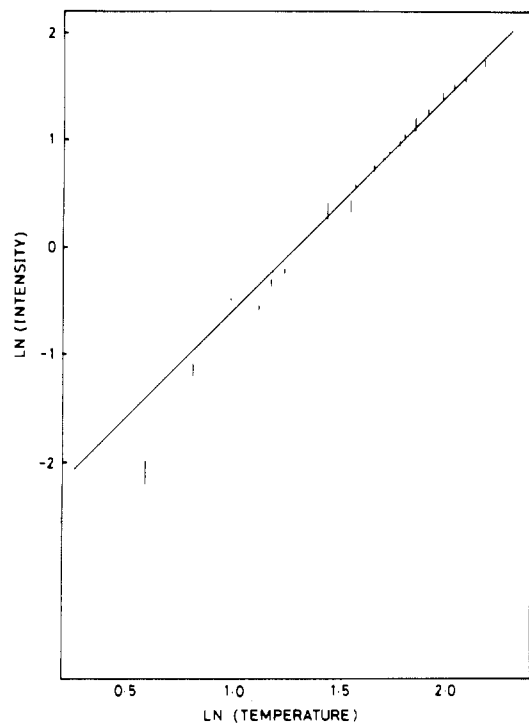


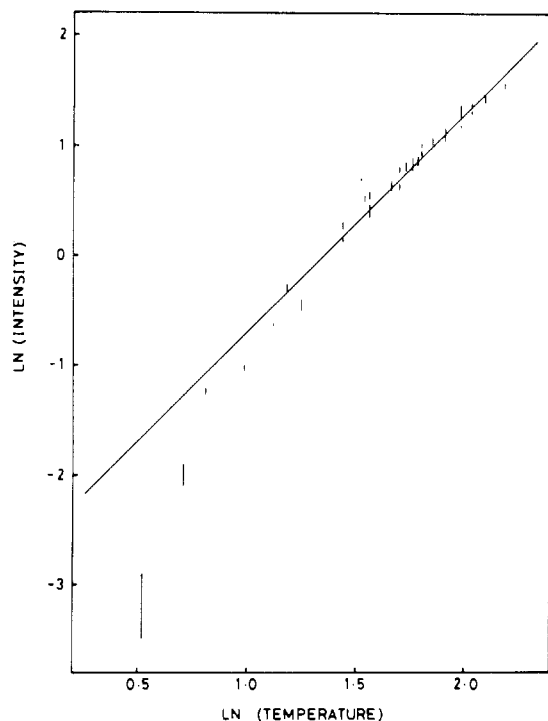
Figure 2. Absorption spectrum of  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  in the 6270-Å region: (a) 8.88–4.75 K; (b) 4.21–1.69 K.

we concentrate on the spectral regions from 5320 to 5350 and 6250 to 6280 Å. Figure 1 shows the former, and Figure 2 the latter. In each case from 8.88 to 4.70 K there is a progressive loss of intensity but no significant variation in the band profile. Below about 3 K, however, it becomes apparent that the bands are composite, and below 2 K, the absorption clearly consists of two components. They are respectively at 5329.0 and 5331.5 Å (Figure 1b) and at 6266.0 and 6268.5 Å (Figure 2b). In both spectral regions the intensity of the shorter wavelength band remains almost temperature independent, so that it becomes increasingly swamped by the longer wavelength band as the temperature increases.

At the lowest temperature accessible to us (1.7–1.8 K), the 5331.5- and 6268.5-Å "hot" bands are still present and are overlapping the cold bands. To obtain a quantitative temperature variation of the hot bands, it was therefore assumed that the contribution of the cold bands to the total intensity was constant over the temperature range 1.7–9 K and this contribution, estimated by curve deconvolution at the base temperature, was



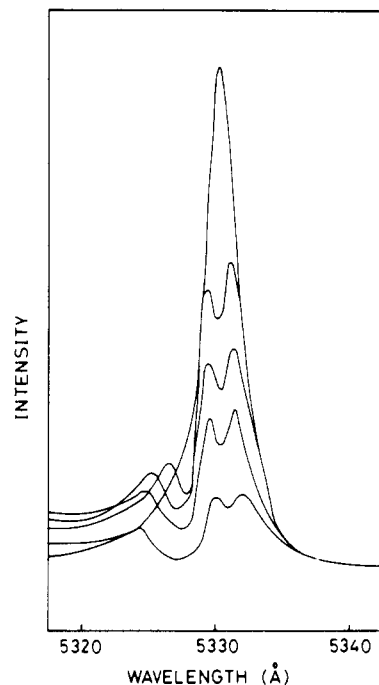
**Figure 3.** Temperature dependence of intensity of the 5331-Å band. The line represents a  $T^2$  dependence.



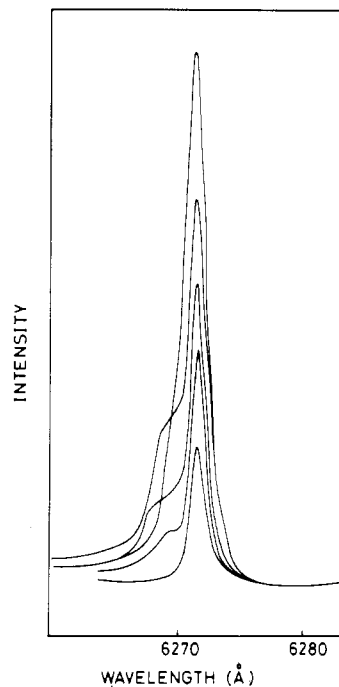
**Figure 4.** Temperature dependence of intensity of the 6268.5-Å band. The line represents a  $T^2$  dependence.

therefore subtracted from the total band area at each temperature. Temperature dependence of the hot-band intensity observed in this way is plotted on a logarithmic scale in Figure 3 (5331.5-Å band) and Figure 4 (6268-Å band). The lines drawn on each figure represent the best fits to a  $T^2$  temperature dependence from 4.2–9 K.

Finally, in Figures 5 and 6 are shown the effects on the 5330- and 6270-Å regions of a magnetic field applied parallel to the Cr layers. With increasing field, the overall intensity of both band systems falls markedly. In the case of the 5330-Å band, the major peak becomes split and a smaller side band also splits off and moves to shorter wavelength with increasing field. The intensity



**Figure 5.** Magnetic field dependence of the absorption in the 5330-Å region with  $H \parallel b$  at 4.2 K. From top to bottom,  $H = 0, 1, 2, 3,$  and  $5$  T.



**Figure 6.** Magnetic field dependence of the absorption in the 6270-Å region with  $H \parallel b$  at 4.2 K. From top to bottom,  $H = 0, 1, 2, 3,$  and  $5$  T.

of the 6270-Å hot band is plotted as a function of field at three temperatures in Figure 7.

#### Discussion

The crystal structure of  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  is related quite closely to those of the corresponding layer perovskite halide salts of Mn(II) and Cd(II), whose structures are known in detail.<sup>13,14</sup> As in the prototype salt  $\text{Rb}_2\text{CrCl}_4$ , though, there is a Jahn–Teller distortion of the corner-sharing  $\text{CrCl}_6$  units in the basal plane, taking the

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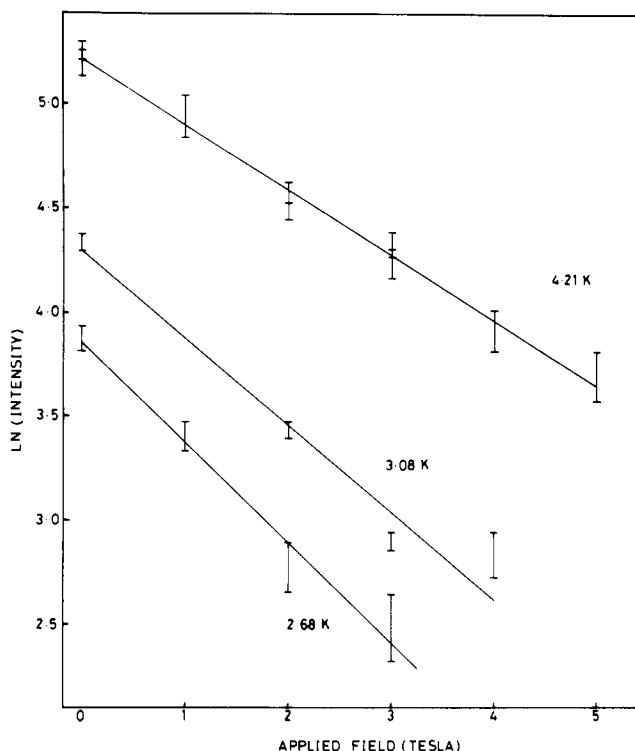


Figure 7. Variation in intensity of the 6270-Å band with applied field.

form of elongations, which, for alternate octahedra, lie in orthogonal directions within the plane.<sup>15</sup> In contrast to those of  $\text{Rb}_2\text{CrCl}_4$ , but like those of the other bis(monoalkylammonium) tetrachlorometalate(II) salts, the planes of  $\text{CrCl}_6$  units are slightly puckered to accommodate the  $\text{CH}_3\text{NH}_3^+$  ion in a favorable H-bonding arrangement, so that the Cr-Cl-Cr angles are  $166.5^\circ$ . The space group is  $Aba2$ , and at room temperature the Cr-Cl bond lengths within the basal plane are 2.41 and 2.82 Å and perpendicular to it, 2.41 Å. These figures should be compared with those in  $\text{Rb}_2\text{CrCl}_4$ , respectively 2.35, 2.70, and 2.38 Å.<sup>3</sup> Heat capacity measurements on  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$ <sup>16</sup> show no evidence of any first-order structural phase transitions associated with reorientation of the weak H-bonds between the  $\text{NH}_3^+$  and  $\text{CrCl}_6$  groups, of the type found in the  $\text{RNH}_3^+$  layer perovskite salts of other metal ions.<sup>17</sup> Apart from the puckering of the  $\text{CrCl}_6$  layers, the biggest difference between  $\text{Rb}_2\text{CrCl}_4$  and  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  is the separation between the  $\text{CrCl}_6$  layers (7.88 Å in the former and 9.41 Å in the latter). This, together with a reduction in the near-neighbor exchange constant  $J$  from 7.55<sup>18</sup> to 6.50 K,<sup>7</sup> is associated with a decrease in the Curie temperature from 52.1 K in the  $\text{Rb}^+$  salt<sup>19</sup> to 41 K in the  $\text{CH}_3\text{NH}_3^+$  one.<sup>20</sup> The small change in the average Cr-Cl bond length also modifies the ligand field strength slightly so that the two main regions of visible absorption are very slightly shifted in the  $\text{CH}_3\text{NH}_3^+$  salt. However, the shifts are so small (about 40 Å) as to reinforce the assignments proposed previously to pure "spin-flip" transitions  $^5B_{1g} \rightarrow ^3B_{1g}$  ( $D_{4h}$ ), unaccompanied by any orbital change.

A spin Hamiltonian that takes into account the cooperative Jahn-Teller distortion in  $A_2\text{CrCl}_4$  lattices with structures based on the  $\text{K}_2\text{NiF}_4$  structure is<sup>12,18</sup>

$$\mathcal{H} = \sum_{ij} J_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j) - \sum_{i1} \bar{P}(S_{i,x})^2 - \sum_{j2} \bar{P}(S_{j,y})^2 + \sum_{i12} \bar{D}(S_{i,z})^2 - g\mu_B \sum_{i12} \mathbf{H} \cdot \mathbf{S}_i \quad (1)$$

where  $i$  and  $j$  are alternate sites,  $\bar{D}$  is an anisotropy constant, which places the moments within the  $xy$  basal plane, and  $\bar{P}$  is the single-ion anisotropy constant arising from the cooperative Jahn-Teller distortion that constrains alternate moments toward the  $x$  and  $y$  directions ( $[100]$  and  $[010]$  of the  $\text{K}_2\text{NiF}_4$  unit cell). The magnetic structure is determined by competition between the ferromagnetic Heisenberg exchange  $J$  and the anisotropic  $\bar{D}$  and  $\bar{P}$ . In  $\text{Rb}_2\text{CrCl}_4$ , inelastic neutron scattering gives  $J = 7.6$  (2),  $D = 1.1$  (1),  $P = 0.12$  (1) K,<sup>18</sup> where  $J_1 = \bar{J}_1 \cos 2\theta$ ,  $P = \bar{P} \sin 2\theta$ ,  $D = \bar{D} + (\bar{P}/2)(1 - \sin 2\theta)$  and  $\theta$  is the canting angle<sup>18</sup> at which the moments are alternately canted to either side of the  $[110]$  direction of the  $\text{K}_2\text{NiF}_4$  unit cell. These values predict a value of  $\theta \sim 1.1^\circ$  compared with  $5 \pm 1^\circ$  observed by neutron diffraction.<sup>3</sup> The moments are canted alternately to either side of the  $\text{K}_2\text{NiF}_4$   $[110]$  direction by about  $5^\circ$ .<sup>3</sup> No inelastic neutron-scattering data are available on the spin waves in  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  because of the difficulty of growing large enough crystals. However, in addition to any canting brought about by the cooperative Jahn-Teller distortion, there will be a further contribution from the fact that the principal axes of the  $g$  tensors of adjacent sites do not coincide because the Cr-Cl-Cr angles are no longer  $180^\circ$ . A corresponding spin canting has been observed<sup>21</sup> in the antiferromagnetic layer perovskite salts  $(\text{RNH}_3)_2\text{MnCl}_4$  where, of course, it introduces a small ferromagnetic component into the spin structure, the inverse of what happens in the Cr case.

Since  $P$  and  $D$  are both small compared with  $J$ , they have their largest effect on the spin-wave energy  $E(k)$  near the Brillouin zone center. In particular  $P$  removes the axial symmetry that would be retained by  $J$  and  $D$  alone and introduces a gap in the spin-wave spectrum at the zone center:<sup>12,18,22</sup>

$$E(0)^2 = 2PS^2(P + 2D) \quad (2)$$

To explain the low-temperature optical results, we are only interested in the spin-wave dispersion near the zone center, which can be written approximately as

$$E(k) = \hbar\omega(k) \sim E(0) + Ak^2 \quad (3)$$

Assuming that the exciton dispersion can be neglected, the intensity of a "hot" exciton-magnon combination band is given by the magnon density of states, weighted by the thermal population of magnons. Thus

$$I(\omega) \propto \int_{E(0)}^{\infty} k^2 [\exp(E(k)/k_B T) - 1]^{-1} d\omega \quad (4)$$

To a good approximation

$$I(\omega) \propto T^2 \exp(-E(0)/k_B T) \quad (5)$$

Equation 5 was fitted to the intensity data for the 6270-Å band in  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$ , after subtraction of the cold-band contribution to each peak. It can be seen from Figure 3 that fewer data were measured at 5335 Å and also that the base temperature was a little higher than for the 6270-Å band. Thus only the two lowest temperature points deviate significantly from the limiting high-temperature  $T^2$  law. For this reason, and because the cold and hot bands overlap more and make deconvolution difficult, attention was concentrated on the 6270-Å band. A total of 41 data were fitted by a least-squares routine to give  $E(0) = 1.80$  (35) K.

In the presence of a field applied in the easy plane the zone-center gap is expected to increase as shown in eq 6. Quantitative

$$E_H(0) = E_0(0) + g\mu_B H \quad (6)$$

measurements of the area of the 6270-Å band were made at temperatures from 4.21 to 1.69 K in fields of 0, 1, 2, 3, 4, and

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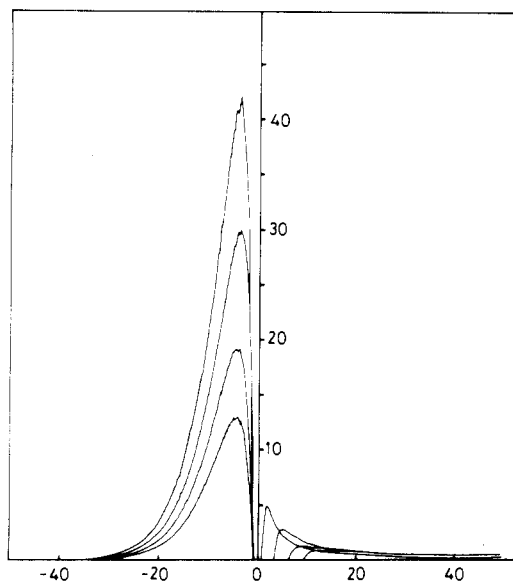
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**Figure 8.** Calculated variation of exciton-magnon absorption profiles in a two-dimensional square Heisenberg ferromagnet with planar anisotropy with field applied in the plane. From top to bottom,  $H = 0, 1, 2, 3,$  and  $5$  T. Zero energy is that of the pure exciton.

5 T to yield a total of 23 data points. On application of a field, the 6270-Å band develops a sideband at 6268 Å, the assignment of which is discussed below. For the purpose of estimating the area of the main band, the sideband was subtracted by assuming that the major absorption profile was symmetrical about the band maximum. The 23 independent data points were fitted to eq 5 and 6 to give  $E(0) = 2.03$  (37) K and  $g = 1.93$  (1). Representative fitted lines are shown in Figure 7. Thus, the zero-field and applied-field data yield estimates of  $E(0)$  in quite good agreement with one another, and an average value of 1.9 K may be adopted. This should be compared with that of 1.20 (15) K found<sup>2</sup> in the Rb salt by similar means. A  $g$  value slightly less than 2 is also anticipated for a high-spin  $d^4$  ion. The larger  $E(0)$  in the  $\text{CH}_3\text{NH}_3$  salt is not surprising in view of the canting of the principal axes of the  $g$  tensors brought about by tilting the  $\text{CrCl}_6$  groups. Lacking experimental spin-wave dispersion data for  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$ , we cannot estimate  $P$  and  $D$  separately, but it is worth noting that from eq 2 the function  $P/(P + 2D)$  is 0.80 compared with 0.28 for  $\text{Rb}_2\text{CrCl}_4$ . If we adopt the hypothesis that  $D$ , which arises primarily from the second-order spin-orbit splitting of the ground  ${}^5\text{B}_{1g}$  term by interaction with excited states, is unchanged on substituting  $\text{CH}_3\text{NH}_3^+$  for  $\text{Rb}^+$ ,  $P$  in the former is calculated as 0.327 (cf. 0.123 in  $\text{Rb}_2\text{CrCl}_4$ ). The spin-canting angle in this model being given by  $\tan^{-1}(P/8J)^{1/2}$ , our estimate for  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  is  $4.5^\circ$ .

At low temperatures the hot and cold bands should be separated by an interval of magnitude  $2E(0)$  since they correspond to the transitions  $\epsilon \pm m$ . The two bands are not so well resolved in  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$  as in  $\text{Rb}_2\text{CrCl}_4$ ,<sup>2</sup> but in the 6270-Å region they are 2.4 Å apart, compared with 1.9 Å for the same bands in the Rb salt.

A final point concerns the marked changes in the absorption band profiles on applying a field. In both spectral regions a sideband splits away from the major hot-band peak, which still dominates the absorption at 4.2 K. Additionally, the 5330-Å band itself splits on applying a weak field, to an extent that then remains invariant up to 5 T (Figure 5). The latter behavior is not that of a conventional linear Zeeman effect, and since the intensity ratio of the two components also remains constant up to 5 T, it appears to be an excited-state rather than a ground-state splitting. No such splitting occurs in the corresponding band of the Rb salt.<sup>2</sup> Since no single-crystal magnetization data are available for  $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$ , we cannot comment further. On the other hand, the splitting off of a sideband is precisely in accord with the theoretical prediction based on the Hamiltonian of example 1.<sup>12,23</sup> Figure 8 shows the absorption profiles of the hot band (left-hand side) and cold band (right-hand side) calculated from the spin-wave dispersion arising from example 1, as a function of increasing field applied in the easy plane by using  $J$ ,  $P$ , and  $D$  parameters appropriate to  $\text{Rb}_2\text{CrCl}_4$ . Exciton dispersion is assumed to be negligible, and the origin of the ordinate (given in units of kelvin) is the energy of the pure exciton. It can be seen that the cold band is predicted to move to higher energy, as confirmed by Figure 5.

### Conclusion

In summary, we have shown that quantitative measurements of absorption band profiles in spin-forbidden ligand field transitions as a function of temperature and applied field can give estimates of the zone-center spin-wave gap and  $g$  value in a prototypic example of an organic-intercalated two-dimensional ferromagnet. Replacing  $A = \text{Rb}^+$  by the bulkier  $A = \text{CH}_3\text{NH}_3^+$  in  $\text{A}_2\text{CrCl}_4$  almost doubles the gap (from 1.1 to 1.9 K), presumably at least in part because the principal axes of the  $\text{CrCl}_4$  units are no longer precisely parallel. An increased canting of alternate moments to either side of the easy axis within the basal plane is also predicted.

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- (23) Harrop, M. C.; D.Phil. Thesis, Oxford University, 1981 (unpublished).  
 (24) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.