Optical and magneto-optical study of the transparent ionic ferromagnet Rb$_2$CrCl$_4$

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Received 5 January 1982

Abstract. The visible absorption spectrum of the transparent ionic ferromagnet Rb$_2$CrCl$_4$ has been recorded as a function of temperature from 0.85 to 50 K and in magnetic fields up to 5 T applied along [100], [110] and [001]. Above 3 K the intensities of all the bands vary approximately as $T^2$, as predicted by Gregson et al for a two-dimensional easy plane ferromagnet. Below 2 K the 631 nm band is resolved into two components, one almost independent of temperature and the other having an intensity which increases with temperature as $T^2 \exp(-E(0)/kT)$. They are assigned respectively as spin wave creation and annihilation sidebands with $E(0)$, the zone-centre gap in the spin wave spectrum, $1.20 \pm 0.15$ K. All the bands lose intensity on applying a magnetic field, following the function $T^2 \exp[-(E(0) + g_\mu_B H/kT)]$, from which $g$-values are derived. The behaviour of the 631 nm band system agrees very well with the calculations of Elliott et al.

1. Introduction

Very few ionic insulators order as ferromagnets and among that small number even fewer are appreciably transparent in the visible region. Of the latter, only one series of compounds, the tetrachlorochromates(II), have discrete resolved absorption bands whose frequencies, intensities and lineshapes can be studied as a function of the magnetic ordering brought about by low temperatures or applied magnetic fields. In fact, cooling these crystals through their Curie temperatures has a spectacular effect on their visible absorption: the bands lose almost all their intensity and the crystals change colour from olive green to pale yellow (Day et al 1973). Following this discovery the crystal and magnetic structures and the magnetic excitations of the tetrachlorochromates have been examined in detail by neutron scattering and susceptibility measurements (Gregson 1974, Gregson et al 1975, Hutchings et al 1976, Fair et al 1977, 1978, Day et al 1979a, b, c). In the present paper we give a detailed account of the behaviour of the visible absorption bands in Rb$_2$CrCl$_4$ at temperatures from 0.85 to 50 K and magnetic fields along [100], [110] and [001] up to 5 T. A preliminary account of some of the measurements between 0.85 and 3.5 K has been given (Day et al 1979b).

Rb$_2$CrCl$_4$ ($T_c = 52.114$ K) has a structure closely related to that of K$_2$NiF$_4$ but the O$_h$ ground state of Cr$^{2+}$ (3d$^4$) is $^5$E$_g$ so there is a strong static Jahn–Teller distortion about the metal ion sites which manifests itself as a tetragonal elongation of the CrCl$_6$ octahedra alternately along the [100] and [010] directions of the K$_2$NiF$_4$ unit cell. Thus in addition
to the Heisenberg exchange between nearest neighbours in the plane \(J = 7.55(3)\)K, Hutchings et al 1981) and the anisotropy term \(D\) arising from second-order spin–orbit coupling which constrains the spins to lie within the basal plane, two further anisotropy terms \(P\) arise from the alternating single-ion anisotropies along [100] and [010]. The result is a planar ferromagnetic structure with an easy axis of magnetisation along [110] but with alternate spins canted to either side of this axis by angles \(\pm \theta\), where \(\tan 2\theta = P/J(0)\) (Elliott et al 1980, Lindgard et al 1980). A further consequence of the weak anisotropy in the \(xy\) plane is to open a small gap in the spin wave excitation spectrum at the zone centre, whose existence has been confirmed by inelastic scattering of long wavelength neutrons (Lindgard et al 1980, Hutchings et al 1981) and also by our preliminary optical measurements (Day et al 1979b). We shall see later that the existence of the gap and the spin canting are crucial to understanding the features of the optical absorption spectrum at low temperature. In broad terms the strong temperature dependence of absorption intensity comes about because creation of a Frenkel exciton \(e(k)\) by photon absorption is accompanied by the annihilation of a thermally populated magnon \(m(-k)\), the so-called ‘hot band’ mechanism of Shinagawa and Tanabe (1971). This comes about because the electronic excited states giving rise to the Frenkel excitons are triplet ligand field states, so to create them from the quintet ground state lowers the spin projection of the crystal. The outline of such a mechanism, as applied to \(K_2\text{CrCl}_4\), was given by Gregson et al (1976). A brief account of a more precise theory of the absorption band profiles, which takes account of the canting of the spins, was given by Elliott et al (1980) and described in more detail by Harrop (1981).

2. Experimental

The visible absorption of all the tetrachlorochromate(II) salts is concentrated into two well defined regions, near 530 and 630 nm, each of which contains several components.

To measure the intensity of the absorption bands at 631 nm and 623 nm as a function of temperature in the range 3.5 K to 0.85 K we used a specially designed Oxford Instruments optical cryostat. The crystal used was a plate of dimensions 5 mm × 5 mm × 2 mm, the light being propagated parallel to [001], i.e. perpendicular to the natural cleavage. It was glued over a hole in a copper block, using silicone vacuum grease. The block and crystal were immersed in liquid helium, pumped by a 4" diffusion pump connected directly to the top of the cryostat by very short 4" diameter pipe. The sample chamber was surrounded by heat shields at 1.3 K, 4.2 K, and 27 K, and the temperature was measured with a carbon resistor. The light source was a Moletron DL 200 tunable dye laser pumped by a Moletron UV 400 pulsed nitrogen laser. Moletron RB dye was the lasing medium. Unpolarised light from the laser was split by a quartz beam-splitter into sample and reference beams whose intensities were measured using two photodiodes. The output from the detectors was fed to a Moletron LP 20 laser photometer, which averaged the heights of 30 pulses in each channel, and ratioed the averages to give a direct measurement of optical density. The effect of an applied magnetic field on the absorption bands was determined with a McPherson 1 m grating monochromator having a spectral bandpass of approximately 0.15 Å. The sample (of about 1 mm thickness) was contained in a Thor Cryogenics split-coil superconducting magnet.

Measurements were made on the 533 nm, 631 nm and 623 nm bands in fields up to 5 T over the temperature range 4.2 K to 2.1 K. The field was applied along both the [100]
and [110] directions, the alignment of the crystal being checked by neutron diffraction. The light was again propagated along [001] which was perpendicular to the crystal face.

The evolution of the shape of the absorption bands with temperature in the range 10 K to 50 K was also studied using the McPherson spectrometer and an Oxford Instruments CF 100 continuous-flow cryostat. Because of the layer structure of Rb$_2$CrCl$_4$, it is difficult to cut samples of good optical quality with the faces parallel to [001]. However, by embedding the crystals in epoxy resin and grinding, thin specimens with faces containing the [001] axis could be produced, for measurements of spectra with the electric vector of the incident light perpendicular (σ) and parallel (π) to this axis.

3. Results

In figure 1 the linearly polarised spectra are shown in the three main regions of absorption, measured at 4.2 K with the incident light perpendicular to [001]. All the bands are much more intense in the σ-polarisation. The same bands are seen in the axial absorption (incident light parallel to [001]) so the dominant absorption mechanism is electric dipole, with polarisation parallel to the basal plane.

All measurements of the variation of intensity with temperature were carried out in the axial polarisation, and spectra measured from $T_c$ down to 12 K are shown in figure 2. The very dramatic reduction in intensity with decreasing temperature is obvious at once. More detailed measurements were made at lower temperatures where the bands are better resolved, and figure 3 contains results for the 623 and 631 nm regions down to a lowest temperature of 0.85 K.
Figure 2. Temperature dependence of the axial absorption spectrum from $T_c$ down to 12 K; A 12.2 K, B 20.7 K, C 27.4 K, D 31.8 K, E 37.4 K, F 44.7 K, G 49.3 K.

Below 4 K the shapes of the bands in the two regions become distinctly different, and they behave quite differently as a function of temperature. The 623 nm band remains broad and keeps the same asymmetric shape down to 1.0 K while its intensity becomes temperature independent below about 1.5 K. On the other hand, the 631 nm band is much sharper and below about 1.7 K becomes resolved into two components. One of them, which is quite broad and almost temperature-independent, dominates the absorption profile at the lowest temperatures while the other, which is much sharper and falls rapidly at lower temperatures, dominates the absorption profile above 1.8 K but becomes

Figure 3. Temperature dependent absorption spectra of (a) the 631 nm band and (b) the 623 nm band at very low temperatures.
almost negligible at 0.85 K. To deconvolute the two components of the 623 nm absorption, we assumed that the broader band was temperature independent over the temperature range of interest. Its area measured at 0.85 K was then subtracted from the total band areas measured at higher temperatures. Above 2 K it made only a very small contribution to the total band area.

Figure 4(a) is a logarithmic plot of the area of the sharp 'hot' band at 631.2 nm against temperature, normalised to unity at 4.2 K. The broken curve represents a $T^2$ variation, so it is clear that at the lowest temperatures the intensity varies much more steeply than $T^2$. Since the 623 nm band cannot be separated into separate temperature-dependent and independent components by curve resolution, we have subtracted the total band area remaining below 1.5 K, which is constant, from the band area measured at higher temperatures and plotted the temperature-dependent contribution on a logarithmic scale in figure 4(b). Clearly, figures 4(a) and 4(b) are very similar.

The effect of a magnetic field applied along [100] on the 631 nm band was illustrated in our preliminary communication (Day et al 1979b) and is not repeated here. Figure 5 shows the effect of applied fields along [100] and [110] on the 623 nm band and figure 6 the effect of a [100] field on the bands near 533 nm. In all cases, when the field is applied parallel to the basal plane the intensity of the absorption falls sharply. With $H \parallel [100]$
new sidebands also appear, to longer wavelength of the 623 nm band, but to shorter wavelength of the two bands near 533 nm. Plotted on a logarithmic scale the band areas in all three spectral regions show an almost linear variation with field, as exhibited in figure 7. The significance of these plots is considered below.
4. Discussion

4.1. Assignment of transitions

In a crystal field of octahedral symmetry the ground state of a high spin $3d^4$ ion is $^5E_g$. There is one other quintet term, $^5T_{2g}$, and a large number of triplets which, for the crystal field strength corresponding to chloride ions, lie above the quintet states (Tanabe and Sugano 1954). In Rb$_2$CrCl$_4$ the point symmetry at the Cr sites is strictly D$_{2h}$, but it approximates very closely to D$_{4h}$ (Day et al. 1979a). A tetragonal crystal field splits the octahedral ground term into $^5A_{1g}$ and $^5B_{1g}$, the latter lying lowest where the octahedron is elongated. The tetragonal components $^3B_{2g}$ and $^3E_g$ of $^5T_{2g}$ are located between 10000 and 12000 cm$^{-1}$ while the $^5A_{1g}$ component of $^5E_g$ has been assigned to a well resolved band near 7800 cm$^{-1}$ (Müninghof et al. 1980). Using these three band energies to fit the cubic and tetragonal crystal field parameters Müninghof et al conclude that the two main regions of absorption in the visible each correspond to a $^3B_{1g}$ upper state. Crystal field calculations in the strong field formalism (Gregson 1974) showed that between 16000 and 19000 cm$^{-1}$ there are two transitions, to $^3E_g$ and $^3A_{2g}$, which are pure ‘spin-flips’ and involve no orbital change. Each leads to a $^3B_{1g}$ state on tetragonal distortion, which likewise is a pure ‘spin-flip’. These assignments also agree with those arrived at from weak field crystal field calculations (Rosseinsky and Dorrity 1977) for CrCl$_2$ in which, also, coordination about the Cr$^{2+}$ is a tetragonally elongated octahedron with equatorial and axial bond lengths 2.40 and 2.91 Å (Tracey et al. 1961), compared with 2.38 and 2.70 Å in Rb$_2$CrCl$_4$ (Day et al. 1979a, b; Müninghof et al. 1980). Since transitions involving no change in orbital occupancy commonly have small Franck-Condon
widths (Orgel 1955) the narrowness of the bands in question, and the absence of phonon sideband structure, appears reasonable.

4.2. Spin waves and sidebands

We have shown earlier (Robbins and Day 1976, Day 1976) that in ionic insulators in which the near-neighbour exchange is ferromagnetic most of the intensity of spin-forbidden crystal field transitions comes from the combination of creating a Frenkel exciton with the annihilation of a thermally populated spin wave. This model accounted for the $T^2$ variation of the intensity of such bands in $K_2CrCl_4$ from 4 to 15 K (Gregson et al 1976) but took no account of the effect which the cooperative Jahn–Teller distortion has on the spin wave spectrum, a crucial factor in understanding the behaviour of the optical absorption bands at very low temperatures. Since alternate $CrCl_6$ octahedra are elongated along [100] ($x$) and [010] ($y$) of the $K_2NiF_4$ unit cell the appropriate spin Hamiltonian is

$$\mathcal{H} = - \sum_q J_q (S_i \cdot S_j) - \sum_i P (S_i^z)^2 - \sum_j P (S_j^z)^2 + \sum n_2 D (S_i^z)^2 - \sum n_2 H \cdot S_i. \quad (1)$$

The easy axis of magnetisation is [110] but, as mentioned in the Introduction, the spins on the two sublattices $i, j$ are canted at a small angle $+\theta$ to this direction. Single-crystal neutron diffraction at 4.2 K gives $\theta \sim 5^\circ$ (Janke et al unpublished). Elliott et al (1980) and Harrop (1981) give the following expression for the spin wave spectrum corresponding to equation (1):

$$[\hbar \omega(k)]^2 = S^2 \{ [J(0) - J(k)] \cos 2\theta + 2P \sin 2\theta \}
	\times \{ J(0) \cos 2\theta - J(k) + P(1 + \sin 2\theta) + 2D \}. \quad (2)$$

Since $P$ and $D$ are both small compared with $J(k)$ they only become important near $k = 0$, where the effect of the $P$ terms is to remove the axial symmetry, which the $D$ term alone would retain, and thus to introduce a gap in the spin-wave excitation spectrum of magnitude

$$[E(0)]^2 = [\hbar \omega(0)]^2 = 2P^2 S^2 (P + 2D)/J(0). \quad (3)$$

A further consequence of the canting brought about by the cooperative Jahn–Teller ordering is to permit zero-point spin deviations, which would not be present in a simple collinear ferromagnet. Thus, in addition to the 'hot band' intensity, the exciton–magnon combination bands are expected to show 'cold band' intensity at the lowest temperatures, because exciton creation can be coupled to magnon creation by destruction of the zero-point deviation.

Finally, calculations of the effect of external magnetic fields on the spin wave excitation spectrum (Harrop 1981) predict that there are significant differences between fields applied along [100], [110] and [001]. For relatively large fields the gap at $k = 0$ increases monotonically, independent of the field direction. At lower fields, however, the gap should increase monotonically when $H \parallel [110]$ but when $H \parallel [100]$ it should decrease at first, becoming zero at the field $2P^2S/J(0)$ required to pull the canted spins into that direction. Thereafter it should increase again. The axial anisotropy requires a field of $(P + 2D)S$ to bring the spins round to the $c$ axis, so the gap should be zero again when an external field along [001] reaches this value, increasing again thereafter, as before. In the following sections we match these predictions to the experimental evidence from the optical spectra.
4.3. Temperature dependence

From a temperature just below $T_c$ down to about 10 K the band areas in the 530 and 630 nm absorption regions (figure 2) follow the $T^2$ law described earlier for K$_2$CrCl$_4$ (Gregson et al 1976). As the temperature is reduced further, however, the intensity of the sharp band near 631.0 nm begins to fall much more steeply until, below 1.0 K, it has all but vanished (figure 3(a)). As the 631.0 nm band diminishes it reveals a much broader asymmetric sideband centred near 630.9 nm which is almost temperature-independent. In contrast, the 623 nm band (figure 3(b)) continues to fall in intensity down to about 1.5 K, after which it, too, remains constant. The temperature-dependent component of the latter, deconvoluted from the constant low-temperature component as described in § 3, follows the same temperature law as the 631.0 nm band. Assuming that this is due to the existence of a gap $E(0)$ in the magnon excitation spectrum at the zone centre the intensity of a magnon annihilation sideband is

$$I(\omega) \propto \int_{E(0)}^{\infty} k^2 \left[ \exp \left( \frac{E(k)}{k_BT} \right) - 1 \right]^{-1} d\omega$$

(4)

where, as an approximation near the zone centre

$$E(k) = \hbar \omega(k) \sim E(0) + A k^2 = E(0) + \hbar \omega'.$$

(5)

Then

$$I(\omega) \propto \int_{0}^{\infty} \hbar \omega' \left[ \exp \left( \frac{E(0)}{k_BT} \right) \exp \left( \frac{\hbar \omega'}{k_BT} \right) - 1 \right]^{-1} d\omega'.$$

(6)

which, with the substitution $\hbar \omega' / k_B T = x$, becomes

$$I(\omega) \propto T^2 \exp \left( \frac{E(0)}{k_BT} \right) \int_{0}^{\infty} \frac{x \, dx}{e^x - e^{-E(0)/k_BT}}.$$  

(7)

The effect of temperature on the integral in equation (7) can be estimated from a standard integral formula (Gradshteyn and Ryzlik 1965). Setting $E(0) \sim 1.4$ K it varies about 25% from 3.5 to 0.8 K, in comparison with the intensity of the 631.0 nm band, which varies by a factor of about 25. Thus we incur little error by fitting the intensities to

$$I(\omega) \propto T^2 \exp \left( \frac{E(0)}{k_BT} \right).$$

(8)

The full curves in figures 4(a) and 4(b) are least squares fits to equation (8), and define a value of $E(0) = 1.4 \pm 0.1$ K. Taking into account the small temperature dependence of the integral in equation (7), the fitted value of $E(0)$ is reduced to $1.2 \pm 0.15$ K, in very satisfactory agreement with the gap at zero wavevector estimated by long-wavelength inelastic neutron scattering which, extrapolated to 0 K, is $1.16 \pm 0.08$ K (Lindgard et al 1980, Hutchings et al 1981).

4.4. Band shapes

Using magnitudes for the exchange and anisotropy constants $J$, $P$ and $D$ in equation (1) close to those determined by inelastic neutron scattering (Janke 1980, Hutchings et al 1981), Elliott et al (1980) and Harrop (1981) calculate absorption profiles $I(\omega)$ for magnon annihilation and creation sidebands by numerical methods. The Brillouin zone was divided into a mesh of 10 points, though for symmetry reasons only one eighth of the zone need be considered. The energy scale was broken into steps of 0.25 K, and at
each square in the mesh $\gamma_k$ and $E(k)$ were evaluated to determine which energy step in
the absorption it would contribute to. The occupation numbers $n(k)$, given by Bose-
Einstein distributions, were evaluated for several temperatures and weight the contribu-
tions of the magnon creation and annihilation sidebands to the total profile at any
particular temperature. While the latter varies as $n(k)$, and so has a very steep temper-
ature dependence, the former varies as $n(k) + 1$, so at low temperature its contribution
is almost constant. Figure 8 is the absorption profile calculated for three temperatures
对应的 to those in figure 3. For this band system agreement between experiment
and theory is excellent, demonstrating the validity of the original hypotheses. In quali-
tative terms the ‘hot’ (magnon annihilation) sideband becomes progressively narrower
as it gets weaker (see also figure 2 at higher temperatures) because it reflects the thermal
population of magnons. With decreasing temperature the population becomes more
and more concentrated towards the low $E(k)$ end of the dispersion curve near the zone
centre where the dispersion is flatter (equation (5)) and the density of states correspond-
ingly larger. By contrast the ‘cold’ (magnon creation) sideband is much broader because
at the lowest temperatures its shape does not depend on the thermal population of
magnons, but rather the wavevector dependence of the transition probability.

Of the three band systems in the visible spectrum, the one at 631 nm is easily the best
resolved, and the absorption profiles of the others cannot be explained so neatly. The
623 nm band is much broader, though also asymmetric in the same sense as the hot band
at 631.0 nm. However, as we showed in § 4.3, it has a cold band contribution which
cannot be separately resolved. The same is true of the 532 and 534 nm bands. One may
speculate that the dispersion of the exciton (neglected in Harrop’s calculation) makes
an appreciable contribution to the overall band shape.

4.5. Magnetic field effects
A simple phenomenological way to describe the effect of applied fields on the optical

![Figure 8. Calculated absorption band profile at (top) 1.74, (middle) 1.05 and (bottom) 0.85 K (Harrop 1981).]
spectrum would be to introduce a field-dependent gap $E_{H}(0)$ in equation (8), i.e. to write

$$E_{H}(0) = E(0) + g\mu_B H.$$  

Data on the variation in area of the 631 nm band with $H \parallel [100]$ up to 5 T, at several temperatures from 4.2 to 2.1 K were least-squares fitted to (8) with the substitution of equation (9) to give $E(0) = 0.9 \pm 0.4$ K and $g = 2.1 \pm 0.1$, in reasonable agreement with $E(0)$ from the zero field experiments (Day et al 1979b). Similar plots for the 623, 534 and 532 nm bands in figure 7, for fields parallel to [100] and [110], lead to comparable estimates. The presence of the spin canting complicates this simple picture, however, and calculations of the effect of an external field on the spin wave spectrum of equation (2) (Elliott et al 1980, Harrop 1981) predict slight differences in the variation of the zone centre gap with field, depending on whether the field is applied along [100] or [110]. As noted in § 4.2, when the field is parallel to the easy axis [110] the mean spin direction is unaffected and $E_{H}(0)$ increases monotonically, as in equation (9), though the canting angle also decreases uniformly since the field merely reinforces the exchange. When the field is along [100], however, the spins have first to be aligned in this hard direction. Thus the gap should decrease and then increase. On the other hand, for the values of $J$, $P$ and $D$ which give the best description of the 631 nm absorption band profile in zero field, the gap is predicted (Harrop 1981) to reach zero at about 0.2 T, i.e. at a lower field than the smallest one (1.0 T) applied in the present experiments. In all our higher field experiments the absorption band area varies quite monotonically with field (e.g. figure 5) and we could not distinguish any difference between the behaviour of the band areas with $H \parallel [110]$ and $H \parallel [100]$ (figure 7). This agrees with the absorption profiles calculated for fields of the same magnitude (figure 9). In figure 9 the small sharp features in the magnon creation sidebands about 120 K above the origin arise from the Van Hove singularity in the magnon density of states at the zone boundary. In zero field the weighting factors multiplying the density of states in this region are vanishingly small, but become slightly accentuated in the presence of a field (Harrop 1981). We have searched the absorption spectrum unsuccessfully for these features, and conclude that they are either too weak to see, or become smeared in the experimental spectra.

Apart from decreasing the intensity of the magnon annihilation sidebands through an increase in the zone-centre magnon gap, the other consequence of an applied field

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**Figure 9.** Calculated absorption band profiles at 4.2 K with (a) $H \parallel [100]$ and (b) $H \parallel [110]$. In order of decreasing intensity the profiles are for $H = 0, 1, 3, 5$ T (Harrop 1981).
predicted by the model of Elliott et al (1980) and Harrop (1981) is a decrease in the intensity of the corresponding magnon creation sidebands which, at the same time, should shift rapidly to shorter wavelength. The magnetic field experiments on the sharp 631 nm band were performed at lower resolution, and did not show this (see figure 2, Day et al 1979b). However, the effect is clearly visible for the 532–534 nm band group (figure 6).

5. Conclusions

The optical and magneto-optical experiments reported here agree quite well with the theoretical predictions for a two-dimensional easy-plane ferromagnet with alternate metal ions having easy axes along orthogonal directions within the plane. The temperature dependence of the absorption profile is particularly well reproduced, and the appearance of a magnon creation sideband, which is almost temperature-independent below 1 K, arises naturally from the small amount of spin canting known to be present in the structure (Hutchings et al 1981). In later papers we shall describe similar experiments on ferromagnetic tetrachlorochromates in which the magnetic layers are separated by organic groups.

Acknowledgments

We thank the Science Research Council for financial support, and Dr P J Walker of the Clarendon Laboratory, Oxford, for supplying the crystals.

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