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## Optical studies of field-induced order in a singlet ground state dimer system

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**Abstract.** Optical Zeeman studies are reported for the ordered region of the singlet ground state dimer system  $\text{Cs}_3\text{Cr}_2\text{Br}_9$ . The results are compared with earlier neutron scattering and AC susceptibility studies, and a model is suggested which not only describes the optical data, but also produces an excellent fit to the phase diagram as defined by the susceptibility results.

### 1. Introduction

The compound  $\text{Cs}_3\text{Cr}_2\text{Br}_9$  belongs to a class of materials where trivalent transition metal ions couple strongly in pairs by exchange interactions to form magnetic dimers. The Cr–Cr separation is 3.3 Å within the dimers and 7.4 Å (same sublattice) and 7.5 Å (different sublattices) between nearest neighbour dimers. Antiferromagnetic coupling between ground state  $\text{Cr}^{3+}$  ions leads to a ground dimer manifold consisting of singlet, triplet, quintet and septet levels at 0, 6.3, 17.5 and 31.0  $\text{cm}^{-1}$  respectively as measured by hot-band optical transitions [1]. The nature of the coupling within the dimers is relatively well understood from optical studies [2], and much of the absorption and Zeeman data may be explained using an isolated dimer model [3]. The one aspect of the Zeeman studies which has not been satisfactorily resolved within an isolated dimer framework is the anomalously low  $g$ -values reported for this material not only in the optically excited states, but also in the dimer ground state which is a well-isolated orbital singlet. An electron delocalization model has been suggested to account for this effect [2], but no detailed calculations for such a mechanism have been carried out. More recently, it has been shown by a series of experiments including neutron scattering studies [4, 5] and AC susceptibility measurements [6, 7], that this material undergoes a field-induced ordering process in large applied magnetic fields at temperatures of less than 2 K. As all the earlier Zeeman work has been carried out at temperatures of 4 K and above, it would seem that the earlier optical data is not relevant to the behaviour of the ordered region. In this paper, we describe the extension of the optical Zeeman measurements into the ordered regime, as defined by our AC susceptibility measurements [7], and examine how these two experimental techniques give some insight into the induced order in this singlet ground state system, as well as suggesting a model for the detailed field behaviour of the optical spectrum which also encompasses some features of the magnetic measurements.

## 2. Experimental evidence for field-induced order

The first strong evidence for inter-dimer coupling in this material came from the neutron scattering studies of Leuenberger *et al* [4, 5], who reported significant dispersion in the singlet-triplet excitations of the ground manifold. Although no evidence of order was observed in their measurements, which went down to temperatures of 1.5 K, the observed dispersion suggested that a transition to magnetic order might be induced by a magnetic field. Attempts to observe such a transition by neutron measurements have proved inconclusive, but AC susceptibility measurements by Leuenberger *et al* [6] over a rather restricted range of temperature (1.5–1.9 K) and field (0–5 T) showed that a field-induced transition to order does exist. Extending these measurements to much lower temperatures (down to 45 mK) and to much higher fields (up to 12 T), Kazmi *et al* [7] were able to map the phase diagram for the transition as shown in figure 1.

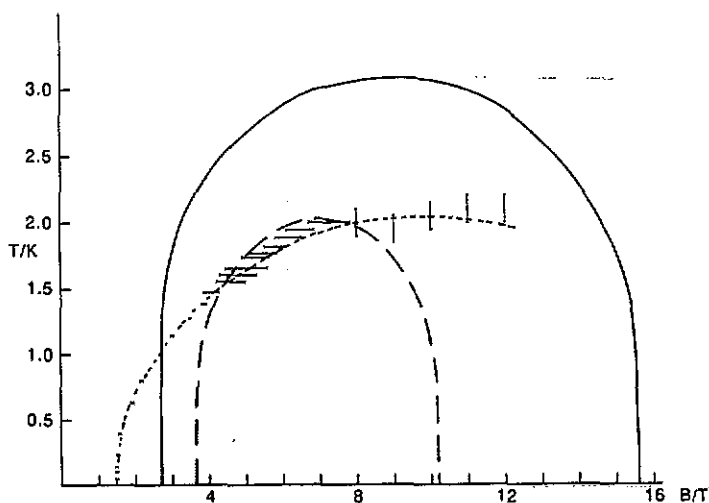


Figure 1. The phase diagram of  $\text{Cs}_3\text{Cr}_2\text{Br}_9$  as measured by AC susceptibility studies [7]. The experimental points are indicated with error bars. The curves indicate the predictions of the present model (---), the soft-mode theory (—) and the molecular field model (- - -).

Several models have been suggested to account for the way in which inter-dimer coupling and the field behaviour of the low-lying levels in  $\text{Cs}_3\text{Cr}_2\text{Br}_9$  give rise to the observed order. A soft-mode theory has been proposed in the random-phase approximation to describe the singlet-triplet excitations measured by inelastic neutron scattering [4] and this theory has later been extended to include the application of field [8]. From the zero-field results, this approach predicts that a component of the acoustic branch of the singlet-triplet excitation near the K symmetry point in  $k$  space will be driven towards zero energy by applied magnetic field giving rise to an ordered phase at  $T = 0$  between fields of 2.5 T and 15.5 T. For higher temperatures the field range of the ordered phase would diminish and no order should be observed above a temperature of 3 K for any applied field. An alternative approach is to use a molecular field model [6] to describe the crossover in field between the ground state singlet and the lowest component of the field-split triplet. The inter-dimer interaction

has non-vanishing matrix elements between the singlet and triplet states and these will become important in the crossover region. If the isotropic inter-dimer exchange is projected on the subspace spanned by the singlet and the lowest component of the triplet, the interaction becomes anisotropic with respect to the direction of the applied magnetic field. The component of the exchange interaction perpendicular to the field becomes larger than the component parallel to the field. The effective field in this subspace becomes very small near the point of level crossing and an ordering of the spin component perpendicular to the field in the vicinity of the point of level crossing should occur at sufficiently low temperatures.

Qualitatively, both the soft-mode and molecular field models give rise to a similarly shaped phase diagram as indicated in figure 1. Both predict the onset of order at  $T = 0$  at a finite value of field and little change in that field for temperatures up to about 1.5 K. Furthermore, both predict a return to the disordered phase at  $T = 0$  for sufficiently large applied fields, with a diminishing range of field for which ordering occurs as the temperature is increased. As may be seen from the phase diagram deduced from our susceptibility measurements, there are a number of features of the experimental results which differ significantly from the predicted behaviour of either model. These include a much less rapid temperature variation with field than predicted, a lower field onset of order at  $T = 0$  and an absence of any evidence for the re-emergence of the disordered state at higher fields. Furthermore, the maximum temperature at which any evidence of order may be detected is lower than the soft-mode theory would suggest. Figure 1 also shows a fit to the experimental data using the empirical formula

$$T^2 = T_0^2 \left[ 1 - \left( \frac{B - B_1}{B_2} \right)^2 \right]$$

with  $T_0 = 2.04$  K,  $B_1 = 10$  T and  $B_2 = 8.5$  T. As can be seen, this expression gives a much better description of the data than either the soft-mode or molecular field theories. This result will be considered in more detail later in the light of the optical results.

### 3. Optical studies

To study the effect of the field-induced order on the energy-level structure of the system, we have extended the earlier Zeeman measurements [2] into the ordered regime. Optical studies in field at temperatures of 4 K and above have previously been carried out on the  ${}^4A_2 \times {}^2E$  [9],  ${}^4A_2 \times {}^2T_1$  [2] and  ${}^4A_2 \times {}^2T_2$  [10] singly-excited states of the dimer. The notation here indicates that one ion in a pair is in the ground state and the other in an optically excited state. The present study concentrates on a few of the sharper lines in the spectrum, and in particular on transitions from the  ${}^4A_2 \times {}^4A_2$  ground manifold to selected states within the  ${}^4A_2 \times {}^2T_1$  manifold. The ground manifold is well described by a Heisenberg-Dirac-van Vleck (HDVV) Hamiltonian of the form

$$\mathcal{H} = -JS_1 \cdot S_2 + j(S_1 \cdot S_2)^2$$

with  $J = -4.9 \pm 0.3$  cm<sup>-1</sup> and  $j = -0.21 \pm 0.06$  cm<sup>-1</sup>, giving a ground state non-magnetic singlet ( $S_g = 0$ ) with the higher spin states  $S_g = 1, 2, 3$  at 6.3, 17.5 and

31.0  $\text{cm}^{-1}$  respectively. Here the subscript denotes states of the ground manifold. It has been shown by Barry *et al* [3] that the  ${}^4A_2 \times {}^2T_1$  manifold is not treatable by the HDVV formalism and a symmetry approach based on ideas of exchange suggested by Stevens [11] is needed to give a satisfactory description of the exchange within the excited manifolds. The  ${}^4A_2 \times {}^2T_1$  manifold consists of 48 states, 30 with spin  $S = 2$  and 18 with spin  $S = 1$ . Before spin-dependent effects are considered, each of these groups comprises two orbital doublets and two orbital singlets. As there are no first-order spin-orbit effects in this manifold, higher order terms must be invoked giving rise to shifts and splittings of the orbital parent states. The resulting states may be divided into two families labelled  $\sigma_b = +1$  and  $\sigma_b = -1$  depending on their transformation properties under the reflection operator of the  $D_{3h}$  group which interchanges the ions in a dimer. These two families may be considered separately as there are no matrix elements of the effective Hamiltonian between them. Individual states are labelled according to their symmetry and spin properties e.g.  $E'(\pm 1)$  represents the degenerate  $m_s = \pm 1$  components of the spin doublet transforming as the irreducible representation  $E'$  of the point group  $D_{3h}$  of the dimer. Where more than one state with the same representation and spin components exists within a manifold, the state may be identified uniquely by a secondary label denoting the orbital parent e.g.  ${}^3A_2''$  is the  $S = 1$  orbital singlet transforming as  $A_2''$ .

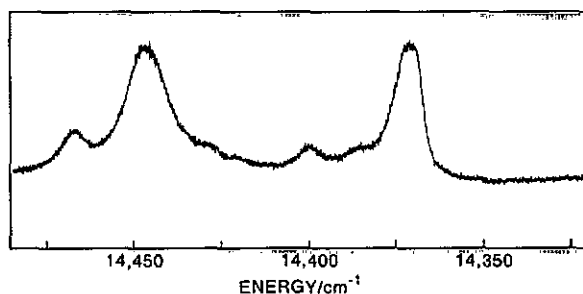


Figure 2 The  $\sigma$ -polarized absorption spectrum of  $\text{Cs}_3\text{Cr}_2\text{Br}_9$  at 4.2 K for part of the  ${}^4A_2 \times {}^2T_1$  region.

In the present study, we concentrate on transitions to a small number of states within the  ${}^4A_2 \times {}^2T_1$  manifold which have been clearly identified in the earlier work of Dean *et al* [2]. Figure 2 shows the  $\sigma$ -polarized absorption spectrum at  $T = 4.2$  K in the  ${}^4A_2 \times {}^2T_1$  region. All of the observed transitions are electric-dipole allowed and are strongly polarized as a consequence of the high dimer symmetry. The line of interest is the strong  $\sigma$ -polarized line at approximately  $14\,370\text{ cm}^{-1}$ . This line is the sharpest feature in the spectrum and has been identified as a transition from the  $S_g = 0$  ground state singlet to the  $E'(\pm 1)$  states which, along with the  $A_1''(0)$  state, makes up the  ${}^3A_2''$  orbital singlet. At 4.2 K, on the application of a magnetic field, either perpendicular or parallel to the  $c$ -axis, this line splits linearly and symmetrically, showing that the  $E'(\pm 1)$  and  $A_1''(0)$  states are degenerate. In axial polarization (radiation along the  $c$ -axis), the transition to the  $A_1''(0)$  component becomes visible in perpendicular field.

Results of the Zeeman studies for the  $14\,370\text{ cm}^{-1}$  line at a temperature of 1.4 K are shown in figure 3 for various fields applied perpendicular to the  $c$ -axis, and the line positions are plotted in figure 4. It is clear that at 1.4 K, where the lines are much sharper than at 4.2 K, there is a substantial departure from the symmetric and linear

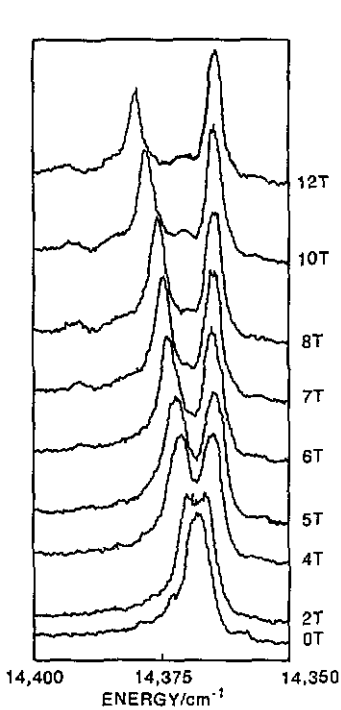


Figure 3. The magnetic-field dependence of the  $14\,370\text{ cm}^{-1}$  line at 1.4 K for field perpendicular to the  $c$  axis.

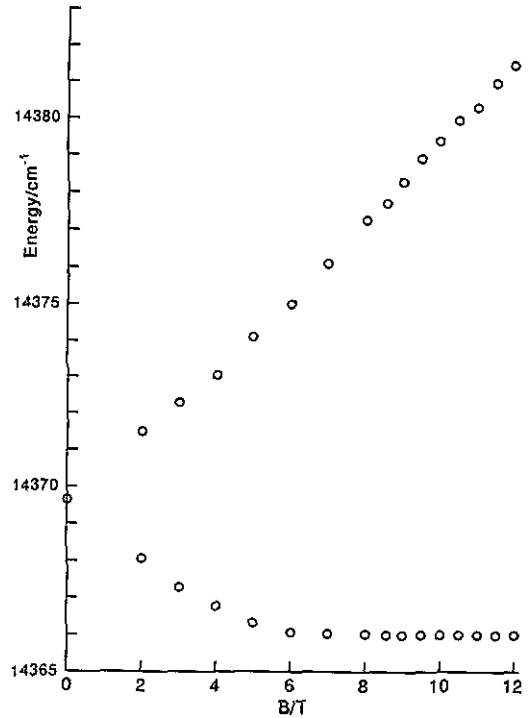


Figure 4. The positions of the field-split components of the  $14\,370\text{ cm}^{-1}$  line at 1.4 K for field perpendicular to the  $c$  axis.

splitting behaviour as observed at 4.2 K, and that this departure occurs at a field of approximately 4 T. When a series of such spectra are recorded at temperatures above 1.4 K, it is found that the derivation from linear behaviour in the temperature range 1.4 to 2.1 K follows the phase diagram of figure 1 which was deduced from the earlier susceptibility measurements. The qualitative change in the spectrum at fixed fields of 8 T and 12 T as the specimen is taken through the transition may be seen in figure 5. Apart from the marked energy shift as a function of temperature particularly in the low-energy component, it is clear that there is a broadening of the lines above 2.1 K at 12 T which is not apparent at the lower field. This broadening is in fact observed for these lines for fields of 9 T and above for temperatures above 2.1 K.

Similar behaviour is also observed in this spectral region for a field applied parallel to the  $c$ -axis. Again a substantial asymmetry in line splitting is observed below 2.2 K with the marked departure from linear behaviour showing agreement with the phase diagram deduced from susceptibility measurements. This is demonstrated in figure 6 where the mean energy of the field-split components is plotted against applied field at various temperatures. On each plot, the field position of the phase change given by the susceptibility measurements is indicated and it is clear that it corresponds in each case to an observable change in slope of the mean energy of the split spectral line. Although the energy of the components of the field-split line are very similar for parallel and perpendicular fields, there is a difference in the line intensities for

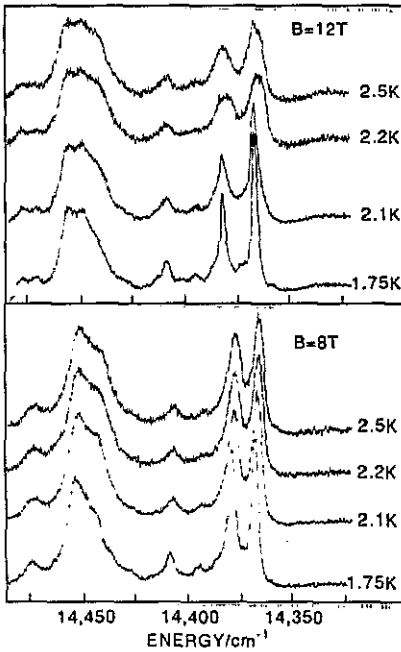


Figure 5. The temperature dependence of the  $\sigma$ -polarized spectrum in the vicinity of the phase boundary at (a) 12 T and (b) 8 T for field perpendicular to the  $c$  axis.

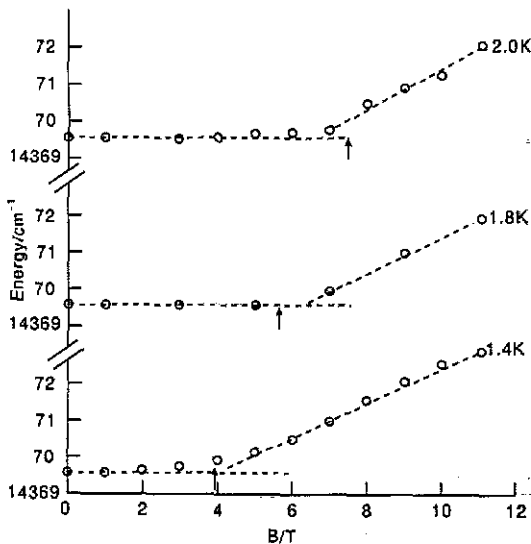


Figure 6. The mean energy of the field-split components of the  $14370\text{ cm}^{-1}$  line plotted as a function of field parallel to the  $c$  axis for several temperatures. The arrows mark the position of the phase boundary as determined from the susceptibility results.

the two field orientations. For perpendicular field, the intensity of the low-energy component is considerably greater than that of the high-energy component at all temperatures in the liquid helium range. The same is true for the parallel field case

only in the temperature range above 2.2 K. Below this temperature, the intensities of the two components are about the same.

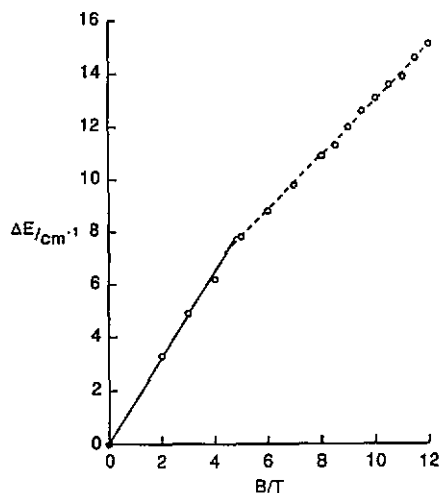


Figure 7. The splitting of the  ${}^3A_2''$  state as a function of field perpendicular to the  $c$  axis at 1.4 K.

The observed splitting in the excited states is similar in both field orientations with  $g_{\parallel}$  and  $g_{\perp}$  each measured to be  $1.4 \pm 0.1$  at 4.2 K. As the temperature is lowered, the lines become much sharper, particularly below 2.2 K and a more detailed analysis may be made of the excited state splitting, which shows two linear regions of different slopes as a function of field as shown in figure 7. For fields up to about 5 T, the splitting indicates a  $g$  factor of  $1.7 \pm 0.1$  whereas in the higher field region,  $g = 1.10 \pm 0.05$ . The accuracy of the lower field gradient is reduced because of resolution and line-pulling considerations, which also make it difficult to ascertain an accurate field at which the gradient changes. In addition to the detailed study of the  $\sigma$ -polarized line at  $14370 \text{ cm}^{-1}$ , it was noted that the spectrum as a whole exhibits a shift towards higher energy by a few wavenumbers as the sample is taken into the ordered region.

#### 4. Discussion of results

Previous attempts to describe the details of the field-induced order in terms of soft-mode or molecular field models have essentially restricted the problem to that of a two-level system, due to the complexity introduced by the inclusion of the remaining spin levels of the ground manifold. However it is clear from our results that effects of the higher lying states of the ground manifold are evident for comparatively modest values of the applied field e.g. the  $S_g = 2$  level is measured at  $17.5 \text{ cm}^{-1}$  in zero field and, with a spin-only splitting factor, one of its components should cross the  $S_g = 0$  level at an applied field of just over 9 T, with a component of  $S_g = 3$  crossing the  $S_g = 0$  level at about 12 T. We believe that the line-broadening observed in the 9–12 T field range for temperatures above 2.1 K (figure 5) is related to the population of these higher spin states, and that models that do not include these states must be treated with caution for fields in excess of about 8 T. The interpretation of the optical work in terms of field-induced order must depend to some extent on an interpretation



of the neutron and magnetic studies referred to earlier. Of central importance is the behaviour of the levels of the ground manifold in the presence of an applied field. All three experimental techniques give information about this, but it is not always obvious how results from the different experiments may be reconciled. In order to study the spin states of the ground manifold other than  $S_g = 0$  by absorption spectroscopy, temperature must be sufficiently high to populate these levels, and observed transitions only occur for  $\Delta k = 0$ . It is usually assumed that such transitions occur at  $k = 0$ , and whereas this is true for the ground state of the system, there is no such constraint on higher states which are thermally populated [12]. In principle, transitions from low-lying excited states may originate from any point in  $k$ -space as long as the  $\Delta k = 0$  rule is obeyed. The neutron studies have generally been carried out at temperatures lower than that required to populate the excited spin states of the ground manifold and the resulting energy dispersion curves show no obvious correlation with the optical energies. The details of the dispersion curves are, however, expected to be temperature dependent and there is some evidence that the total density of states of the singlet-triplet excitation peaks at an energy value close to the optical result for  $S_g = 1$  at temperatures around 10 K and above [13]. Thus although the optical result gives a well-defined and apparently temperature-independent energy for the  $S_g = 1$  state, the neutron result would indicate that the optical measurement is the mean energy of a narrow band, the structure of which is temperature and field dependent. This would indicate that the  $S_g = 1$  level does not behave in applied field as a simple triplet with a spin-only splitting factor but that it should be represented as a magnon band exhibiting dispersive character i.e. the coupling between dimers leads to a collective excitation of the system. The excited states may also be expected to have a dispersive character and should be formally described as excitons. To understand the optical spectrum, we must therefore consider the excitations of the system.

The form of the ground state for a three-dimensional antiferromagnet is an unsolved problem in theoretical physics and it is therefore impossible to give a rigorous description of this system. However it is possible to construct a self-consistent approximation capable of describing and linking together the thermal, optical and magnetic properties of the system.

At low temperatures and moderate fields, it is only necessary to include the  $S_g = 0$  and 1 states of the chromium dimers with zero-field separation of  $W$ . The isotropic exchange interaction commutes with the total spin of the coupled dimers, and the applied magnetic field interaction commutes with the component of total spin parallel to  $B$  (taken as the axis of quantization). Thus the ground state of the system takes the form

$$\Psi_n = \sum_p c_p P|0, 0, \dots; -1, -1, \dots\rangle$$

where  $n$  dimers are in the  $M_S = -1$  state, and  $(N - n)$  dimers have  $S_g = 0$ .  $P$  permutes the spin deviations over the dimers and the amplitudes  $c_p$  are unknown. In this representation, the magnetic field interaction is diagonal

$$E_{\text{mag}} = n(W - g\mu_B B).$$

The exchange interaction between the dimers has the effect of moving the spin deviations from one dimer to another, but it does not change their number  $n$ . This

leads to a depression of the ground state energy proportional to the inter-dimer exchange. Motion of the spin deviations cannot occur when  $n$  is equal to  $N$  or zero. We therefore assume an exchange contribution to the ground state energy of the form

$$E_{\text{ex}}^{(1)} = \frac{J_1 n(N - n)}{N}$$

with  $J_1 < 0$  for antiferromagnetic interactions. A second smaller contribution to the exchange energy arises when adjacent dimers are both in the  $M_S = -1$  state. For an antiferromagnetic interaction, this gives an energy increase of the form

$$E_{\text{ex}}^{(2)} = -\frac{J_2 n^2}{N}$$

At low temperature, the number of spins deviations,  $n$ , will minimize the ground state energy

$$E_n = E_{\text{mag}} + E_{\text{ex}}^{(1)} + E_{\text{ex}}^{(2)}.$$

This leads to three regions of magnetic field with different behaviour.

(i)

$$\begin{aligned} g\mu_B B &< W + J_1 \\ n = 0 \quad E_n &= 0 \end{aligned}$$

(ii)

$$\begin{aligned} W + J_1 &< g\mu_B B < W - J_1 - 2J_2 \\ n = \frac{N(W + J_1 - g\mu_B B)}{2(J_1 + J_2)} \quad E_n &= \frac{N(W + J_1 - g\mu_B B)^2}{4(J_1 + J_2)} \end{aligned}$$

(iii)

$$\begin{aligned} g\mu_B B &> W - J_1 - 2J_2 \\ n = N \quad E_n &= N(W - g\mu_B B) - NJ_2 \end{aligned}$$

At higher magnetic fields, the  $S_g = 2$  and 3 states of the dimer may become involved.

The low-temperature magnetic susceptibility can easily be calculated from these results. The magnetic moment is proportional to  $n$  and therefore

$$\chi \propto \frac{\partial n}{\partial B}.$$

In field regions (i) and (iii),  $\chi = 0$  and in region (ii),  $\chi$  is a constant. This may be compared with the results of Fletcher *et al* [14] on this material, which show a very small increase of  $\chi$  with increasing field in this region. There is some evidence to suggest that this increase is due to instrumental drift, a result that does not materially affect the conclusions of that paper, and is in agreement with the above theory. Further evidence comes from the very high field work of Ajiro *et al* [15]

on the isomorphous chloride compound where an approximately constant value of the susceptibility is reported for the ordered region. As the temperature is raised, the thermal fluctuations break the exchange-induced order. The order parameter is off-diagonal, having a matrix element coupling the  $S_g = 0$  state of the dimer to the  $M_S = -1$  state. In the field regions (i) and (iii) at low temperatures, all dimers are in the  $S_g = 0$  and  $M_S = -1$  states respectively, and the order vanishes. In region (ii), the exchange energy can be thought of as due to the interaction of the order parameter of each dimer with an internal field proportional to the order parameter of the other dimers. Thus the internal field is proportional to  $[E_{\text{ex}}^{(1)}]^{1/2}$ . The thermal energy needed to disorder the dimers is proportional to the internal field and the resulting equation of the phase boundary is:

$$T \propto \sqrt{n(N-n)}.$$

In field region (ii) this leads to

$$T^2 = T_0^2 \left[ 1 - \left( \frac{B - B_1}{B_2} \right)^2 \right]$$

where  $B_1 = (W - J_2)/g\mu_B$  and  $B_2 = -(J_1 + J_2)/g\mu_B$ . Here, at  $T = 0$ ,  $(B_1 - B_2)$  and  $(B_1 + B_2)$  give the lower and upper field limits for order respectively, assuming that no other spin states are involved, an assumption that is only likely to be valid for fields of about 8 T or less.  $T_0$  is an empirical parameter which gives a measure of the maximum temperature at which order is possible. This expression has been shown to give an excellent fit to the data of figure 1 with  $T_0 = 2.04$  K,  $B_1 = 10$  T,  $B_2 = 8.5$  T.

In optical absorption at low temperature, a dimer makes a transition from state  $\Psi_n$  to an electronically excited state. This excited state is also affected by the exchange interaction between dimers, allowing the excitation to travel from one dimer to another. This results in a band of excitons with a width proportional to the inter-dimer exchange. If the initial state has  $n = 0$ , the exciton is travelling through a lattice of dimers in the  $S_g = 0$  state. On the other hand, if  $n = N$ , the exciton travels through dimers in the  $S_g = 1$ ,  $M_S = -1$  state, resulting in a different width for the exciton band. In the general case, the initial state is intermediate between these extremes, and the simplest assumption is that the exciton band width varies linearly with  $n$ . The optical transition has the selection rule for momentum,  $\Delta k = 0$ , and the sharp optical line at low temperatures arises from the  $k = 0$  point of the exciton band. Thus the energy of the appropriate excited state for optical absorption includes the terms  $\Delta + J_4 n/N$ , where  $J_4$  is proportional to the off-diagonal part of the inter-dimer exchange for the excited states, and  $\Delta$  is the zero-field energy of the transition between ground and excited states.

The diagonal part of the exchange couples the parallel component of the dimer spins to those of its near neighbours. The average number of neighbours in the  $M_S = -1$  states is proportional to  $n$ , giving an additional energy contribution of  $J_3 M_S^e n/N$  where  $M_S^e$  is the parallel spin component of the electronic excited state, and  $J_3$  is the strength of the diagonal part of the inter-dimer exchange. The energy of the excited state includes the energy  $E_n$  of the  $n$  dimers in the state  $M_S = -1$  and the optical absorption energy is

$$h\nu = \Delta + g_e \mu_B B M_S^e + \frac{n}{N} (J_3 M_S^e + J_4)$$

where  $e$  indicates the excited state. At low temperatures and fields,  $n$  is approximately zero and, for  $g\mu_B B < J_1 + W$ , the spectrum has the simple form

$$h\nu = \Delta + g_e\mu_B B M_S^e.$$

As the applied field is increased beyond the phase transition into region (ii),  $n$  becomes field dependent, as above, and for  $g\mu_B B > J_1 + W$ ,

$$h\nu = \Delta + g_e\mu_B B M_S^e - \frac{(g\mu_B B - W - J_1)(J_3 M_S^e + J_4)}{2(J_1 + J_2)}.$$

There is thus a change of slope in the graphs of frequency versus field, when the applied field is strong enough to cause ordering of the ground state. The splitting of the  $M_S^e = \pm 1$  components at high fields is described by

$$2g_{\text{eff}} = 2g_e - g \left( \frac{J_3}{J_1 + J_2} \right).$$

These predictions are in accord with the low-temperature observations. At low fields, the  $\sigma$ -polarized line splits symmetrically with  $g$  close to 2. At high fields,  $g_{\text{eff}}$  approaches 1 indicating that  $J_3 \approx (J_1 + J_2)$  assuming  $g$  and  $g_e$  have spin-only values. For antiferromagnetism  $J_1$  is negative,  $J_2$  is small, and  $J_3$  is thus negative.

The slope of the  $M_S^e = +1$  component becomes approximately independent of field at low temperatures. This indicates that the  $(J_3 M_S^e + J_4)$  factor in the expression for the absorption energy is small for this state, and  $J_3 \approx -J_4$ . Thus  $J_4 \approx -(J_1 + J_2)$  and is positive. The position of the centre of gravity of the two lines to  $M_S^e = \pm 1$  is given by

$$h\nu = \Delta + n \frac{J_4}{N}.$$

At temperatures low enough for ordering to occur, we therefore expect to see an increase of slope in the graph of line position against field at the onset of magnetic ordering. At higher temperatures, the variation of  $n$  is less abrupt and a gradual change of slope occurs. The sign of this change of slope is consistent with a positive value of  $J_4$  deduced from the low temperature behaviour. This is also consistent with the general shift of the spectrum to higher energies with increasing field.

## 5. Conclusions

The optical absorption and Zeeman studies reported here have been used to discuss the field-induced order observed in the singlet ground state dimer system  $\text{Cs}_3\text{Cr}_2\text{Br}_9$ . The optical measurements are shown to be consistent with earlier magnetic and neutron scattering measurements, and a model is developed that not only explains the optical measurements, but also suggests a basis for an empirical formula that has been found to give a much better fit to the magnetic phase diagram than either the soft-mode or molecular field approaches previously considered. The proposed model considers essentially a two-level system and is therefore applicable only in the experimental regime where the effects of the higher lying spin states may be ignored.

The effect of these states is observed on the optical spectrum for fields in excess of 9 T.

As the temperature is raised, thermal excitations in the form of magnons are produced. There is then no single state for optical absorption. The initial states with thermally excited magnons no longer have a single value of  $n$  or of  $k$  (momentum) and therefore the final states for the optical transitions will also involve a range of values of  $n$  and  $k$ , the distribution of which will be field dependent. As the energies of the final states depend on  $n$  and  $k$ , this introduces a temperature and field dependent broadening and shift of the absorption frequencies. The details of the higher temperature behaviour have not been explored here as this would introduce a new range of unknown parameters. However, the expected broadening and shift of absorption frequencies may well account for the unusually small values for apparent splitting factors reported from the optical studies for both the ground and excited states in this material at temperatures of 4.2 K. In contrast, the isomorphous chloride compound shows spin-only  $g$  values at this temperature, but requires very much higher fields (of order 15 T) to induce order, indicating the much lower ratio of inter- to intra-dimer coupling in this material than in the bromide.

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