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OPTICAL STUDIES OF THE MAGNETIC PHASE DIAGRAM OF  $\text{MnBr}_2$ 

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**Résumé.** — Le bromure de manganèse est un composé ionique isolant transparent, qui présente un ordre magnétique en champ nul à très basse température. Des mesures d'absorption optique des transitions internes de l'ion  $\text{Mn}^{2+}$  sont combinées avec des études de dichroïsme pour déterminer le diagramme de phase magnétique. Comme dans le cas de  $\text{MnCl}_2$ , trois régions d'ordre magnétique sont mises en évidence et étudiées en fonction de la température et du champ magnétique. Ces données sont comparées aux résultats des études de diffraction de neutrons et un modèle d'ordre magnétique est discuté.

**Abstract.** — Manganous bromide is a transparent ionic insulator which exhibits magnetic ordering in zero field at temperatures below circa 2.2 K. Experiments are reported in which optical absorption measurements of internal transitions of the Mn ion are combined with dichroism studies in these same absorption bands to determine the magnetic phase diagram. As for the case of  $\text{MnCl}_2$ , three regions of magnetic order are found and studied as a function of magnetic field and temperature. The present data are compared to previous neutron diffraction studies and a model of the magnetic ordering is discussed.

1. **Introduction.** — Manganous bromide is a transparent ionic insulator that crystallizes in the layer type hexagonal structure of  $\text{CdI}_2$ . The crystal is, therefore, comprised of layers of  $\text{Mn}^{2+}$  ions separated by two layers of bromine ions (Fig. 1). The  $(c/a)$  ratio is 1.622 and there is one molecule of  $\text{MnBr}_2$  per unit cell, all the  $\text{Mn}^{2+}$  ions being crystallographically equivalent. Neutron diffraction studies [1] have indicated that at circa 2.16 K, under zero magnetic field conditions, the high temperature paramagnetic phase converts to an antiferromagnetic phase. If the spins on the  $\text{Mn}^{2+}$  are taken into account, the  $\text{Mn}^{2+}$  ions may be regarded as occupying two equivalent interpenetrating sublattices with origins displaced by  $(\frac{1}{2}, \frac{1}{4}, 0)$  in terms of the orthorhombic unit cell chosen by Wollan *et al.* [1] and shown in figure 1.

The neutron data suggests that, in the antiferromagnetic phase, all the  $\text{Mn}^{2+}$  spins lie in the basal planes of the orthorhombic unit cell. Strong antiferromagnetic exchange coupling between  $\text{Mn}^{2+}$  ions in adjacent basal planes occurs through the bromine ions along the  $\langle 611 \rangle$  directions of the orthorhombic cell. These directions have a three fold symmetry

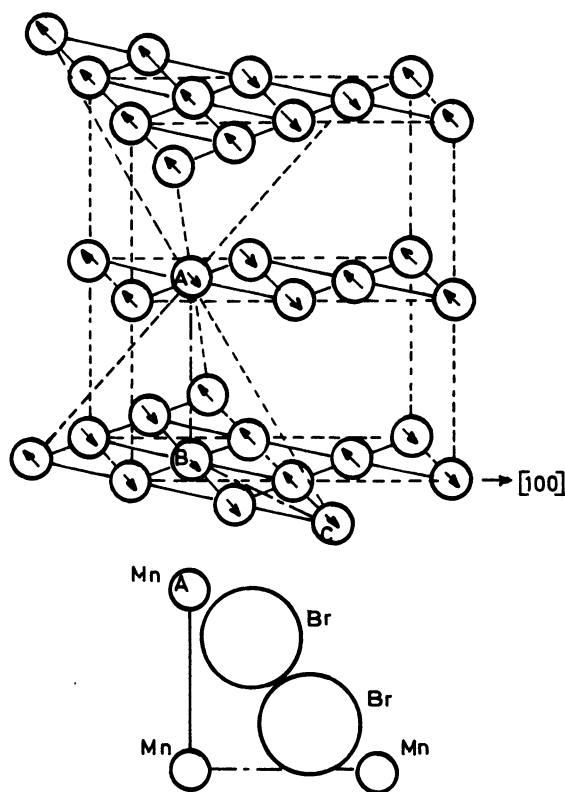


FIG. 1. — The magnetic structure of  $\text{MnBr}_2$  as determined by Wollan *et al.* [1].

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with respect to the  $c$ -axis of the unit cell and three equivalent antiferromagnetic domains can be formed, each having one of these directions as a characteristic axis. When the magnetic field is arranged to be at an angle to the  $c$ -axis, so that a component is along one of these directions, it is possible to organize the antiferromagnetic phase into a single domain. Similar behaviour has been observed in the crystallographically similar  $\text{MnI}_2$  [2] and  $\text{MnCl}_2$  [3, 4] structures, the favored domain being that for which the field component is perpendicular to the magnetic moments. In contradistinction to the case of  $\text{MnBr}_2$  the preferred domain in these other structures was not stable when the magnetic field was reduced to zero.

In  $\text{MnCl}_2$  a study [4] of the dependence of the neutron scattering intensity as a function of magnetic field and temperature indicated the possible presence of two antiferromagnetic structures. The transition from the paramagnetic to the high temperature structure was always sharply defined but the transition between the high and low temperature antiferromagnetic phase occurred over a temperature range that became larger as the applied magnetic field was increased. The presence of these two antiferromagnetic states was also indicated by measurements [5] of the specific heat of single crystals of  $\text{MnCl}_2$  in an applied magnetic field. The optical measurements reported in the previous paper [6] also clearly revealed the presence of the two antiferromagnetic phases. The neutron data provided no indication of two antiferromagnetic phases for the case of  $\text{MnBr}_2$ .

Single crystals of  $\text{MnBr}_2$  exhibit an onset of strong optical absorption in the region of 2 700 Å indicating an electronic band gap of circa 4.6 eV. As in  $\text{MnCl}_2$  the spectral region between 6 500 Å and 2 700 Å has a complex absorption spectrum consisting of bands with considerable interval structure that are associated with transitions in the  $\text{Mn}^{2+}$  ion between the  ${}^6A_{1g}$  ground state and higher excited states. These transitions have been extensively studied by Stout [7] and Pappalardo [8, 9] in both  $\text{MnBr}_2$  and  $\text{MnCl}_2$ . As in the previous paper on  $\text{MnCl}_2$ , the band at about 4 340 Å which corresponds to the  ${}^6A_{1g} \rightarrow [{}^4E_g, {}^4A_{1g}]$  transition is of particular interest. All these transitions are spin and parity forbidden in the free ion but exciton-magnon interactions induce non zero oscillator strengths in the solid, following the mechanisms proposed and extensively discussed by Sell *et al.* [10] for the case of  $\text{Mn}^{2+}$  in  $\text{MnF}_2$ .

In this paper measurements are reported on the optical absorption and dichroic properties of  $\text{MnBr}_2$  in the region of the Néel temperature ( $\sim 2.16$  K). A magnetic phase diagram, similar to that measured for  $\text{MnCl}_2$  is derived from this data. The present results are compared to those of the previous neutron diffraction studies.

**2. Experimental results.** — The experimental configuration used for these measurements was the same

as that reported in the previous study of  $\text{MnCl}_2$  [6]. Samples of  $\text{MnBr}_2$  were cleaved from ingots grown by D. Legrand <sup>(1)</sup>.

**2.1 THE OPTICAL ABSORPTION OF  $\text{MnBr}_2$ .** — Three series of absorption lines have been studied; the first between 3 600 and 3 650 Å corresponds to the  ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$  transitions of the Mn ion in the cubic field description, the second between 3 700 and 3 850 Å corresponds to the  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  (II) transitions and the third between 4 300 and 4 350 Å to the  ${}^6A_{1g} \rightarrow [{}^4E_g, {}^4A_{1g}]$  transitions. These measurements are in agreement with those of Pappalardo [9] but have better resolution due to the lower temperatures employed in the present measurements. It is not the purpose of this paper to give a full interpretation of the optical spectrum but to emphasize those features of the transitions which will be used to study the magnetic properties of  $\text{MnBr}_2$ .

**2.1.1 Absorption between 3 600 and 3 650 Å [ ${}^6A_{1g} \rightarrow {}^4E_g$ ].** — The absorption spectrum of  $\text{MnBr}_2$  in this energy range is shown in figure 2 above and below the Néel temperature. In this figure, the bands are labeled as  $\alpha_1, \beta_1, \gamma_1$ , for the first triplet,  $\alpha_2, \beta_2, \gamma_2$  for the second and  $\alpha_3$  for the broad peak at higher energy. The energy difference between  $\alpha_1, \alpha_2$  and  $\alpha_3$ ,

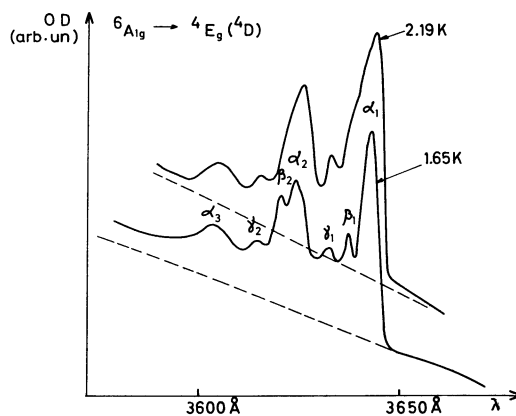


FIG. 2. — The optical absorption of  $\text{MnBr}_2$  corresponding to the  ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$  transition.

$\beta_1$  and  $\beta_2$  and  $\gamma_1$  and  $\gamma_2$ , is about the same and is approximately equal to  $140 \text{ cm}^{-1}$ . Within a given triplet, below  $T_N$ , the  $\beta$  and  $\gamma$  peaks are separated from the  $\alpha$  peak by  $40 \text{ cm}^{-1}$  and  $75 \text{ cm}^{-1}$  respectively. The  $\alpha$  and  $\beta$  peaks are only separated below the Néel temperature where the magnetic ordering changes the optical absorption spectrum. This was also seen for the  ${}^6A_{1g} \rightarrow ({}^4A_{1g}, {}^4E_g)$  transition in  $\text{MnCl}_2$  [6] and by Marzacio and McClure [11] in  $\text{MnCl}_2 \cdot 2 \text{H}_2\text{O}$ .

In  $\text{MnBr}_2$  the Néel temperature, and consequently the magnon energy, is low and it is therefore difficult to separate purely dipolar transitions from electric

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dipolar-exciton-magnon transitions. In interpreting the spectrum it has been assumed that the  $\alpha_1 \beta_1$  and  $\gamma_1$  peaks are due to exciton-magnon transitions and correspond to three purely excitonic transitions;  $\alpha_2 \beta_2$  and  $\gamma_2$  are assigned to exciton-magnon-phonon transitions with the phonon having an energy of  $140 \text{ cm}^{-1}$ ;  $\alpha_3 \beta_3$  and  $\gamma_3$  correspond to the same type of transition but with two phonons of the same energy.

The above assignments raise two questions: why are three levels observed for the  ${}^4E_g$  state and why does one of these levels behave in the observed manner in the ordered and disordered phases? The present experimental results do not answer the first question and it is necessary to speculate about the relative strengths of the spin-orbit coupling, the exchange field and the Jahn-Teller (J.T.) coupling. It can be assumed that the small  $C_{3v}$  contribution to the crystal field does not split the orbital doublet. In the presence of a strong J.T. coupling the energy degeneracy is not lifted and the exchange field, acting only on the spins, lifts the spin degeneracy. The only allowed transition is then between the  $m_s = -\frac{5}{2}$  ground state and the  $m_s = -\frac{3}{2}$  excited state of the  ${}^4E_g$  level and only the one exciton-magnon transition is observable. If the J.T. coupling is very small the spin orbit interaction predominates and splits the  ${}^4E_g$  state into three levels giving rise to three absorption peaks of practically the same intensity. From the data of figure 2 it is evident that MnBr<sub>2</sub> represents an intermediate case. The splitting between the  $\alpha$ ,  $\beta$  and  $\gamma$  peaks is too small to be analysed only in terms of a spin orbit interaction [12] and the J.T. effect is certainly reducing the orbital angular momentum of this level. The change in the  $\alpha$  and  $\beta$  peaks above and below the Néel temperature is more difficult to interpret. As will be seen later, the  $\beta$  peak disappears completely above  $T_N$  and it is probable that a rapid change occurs around  $T_N$ .

2.1.2 *The absorption at 4 300 Å [ ${}^6A_{1g} \rightarrow ({}^4E_g, {}^4A_{1g})$ ].* — Figure 3 shows the optical absorption spectrum of MnBr<sub>2</sub> above and below  $T_N$  in the 4 300 Å region. The first two peaks  $A_1$  and  $A_2$  behave in the same manner as the  $\alpha$  and  $\beta$  peaks in the U.V.

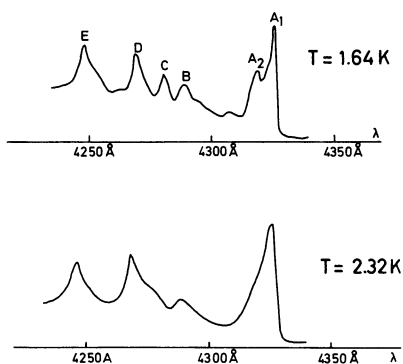


FIG. 3. — The optical absorption of MnBr<sub>2</sub> corresponding to the  ${}^6A_{1g} \rightarrow ({}^4E_g, {}^4A_{1g})$  transitions.

absorption which suggests that they correspond to the exciton-magnon  ${}^6A_{1g} \rightarrow {}^4E_g$  transitions with the  ${}^6A_{1g} \rightarrow {}^4A_{1g}$  transition corresponding to one of the higher energy peaks. This assignment is in good agreement with the results of Schwartz *et al.* [13] who observed a  ${}^6A_{1g} \rightarrow {}^4A_{1g}$  transition at higher energy than the  ${}^6A_{1g} \rightarrow {}^4E_g$  transition in K<sub>2</sub>MnF<sub>4</sub> and MnF<sub>2</sub>. The C peak is related to the A<sub>2</sub> peak and disappears above the Néel temperature. The energy difference between C and A<sub>2</sub> is the same as that between B and A<sub>1</sub> (ca.  $170 \text{ cm}^{-1}$ ) and could correspond to a phonon energy. This suggests that the A<sub>1</sub> and A<sub>2</sub> peaks correspond to exciton-magnon transitions. These two peaks can correspond to exciton-magnon transitions from the same excitonic transition  ${}^4E_g$  level or to exciton-magnon transitions from two excitonic transitions to the two  ${}^4E_g$  levels split by the spin-orbit interaction; such a splitting has been observed in MnF<sub>2</sub> and K<sub>2</sub>MnF<sub>4</sub> and are respectively  $14.5 \text{ cm}^{-1}$  and  $25 \text{ cm}^{-1}$  [13].

2.1.3 *The absorption between 3 700 Å and 3 850 Å [ ${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{II})$ ].* — As shown in figure 4 this absorption does not change on going through the Néel temperature. The spectrum is simple, being a series of quartets (*a, b, c, d*) with a spacing of about  $160 \text{ cm}^{-1}$  and an intraquartet spacing of about  $33 \text{ cm}^{-1}$ . It is suggested that the *a, b, c, and d*, peaks correspond to exciton-magnon transitions with four spectral origins (*a<sub>0</sub> b<sub>0</sub> c<sub>0</sub> and d<sub>0</sub>*) that are too weak to be observed. The (*a<sub>i</sub> b<sub>i</sub> c<sub>i</sub> d<sub>i</sub>*) peaks correspond to an exciton-magnon transition with *i* phonons. Only one kind of phonon is involved having an energy of  $160 \text{ cm}^{-1}$ , a value close to that observed in the two previous cases.

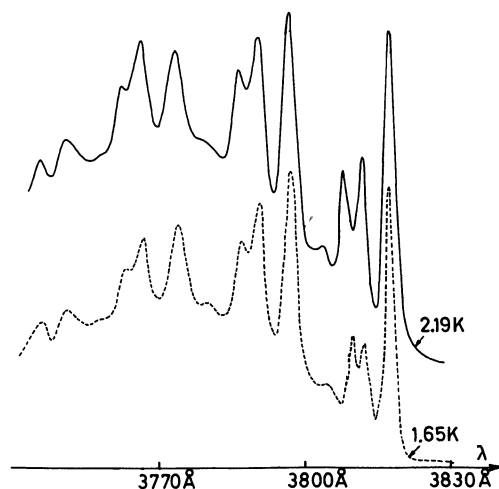


FIG. 4. — The  ${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{II})$  absorption in MnBr<sub>2</sub>.

This spectrum is simpler than the spectrum corresponding to the same transition in RbMnF<sub>3</sub> studied by Solomon and McClure [12]: in MnBr<sub>2</sub> as only one phonon is involved. Solomon and McClure have made detailed calculations to interpret the  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  absorptions in RbMnF<sub>3</sub> taking

into account the phonon coupling with Jahn-Teller distortions, spin-orbit effects and exchange interactions. They have shown that for the  ${}^6A_{1g} \rightarrow {}^4T_{1g}(\text{II})$  transition, the J.T. distortion is very small and that the splitting of the  ${}^4T_{2g}(\text{II})$  levels arises from the spin-orbit interaction. In  $\text{MnBr}_2$ , the splitting of the levels gives equally spaced peaks ( $33 \text{ cm}^{-1}$ ) and it could be concluded that a strong J.T. distortion quenches the orbital momentum and that the exchange field makes the largest contribution to the splitting of the orbital triplet. However, this splitting should decrease to zero when the sample, in the antiferromagnetic phase, reaches the Néel temperature. This is not the case (Fig. 4), the same splitting being observed up to 80 K. The only effect of the magnetic ordering is seen to be a small decrease in the oscillator strength in going from the paramagnetic to the antiferromagnetic phase.

The observed splitting might also be explainable in terms of a slight  $C_{3v}$  distortion of the crystal field as in  $\text{FeCl}_2$  [14]. Such a distortion should give rise to strong dichroic effects as observed in  $\text{MnF}_2$  [15] or other trigonally distorted manganese salts [16]. However, such dichroism was not observable in a  $\text{MnBr}_2$  sample which had its  $c$ -axis alligned at  $45^\circ$  to the direction of the incident light.

The most satisfactory explanation of the observed behaviour can be given by assuming the full quenching of the orbital momentum of this level by a Jahn-Teller distortion which results in a single pure dipolar magnetic zero phonon line. In this picture, the splitting of the quartet comes from a very low frequency even phonon which couples with a magnon (or the spin disorder) to give the  $a, b, c, d$  optical spectrum. The assumption is in good agreement with the fact that the  $(a_1, b_1, c_1, d_1)$  quartet shifts to higher energy by about  $4 \text{ \AA}$  ( $\approx 30 \text{ cm}^{-1}$ ) when the temperature goes down from 4.18 K to 1.7 K. This fact suggests that all these lines are combinations of a very low frequency phonon, a magnon and normal phonons. Such a phonon will not likely exist at  $k = 0$  in crystals with this structure : it has not been observed by Raman scattering or infrared absorption on crystals of the same structure [17]. A bimolecular unit cell would allow such low frequency vibrations and such a mode has probably been observed by Raman spectroscopy in  $\text{MoS}_2$  which could correspond to vibrations between rigid layers [18]; but there is no evidence of such a cell in  $\text{MnBr}_2$ . However, an acoustic mode of the zone boundary will have even symmetry and could have a frequency of  $33 \text{ cm}^{-1}$ . A very low frequency phonon has been observed in  $\text{CdCl}_2 : \text{CO}^{2+}$  which could come from such vibrations [19]. Then, even if the origins of such low frequency phonons have not been satisfactorily resolved, they have been observed in similar materials. Unfortunately, the assumption of the combination of such a phonon with a magnon to explain the first quartet is in disagreement with the observed relative intensities of these four peaks

which should decrease according to the well known law in the low temperature range [20] :

$$I = (e^{-s} S^n / n !)$$

$n = 1, 2, 3, 4$  respectively for  $a_1, b_1, c_1, d_1$ . Furthermore, the intensity ratio between the  $b_1$  and  $c_1$  lines changes above and below  $T_N$ .

In view of the above discussion it seems that no entirely satisfactory explanation is presently available for the fine structure of the  ${}^6A_{1g} \rightarrow {}^4T_{2g}(\text{II})$  absorption in  $\text{MnBr}_2$ .

**2.2 CIRCULAR DICHROISM OF THE  ${}^6A_{1g} \rightarrow {}^4E_g(4D)$  TRANSITION.** — As in the case of  $\text{MnCl}_2$ , two kinds of experiments have been performed using the techniques of circular dichroism. In the first, the sample has its  $c$ -axis parallel to the magnetic field, and in the second, the  $c$ -axis is at  $45^\circ$  to the magnetic field in order to establish a monodomain in the crystal. On the basis of these measurements it has been possible to conclude that two magnetic phases exist in  $\text{MnBr}_2$  which have characteristics that are similar to those observed for  $\text{MnCl}_2$ .

**2.2.1 Circular dichroism with the magnetic field along the  $c$ -axis.** — The  $A_1$  and  $A_2$  peaks are better resolved in  $\text{MnBr}_2$  than they are in  $\text{MnCl}_2$ , consequently linear and circular dichroism measurements are more easily performed on this material. Figure 5 shows the circular dichroism of the  $A_1$  peak as a function of temperature for several applied magnetic fields. These curves have the same form as those obtained for  $\text{MnCl}_2$ . As discussed in the previous paper, the magnetic circular dichroism (MCD) gives a direct measure of the magnetization and, for a given field, of the transverse susceptibility. A low temperature phase of constant susceptibility is seen to exist below 2 K and in this phase the MCD is proportional to the product of the normal susceptibility and the applied field. This low temperature phase is fully ordered with the spins lying in the  $c$ -plane. Between 2.2 and 2.0 K the MCD of the  $A_1$  peak behaves in the same manner as the corresponding peak in  $\text{MnCl}_2$ ,

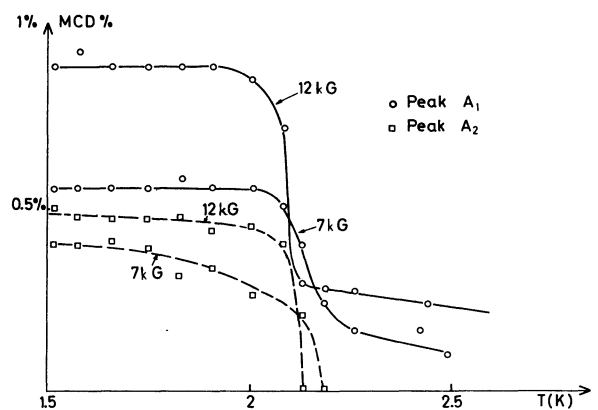


FIG. 5. — The magnetic circular dichroism of the  $A_1$  and  $A_2$  peaks versus temperature. The applied magnetic field is parallel to the  $c$ -axis.

a probable indication of the existence of another phase in  $\text{MnBr}_2$  that is similar to phase I in  $\text{MnCl}_2$  [6]. Experiments with the magnetic field at  $45^\circ$  to the  $c$ -axis confirm this hypothesis.

The MCD signal of the  $A_2$  peak is particularly interesting since it goes abruptly to zero with increasing temperature (Fig. 5). As discussed later, this behaviour is related to the transition from a fully ordered magnetic phase II to an intermediate phase I. This fact has been used to measure the magnetic phase diagram of  $\text{MnBr}_2$  as shown in figure 6 where the curve represents the boundary between phase II and phase I in the  $H$ - $T$  plane with the applied magnetic field parallel to the crystalline  $c$ -axis.

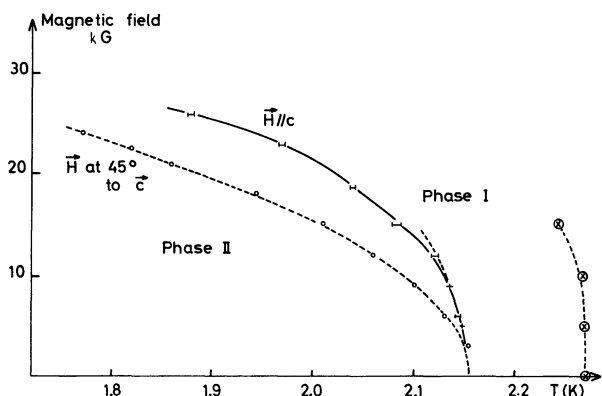


FIG. 6. — The magnetic phase diagram of  $\text{MnBr}_2$  determined optically (+ indicate neutron measurements of Wollan *et al.* [1] with the applied field parallel to the  $c$ -axis).

**2.2.2 Circular dichroism with the magnetic field at  $45^\circ$  to the  $c$ -axis.** — As shown above, changes in the optical absorption near certain critical temperatures gives a strong indication of the existence of two magnetic phases in  $\text{MnBr}_2$ , one stable below 2.15 K and the other below 2.30 K. Experiments in this new geometry confirm this assignment. In this configuration the MCD signal always corresponds to a zeroth moment change of the  $A_1$  and  $A_2$  lines, but, as is shown in figure 5 the  $A_2$  signal goes to zero when the crystal goes from phase II to phase I at a temperature  $T_2$ . It has been carefully verified that the MCD signals corresponding to the  $A_1$  and  $A_2$  peaks are proportional to their optical absorption and that the decrease of  $A_2$  at temperature  $T_2$  is proportional to the increase of  $A_1$  at that temperature. This result indicates that the oscillator strength of the  $A_2$  line is given to the  $A_1$  line when the temperature of the sample increases through  $T_2$ .

In figure 7 the MCD of the  $A_1$  line is plotted as a function of temperature for an applied field of 5 kG. The signal exhibits two strong changes in slope, one at  $T_1$  and the second at  $T_2$ . The change at  $T_1$  is a good indication of a previously unreported phase transition. Using this change in slope of the MCD signal of the  $A_1$  peak a function of temperature,

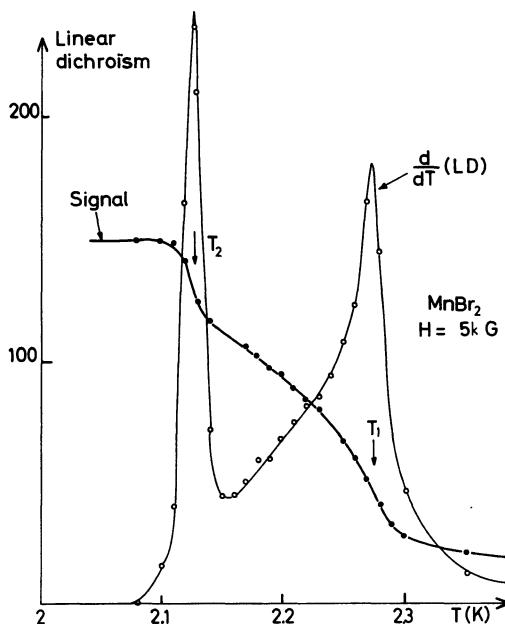


FIG. 7. — Linear dichroism of the  $A_1$  peak and its derivative versus temperature with the applied field and the direction of light propagation at  $45^\circ$  of the  $c$ -axis.

$T_1(H)$  was determined and is shown in figure 6 as a dotted line.

In figure 8 the MCD signal of the  $A_2$  peak as a function of temperature is shown for different applied fields. If the point at which this signal starts to go to zero is taken to indicate a phase transition, the phase diagram of  $\text{MnBr}_2$  as a function of field can be obtained. This is shown as a dotted line in figure 6 and it is clear that the  $T_2(H)$  curve is different for the applied field either parallel or at  $45^\circ$  to the  $c$ -axis.

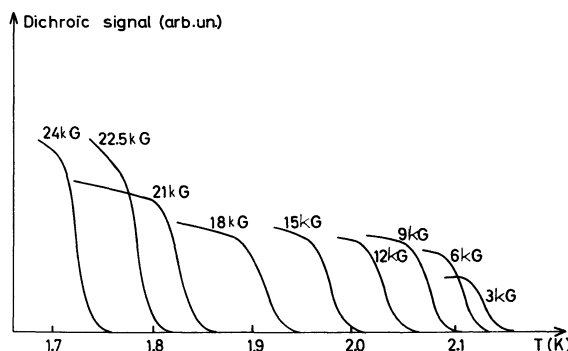


FIG. 8. — Variation of the linear dichroism of the  $A_2$  peak versus temperature with the same geometry as figure 7.

i) *The linear nature of the observed dichroism.* — As indicated in the discussion of the  $\text{MnCl}_2$  data in the previous paper, circular dichroism experiments are always difficult on a birefringent crystal which can transform circularly polarized light into light of linear polarization and *vice versa*. In the  $45^\circ$  geometry  $\text{MnBr}_2$  is indeed birefringent and it was necessary to decide if the observed behaviour came from linear or circular dichroic behaviour. In order

to separate the two effects a quarter wave plate was placed in the light beam after the elasto-optic modulator and before the sample. This plate changes a circularly polarized signal into a linear one and, by rotating the plate, it was possible to analyze the linear dichroism and the angular distribution of this dichroism. The measured signal as a function of the orientation of the quarter wave plate is shown in figure 9 for the  $A_1$  and  $A_2$  lines. From this curve it can be concluded that the signal is linearly dichroic as there should be no angular dependence of circular dichroism. As shown by Wollan *et al.* [1] the magnetic field induces a monodomain in  $MnBr_2$  in one of three equivalent orientations. In this particular experiment, the orientation of the domain is clearly at  $80^\circ$  to the horizontal.

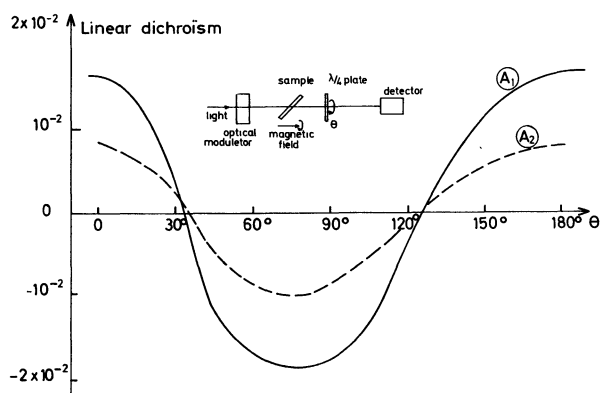


FIG. 9. — Analysis of the linear dichroism induced by the  $A_1$  and  $A_2$  peaks : in this experiment a quarter wave plate is inserted between the sample and the detector and can rotate by the angle  $\theta$  around the direction of the light and the magnetic field.

This domain effect can also be seen in figure 10 where the dichroic signal of the  $A_1$  peak is plotted versus magnetic field at 1.76 K. A field of 3 kG induced

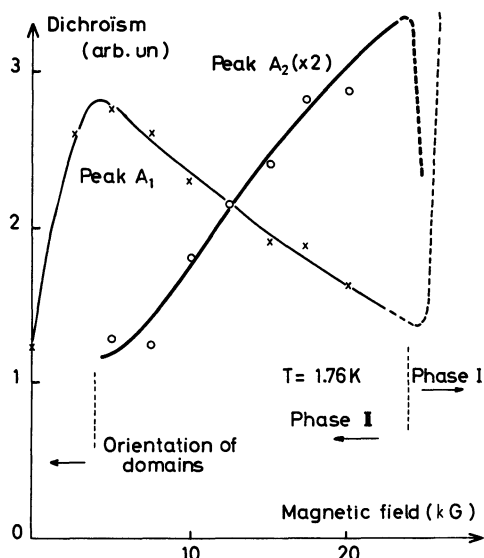


FIG. 10. — Variation of the dichroism in the phase II versus magnetic field when a monodomain has been formed, this dichroism is proportional to the absorption.

a monodomain in the sample and the  $A_1$  signal increased strongly. The zero field signal shown in this figure is not zero since the individual randomly oriented domains are large enough to avoid complete compensation. This could be demonstrated by varying the size of the light beam on the sample which resulted in a change in both the magnitude and the sign of the zero field signal.

The proportionality of the dichroic signal to the absorption coefficient of the peak and the angular distribution of this signal, which is directly related to the presence of domains, indicates that the observed signal is due to linear dichroism. Similar behaviour is exhibited by  $MnCl_2$  in the same geometry. As discussed in the previous paper, the linear dichroism could come from two effects : either from magnetostriction, which always occurs during magnetic ordering, or from the Cotton-Mouton effect which should occur because the spins are in the  $c$ -plane at  $45^\circ$  to the magnetic field. In the first case, the dichroic signal, normalized by the intensity of the transition, should be proportional to the magnetic energy [21, 22]. In the second case, the same quantity is proportional to the square of the local field [22, 23]. The fact that the dichroic signal is proportional to the oscillator strength of the transition strongly favors the first mechanism. In this case the dichroic signal is proportional to the product of the local distortion and the oscillator strength of the transition. The dichroism therefore provides a measure of the magnetic energy and consequently of the specific heat.

ii) *The specific heat of  $MnBr_2$ .* — The derivative of the dichroic signal as a function of temperature is plotted in figure 7. Two well defined peaks are exhibited which indicate the existence of two phase transitions in  $MnBr_2$ . These phase transitions are similar to those in  $MnCl_2$  but are more clearly resolved. The data indicates that short range order remains above  $T_1$ , as is also the case for  $MnCl_2$ , however the entropy tends to zero above 2.5 K. Specific heat measurements of  $MnBr_2$  have been performed by Stout [24] : he has not observed the two peaks that we measured with our optical technics. From his results, it seems, in fact, that the temperature resolution in his experiments was not good enough to resolve the two peaks.

iii) *The critical behaviour of the  $A_2$  line.* — The proportionality between the absorption of the  $A_2$  line and its dichroic signal allowed a more detailed study of this line to be made. At  $T_2$  the line goes rapidly to zero and it is possible to measure a critical exponent,  $x$ , from the relationship

$$A_2 \propto \left( \frac{T_c - T}{T_c} \right)^x.$$

This  $x$  was determined to be about 2 : however we cannot present here a physical signification of this critical exponent.

**3. Discussion.** — 3.1 MAGNETIC ORDERING. —  $\text{MnBr}_2$  has been found to exhibit two magnetic phase transitions similar to those reported in the previous paper on  $\text{MnCl}_2$  [6]. Wollan *et al.* [1] have previously detected only one of these transitions in their neutron scattering experiments. In zero field these transitions occur at 2.3 and 2.15 K. In the ordered phase magnetic domains were easily observed and magnetostriction induces linear dichroism in the optical transitions. The linear dichroism is proportional to the magnetic energy and was used in optical measurements of the specific heat which showed two sharp peaks at the phase transitions. These were more pronounced than the corresponding peaks in  $\text{MnCl}_2$ .

The difference in the phase diagrams obtained with the magnetic field along the  $c$ -axis or at an angle of  $45^\circ$  to this axis is also in good agreement with a model in which the spins are in the  $c$ -plane. On the basis of the magnetic phase diagram for these two orientations it could be assumed that the transition to phase II involves a spin-flop. This is, however, in disagreement with the experimental results since in a spin-flop transition at a given temperature, the magnetization increases with magnetic field and saturates when the paramagnetic phase is reached. Furthermore, short range order remains important in a spin-flop transition and the optical specific heat data indicates that this is not the case here.

The very sharp decrease of the  $A_2$  line at  $T_2$  strongly suggests that a change in the magnetic structure occurs between phases I and II. In such a change the first magnon Brillouin Zone changes, as does the magnon density of states. This point is discussed further below. However, even if the magnetic structure is different between phases I and II, phase I is not exhibiting the properties of a normal antiferromagnetic phase. It is therefore probable that phase I is not a fully ordered phase in  $\text{MnBr}_2$ , as it is in  $\text{MnCl}_2$ .

The strong similarity with  $\text{MnCl}_2$  could indicate that the magnetic structures are the same. In the previous paper, we assumed for  $\text{MnCl}_2$  that phase II is certainly an ordered phase and phase I a partly disordered phase. The same assumption applies for  $\text{MnBr}_2$  where the same behaviour has been observed. More precisely, the sharpness of the specific heat peak at 2.15 K is an indication of a first order phase transition when the width of the second peak between 2.2 K and 2.3 K is an indication of an higher order phase transition. Wollan *et al.* [1, 2] had observed a different magnetic structure for  $\text{MnCl}_2$  and  $\text{MnBr}_2$ ; the identical behaviour of these two salts in our experiments indicates that errors could have been made in the neutron scattering experiments. Further neutron diffraction experiments are desirable to resolve their structure.

**3.2 THE NATURE OF THE  $A_1$  AND  $A_2$  PEAKS.** — Experimental results on these two peaks are the following :

i) the energy difference  $\Delta E$  between the two peaks

is  $42 \text{ cm}^{-1}$  at low temperature and decreases to  $30 \text{ cm}^{-1}$  at the Néel temperature in zero field ;

ii)  $\Delta E$  decreases quadratically with an applied magnetic field ;

iii) the peak  $A_2$  exists only in phase II ;

iiii) the total oscillator strength is constant.

There are two possibilities to explain the behaviour of the  $A_1$  and  $A_2$  peaks. In the first one, the  ${}^4E_g$  level remains degenerate and the two peaks are magnon sidebands, the  $A_1$  peak corresponding to a very low energy maximum in the magnon density of states and the  $A_2$  peak to a maximum at the zone boundary. With this interpretation, the decrease of  $\Delta E$  with temperature corresponds to the renormalization of magnons ; effectively the change of  $\Delta E$  with temperature is the same as the thermal shift of the  $3880 \text{ \AA}$  band which is indeed coming from renormalization of magnons. With this model, one can analyze the disappearance of the  $A_2$  peak as follows : Sell, Greene and White [10] have shown that, in an exciton magnon transition, the selection rules are such that only magnons of given symmetry can appear with a given energy of the magnon and a given symmetry of the initial and final electronic states. If the magnetic cell is changed, the energy and the symmetry of magnons at the zone boundary will also change and, a maximum in the magnon density of states can disappear, or its new symmetry can be such that it cannot couple to a given excitonic transition ; such a process can occur during the transition from phase I to phase II.

In the second mechanism, the  ${}^4E_g$  level is split by second-order spin-orbit interaction and the two peaks are magnon sidebands corresponding to two purely excitonic transitions. As we said previously, such a splitting has been observed in  $\text{MnF}_2$  and  $\text{K}_2\text{MnF}_4$  [13]. As in the previous model, a change in the symmetry of the magnetic cell between phase I and phase II can explain the disappearance of  $A_2$  peak in phase I. However, with this model, it is more difficult to understand the thermal behaviour of the shift  $\Delta E$  between the two peaks.

To choose between these two possibilities, it is evident that new neutron scattering experiments are needed.

**4. Conclusions.** — Optical experiments have been used to show the existence of two magnetic phases in  $\text{MnBr}_2$ . The magnetic phase diagram has been determined and is found to be very similar to that of  $\text{MnCl}_2$ . The low temperature magnetic phase is certainly fully ordered and the intermediate phase is either an ordered phase with a different magnetic unit cell or a partially disordered phase. The experimental data suggests that most probably both of these factors are operative at the same time. As in  $\text{MnCl}_2$ , magnetostriction occurs in  $\text{MnBr}_2$  and this induces a linear dichroism in the  ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$  transition that is proportional to the magnetic energy.



This fact has been used to study the magnetic contribution to the specific heat which is found to exhibit two sharp peaks at the transition temperatures between the magnetic phases at  $T_1$  and  $T_2$ .

It is difficult to obtain more information about the magnetic structure from these optical experiments and new neutron scattering measurements are desirable to give the magnetic structure of the observed phases and the magnon density of states. It would

also be of interest to perform X-ray scattering experiments to look for substructures, related to lattice distortions associated with the different phases, which cancel the equivalence between the  $Mn^{2+}$  ions in this salt.

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