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MAGNETIC PHASE DIAGRAM OF $MnBr_2 4H_2O$

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ABSTRACT

The magnetic phase diagram of the monoclinic antiferromagnet $MnBr_2 4H_2O$ (obtained from differential magnetization measurements) is presented for temperatures down to $T=0.3$ K, and for applied magnetic fields parallel to the crystallographic axes $\underline{a}'$, $\underline{b}$ and $\underline{c}$. For $H \| \underline{c}$ an unusual behavior is observed below $T \sim 0.55$ K where the antiferro-paramagnetic boundary apparently splits into three others. It is shown that our critical fields extrapolated to $T=0$ are consistent with a recent theory proposed by Becerra and Ferreira.

MAGNETIC PHASE DIAGRAM OF $MnBr_24H_2O$

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RESUMÉ

On présente le diagrame de phase magnetique de l'antiferromagnet monoclinic $MnBr_24H_2O$ (obtenu a partir de mésures de suceptibilité magnetique) entre $T = 0.3$ K et T_N, et pour un champ magnetique appliqué au long des axes cristalografiques $\underline{a}'$, $\underline{b}$ et $\underline{c}$. Pour $H \| \underline{c}$, on observe un comportement anormale au dessous de $T \sim 0.55$K, où, la frontiére de phase antiferro-paramagnetique se separe en trois autres. On montre que les champs crítiques extrapolés a $T = 0$ sont consistant avec la théorie qui a eté proposé par Becerra et Ferreira.

MAGNETIC PHASE DIAGRAM OF $MnBr_2 4H_2O$

The $MnBr_2 4H_2O$ is a monoclinic salt which orders antiferromagnetically at $T_N = 2.13$ K. It shows spin-flop transition only for temperatures below 0.57 K ($0.27\ T_N$) (1) and this fact contrasts with the properties of the two structurally and magnetically isomorphous salts $MnC\ell_2 4H_2O$ and $NiC\ell_2 4H_2O$, in which the spin-flop phase is already observed at $0.80\ T_N$ (2) and $0.73\ T_N$ (3) respectively. The spin-flop field is related to the anisotropy interaction which seems to be considerably higher in this salt than in its two isomorphs. To further investigate this point, we have examined the magnetic field dependence of the differential magnetization (dM/dH) of single crystals of $MnBr_2 4H_2O$, and thereby determined its magnetic phase diagram, down to 0.3 K.

The dM/dH was measured by a Hartshorn-type bridge operating at 155 H_z. An external magnetic field (H), parallel to the modulating field, was provided by a superconducting solenoid capable of producing up to 75 kOe. The single crystals, of about 100 to 200 mg, were grown from aqueous solution. Once out of the solution, they were readily coated with silicone grease and cooled down because of their hygroscopicity. To orient them, suitable supports were provided for the crystal faces in the sample rod. The accuracy of this procedure was estimated to be better than 5^o , and the repeatability of the data taken with different samples, always inside the experimental error (better than 2% in the critical fields), corroborates that.

It has been suggested that the easy-axis of $MnBr_2 4H_2O$ lies in the $\underline{a}$-$\underline{c}$ plane between the $\underline{c}$ and $\underline{c}'$ axes which make an angle of about 10° (c' being the axis perpendicular to a and b) (4,5). We have made measurements with H parallel to c, c' and an intermediate direction, obtaining always essentially the same results, thus making it impossible to distinguish the easy-axis from our data. We have also made measurements with H parallel to b and a' (axis perpendicular to b and c). Fig. 1 shows traces of dM/dH versus H at several temperatures for H parallel to c and b. For $H\|c$, a single peak marks the transition from the antiferromagnetic (AF) to the paramagnetic (P) phase, from T_N down to ∿ 0.55 K. Below ∿ 0.55 K this single peak splits into three others, the separation being quite evident at the lowest temperatures measured. Several runs were made with different single crystals, sweeping the field up and down at very different rates, always with consistent results. For $H\|b$ (and similaly for a') just one peak is observed at all temperatures, marking the transition to the P phase. Fig. 2 shows the phase-boundaries thus determined. As expected, the phase diagram shows a high anisotropy, however, the splitting of the AF-P boundary for $H\|c$ below 0.55 K (detail of fig. 2) into three others is surprising.

The properties of $MnC\ell_2 4H_2O$ and $MnBr_2 4H_2O$ have been interpreted by Gijsman *et al* (2) in terms of the following Spin-Hamiltonian:

$$\mathcal{H} = A_x S_x^{(1)} S_x^{(2)} + A_y S_y^{(1)} S_y^{(2)} - \frac{1}{2} D_x \left(S_x^{(1)} S_x^{(1)} + S_x^{(2)} S_x^{(2)}\right) -$$

$$- \frac{1}{2} D_y \left(S_y^{(1)} S_y^{(1)} + S_y^{(2)} S_y^{(2)}\right) - g\mu_B H \cdot \left(S^{(1)} + S^{(2)}\right) + \text{terms in } z \qquad (1)$$

where the superscripts indicate the sublattice, D_x and D_y are the intrasublattice exchange parameters, and the other symbols have their usual meaning. Choosing x as the preferred axis for antiferromagnetic order implies: $A_x + D_x > A_y + D_y$ and $A_x > 0$. The z-axis is the hardest so that a spin-flop phase (SF) must occur in the x-y plane.

The $H \| \underline{c}$ boundaries below 0.55 K suggest the presence of an "intermediate" phase between the AF and SF. It has been shown by several authors that when $D_x - D_y < 0$, an "intermediate" phase, with the sublattice magnetizations forming two different angles with H, can be stable (6-8). The above inequality, however, implies that the T = 0 transition to the P phase for $H \| x$ ($\underline{c}$ in fig. 2) occur at a critical field bigger than for $H \| y$ ($\underline{b}$ in fig. 2), since they are respectively given by $(S/g\mu_B)(A_x + A_y - D_x + D_y)$ and $(S/g\mu_B)(A_x + A_y + D_x - D_y)$. This is not the case in fig. 2.

Another possibility has been pointed out recently by Becerra and Ferreira (9). They have shown that assuming just an intrasublattice antiferromagnetic interaction $D_x < 0$, an instability of the antiferromagnetic order occurs at a critical field where H_{eff} acting on one sublattice vanishes, thus giving rise to a more complicated order which they called the Reduced Spin (RS) phase. This is not incompatible with our data and in fact it is possible to find a set of parameters of (1) that can explain the T = 0 transitions (reasonably extrapolated in fig. 2 for $H \| \underline{c}$) in terms of: - a AF followed by a RS, a SF and a P phases. Fig. 3 shows the calculated energies for such phases matching very well our data. The values used for the parameters are: $A_x = 1.00$; $A_y = 0.75$; $D_x = -0.11$ and $D_y = -0.63$ (in units of 10^{-16} erg). Of course these parameters were chosen to predict a T = 0 critical field for $H \| y$ (the cristallographic $\underline{b}$-axis) equal to 31 kOe in agreement with fig. 2.

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FIGURE CAPTIONS

Fig. 1 - (dM/dH) × H traces at constant temperatures, for $H\|\underline{c}$ and $H\|\underline{b}$.

Fig. 2 - Magnetic phase boundaries measured by a.c. susceptibility. Different symbols reffer also to different samples. The open triangles reffer to a needle shaped sample. The axis $\underline{a}'$ is perpendicular to the axes $\underline{b}$ and $\underline{c}$, and the (dM/dH) traces for $H\|\underline{a}'$, from which the present boundary was obtained, are similar to those for $H\|\underline{b}$.

Fig. 3 - Calculated energy versus field at $T = 0$ for $H\|\underline{c}$.

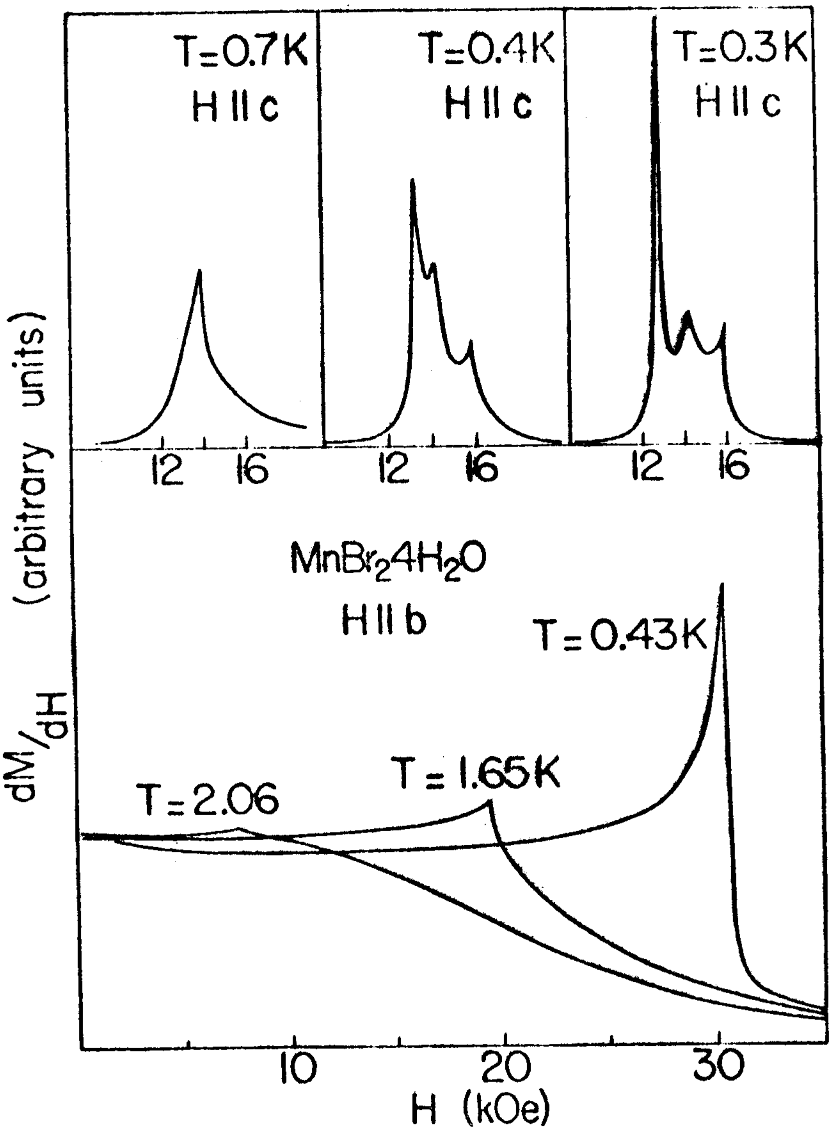
T=0.7K
H ll c
T=0.4K
H ll c
T=0.3K
H ll c
12
16
12
16
12
16
MnBr2 4H2O
H ll b
T=0.43K
T=1.65K
T=2.06
dM/dH (arbitrary units)
10
20
30
H (kOe)

FIG. 1

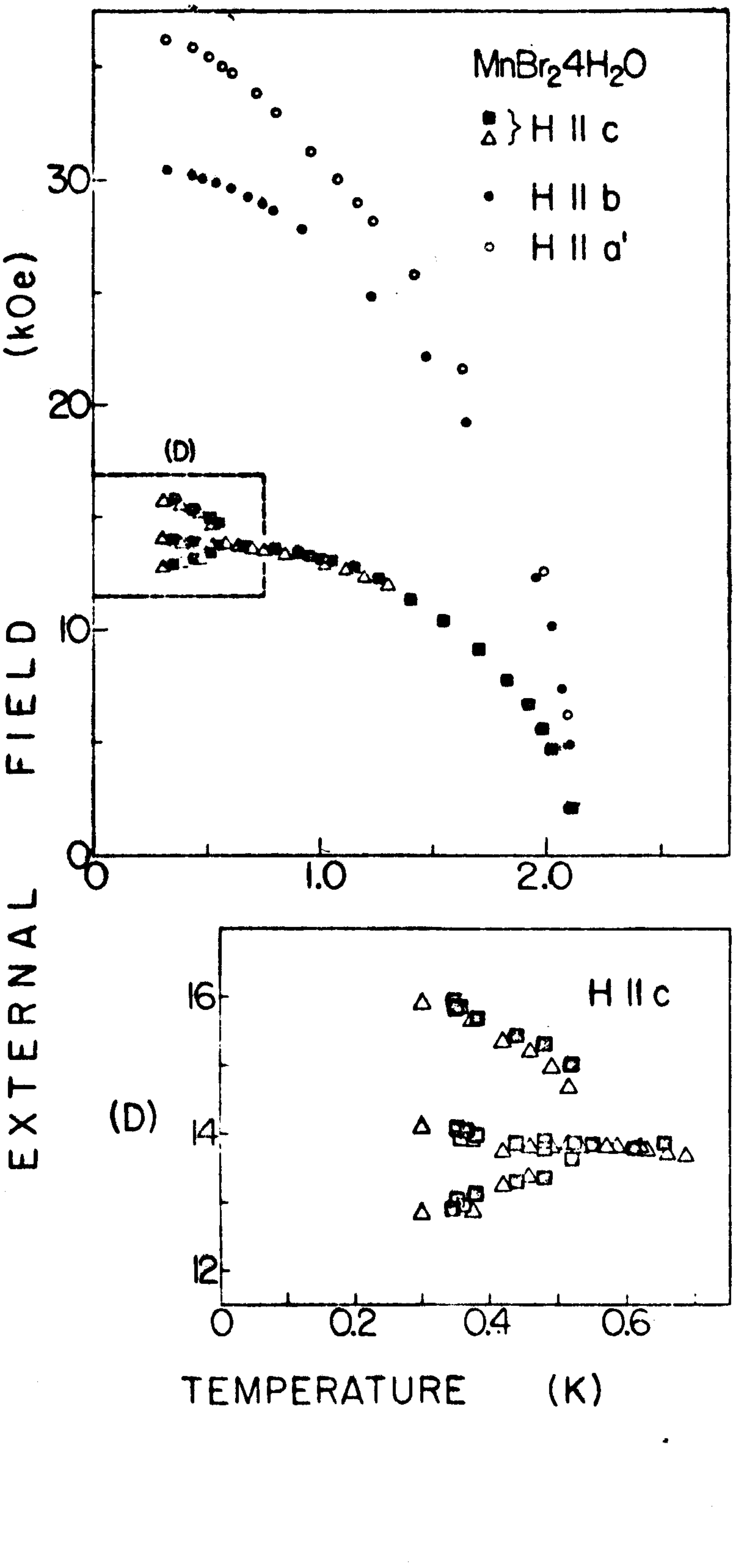
MnBr2 4H2O
■ △ } H ll c
● H ll b
○ H ll a'
(D)
EXTERNAL FIELD (kOe)
0
10
20
30
0
1.0
2.0
H ll c
(D)
12
14
16
0
0.2
0.4
0.6
TEMPERATURE (K)

FIG. 2

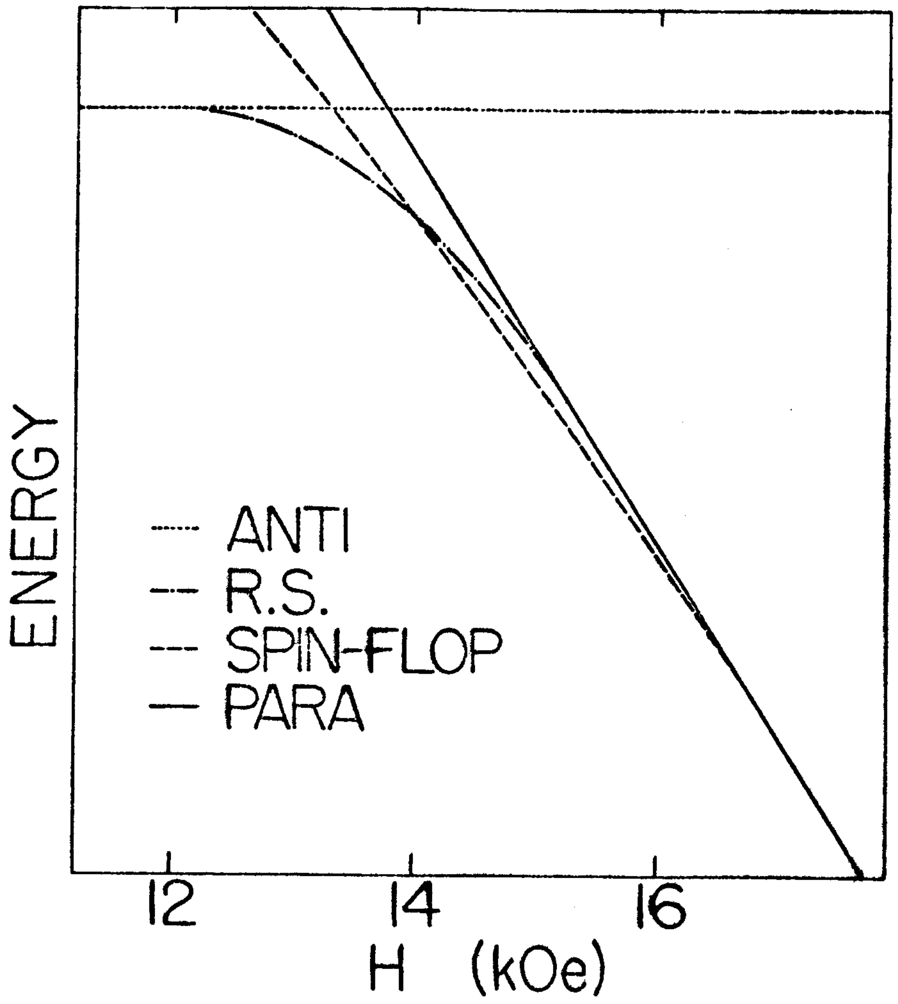

FIG. 3