

Pressure dependence of the Néel temperature of $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$

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From magnetization measurements at hydrostatic pressures up to $P \sim 10$ kbar, we have determined the pressure dependence of the Néel temperature T_N of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$. For $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ we found $dT_N/dP = +(0.029 \pm 0.003)$ K/kbar, while for $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$ we obtained $dT_N/dP = +(0.019 \pm 0.002)$ K/kbar. These results are comparable in magnitude to and have the same sign as dT_N/dP for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, as determined from a comparison of thermal-expansion and specific-heat measurements. For $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, however, a comparison of specific-heat and thermal-expansion singularities would suggest a *negative* sign for dT_N/dP . We suggest an explanation for this discrepancy in terms of the different magnetic interactions in these compounds.

I. INTRODUCTION

The antiferromagnets $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ($T_N = 1.62$ K) and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ ($T_N = 2.12$ K) have long been favorite objects of study^{1,2} due to their readily accessible Néel temperatures and the large moment of the Mn^{2+} ion ($S = \frac{5}{2}$). The chloride, a good example of a low-anisotropy antiferromagnet, has been extensively studied by many techniques and various attempts have been made to determine the exchange interactions in this material.³⁻⁷ The structurally isomorphic bromide possesses a much greater anisotropy and transitions to a spin-flop phase are observed^{6,8} only at temperatures below 0.57 K. A recent study of the mixed compounds⁹ $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$ has shown that both anisotropy and exchange interactions vary continuously with composition in these materials.

In the present work, we present measurements of the pressure dependence of the Néel temperature T_N of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$ for hydrostatic pressures up to $P \sim 10$ kbar. Taken by themselves, these results provide information about the volume dependence of the exchange interactions in these materials. In certain cases, it is also possible to obtain dT_N/dP from a comparison of specific-heat and thermal-expansion measurements.¹⁰⁻¹⁵ Thus, in the case of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, a comparison of high-resolution specific-heat¹⁶ and thermal-expansion^{17,18} measurements in terms of a simple thermodynamic relation furnished values of $d \ln T_N/dP$ which essentially agree in magnitude and sign with our direct measurements of this quantity for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$. However, a comparison of the specific-heat and thermal-expansion singularities in $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ would furnish a result in disagreement with the *sign* of our direct measurements. This

unexpected finding is discussed in terms of the magnetic interactions in these materials and may indicate certain limits on the usefulness of the simple thermodynamic relations between specific-heat and thermal-expansion coefficients.

II. EXPERIMENT

The single crystals used in these experiments were obtained by slow evaporation from an aqueous solution maintained at 10 °C. The starting solution for $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$ was prepared from controlled amounts of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Afterward a chemical analysis was performed which permitted a determination of the relative percentage of Br and Cl to better than 2%. The crystallographic axes were determined visually from the crystal habit.

Hydrostatic pressure was applied using binary beryllium-copper pressure cells, similar to those described by Guertin and Foner.¹⁹ The pressure-transmitting fluid was Dow-Corning 200 silicone oil with a viscosity of 30 000 centistokes at 25 °C. Separate measurements up to $P \sim 10$ kbar showed that the superconducting transition of the tin manometer was always narrower with the silicone oil than with the usual pressure transmitting fluid, 1:1 isoamyl alcohol and *n*-pentane. The pressure cell was attached to the drive rod of a Princeton Applied Research vibrating sample magnetometer,^{19,20} permitting measurements of the magnetization as a function of external field for a fixed temperature and pressure. Temperatures were measured using a capacitor obtained from Lakeshore Cryotronics Inc., which was, in turn, calibrated against the vapor pressure of ⁴He. Pumping on the helium bath, we were able to reach temperatures down to $T \sim 1.6$ K. This fact limited

our study of the $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$ to the Br-rich compositions.

III. RESULTS

In Fig. 1 we show curves, for a pressure $P = 9.3$ kbar, of the magnetization M vs external magnetic field H for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$. The external field was applied along the c' axis (perpendicular to the plane formed by the a and b axes). The various curves, which are displayed vertically for visual clarity, were obtained for temperatures in the vicinity of T_N . We notice a clear break in curves 1–5, corresponding to transitions from the antiferromagnetic to paramagnetic phases. The curves of Fig. 1 are very similar to those presented by Schmidt and Friedberg²¹ for this same material.

The transition fields, determined from curves such as those of Fig. 1, were then converted to internal fields (H_i) by applying a demagnetization correction, estimated from the data of Schmidt and Friedberg. In practice, this correction never amounted to more than 2% of the measured transition field and had a completely negligible effect on our determination of T_N .

In order to determine T_N for each pressure, the transition fields were extrapolated to $H = 0$. It has been shown experimentally²² that the antiferro-para phase boundary of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ may be represented near T_N by a parabola as $T_N(H) = T_N(0)(1 - \gamma H^2)$.

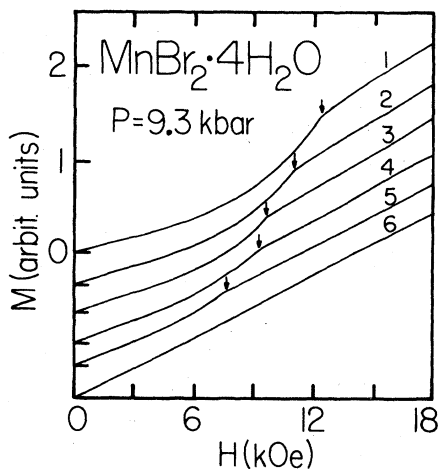


FIG. 1. Magnetization M vs applied field H for various temperatures (1: $T = 1.76$ K; 2: $T = 1.92$ K; 3: $T = 2.04$ K; 4: $T = 2.14$ K; 5: $T = 2.20$ K; 6: $T = 2.43$ K). The arrow marks the transition from antiferromagnetic to paramagnetic phases. The zeros of the curves have been displaced for visual clarity.

That the boundary should be nearly parabolic is consistent with molecular field treatments²³ as well as with the calculations of Bienenstock,²⁴ who considered several Ising models in large applied magnetic fields. In Fig. 2 we show H_i^2 (where H_i is the internal field) versus T for several values of the hydrostatic pressure. The parabolic relation evidently gives a good description of the phase boundary near T_N . The dashed lines of Fig. 2 are least-squares fits to the experimental points of the figure, and the extension of these dashed lines to $H_i = 0$ allows us to determine T_N for each pressure. For $P = 1$ atm we obtained $T_N = 2.12$ K, in good agreement with other workers.

The values of $T_N(P)$ so obtained for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ are shown in Fig. 3 along with data obtained in a similar manner for $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$. For both of these materials, T_N increases with pressure. The dashed lines of Fig. 3 represent least-squares fits to the points shown in the figure. For $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ we find $dT_N/dP = +(0.029 \pm 0.003)$ K/kbar, while for $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$ the result is $dT_N/dP = +(0.019 \pm 0.002)$ K/kbar. For $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, we calculate $d \ln T_N/dP = +(0.013 \pm 0.001)$ /kbar. Using our value $T_N(0) = 1.99$ K, in agreement with Ref. 9, we calculate $d \ln T_N/dP = +(0.010 \pm 0.001)$ /kbar for $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$.

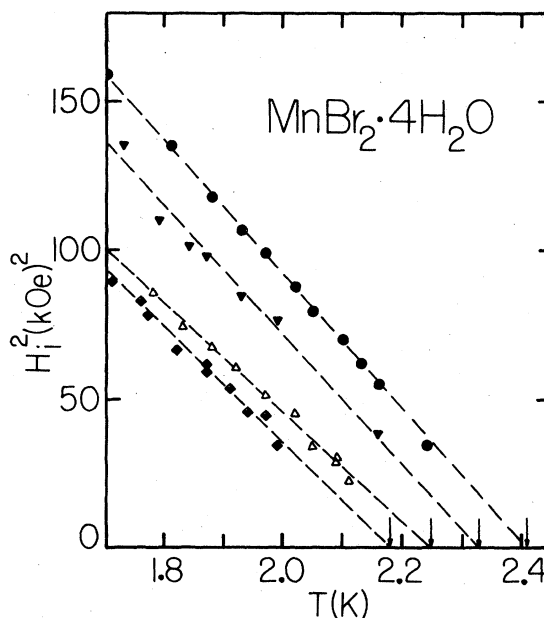


FIG. 2. Square of internal field H_i^2 vs temperature T for several pressures (\diamond : $P = 0.4$ kbar; Δ : $P = 4.7$ kbar; ∇ : $P = 6.9$ kbar; \bullet : $P = 9.3$ kbar). The dashed lines are least-squares fits to the points shown in the figure. The arrows mark $T_N(P)$.

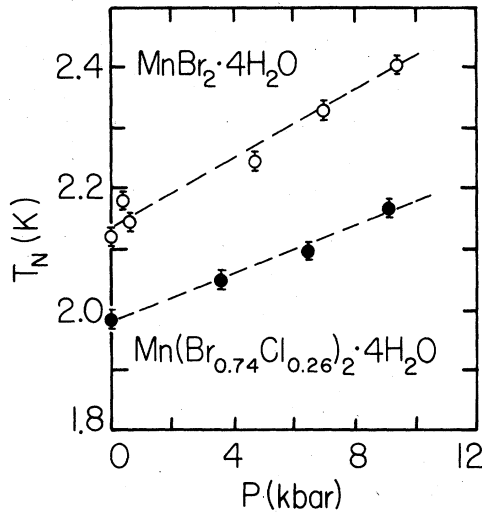


FIG. 3. Néel temperature T_N as a function of pressure P for the compounds studied. The dashed lines are least-squares fits to the data points.

IV. DISCUSSION

A. Exchange interactions in $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$

Before comparing our measurements of dT_N/dP with results obtained from thermal-expansion and specific-heat experiments, it is interesting to consider the magnetic interactions in terms of a phenomenological spin Hamiltonian. Due to the small departure of the monoclinic unit cell from orthorhombic symmetry, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ have frequently^{3,4,6,8} been treated in terms of a spin Hamiltonian of the type,

$$H = \sum_{i=x,y,z} \left[J_i S_i^x S_i^{x'} - \frac{K_i}{2} (S_i^x S_i^x + S_i^{x'} S_i^{x'}) - g \mu_B H_i (S_i^x + S_i^{x'}) \right]. \quad (1)$$

In this equation S_i^x and $S_i^{x'}$ are spin components for different sublattices, J_i represent interactions between spins on different sublattices, the K_i represent interactions between spins on the same sublattice, H_i are the components of the external magnetic field, and the g factor is isotropic for this S -state ion. According to the usual notation,^{3,4,6,8} the x axis is the easy magnetic axis, the y axis is intermediate and the z axis is magnetically hard. For these materials, the easy axis is approximately²⁵ parallel to the c' axis, the b axis is the intermediate axis, and the a axis is the hard axis.

$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ has been studied in terms of this Hamiltonian by various authors. The values of J_i and K_i obtained from their data are shown in Table I. We immediately note that the J_i are nearly an order of magnitude larger than the K_i , suggesting that next-nearest-neighbor interactions are relatively unimportant in this material. The case of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ has been studied by Becerra,^{6,8} and his results are also shown in Table I. Here we find that J_x is about 30% larger than J_y . However, K_y is quite comparable with both J_x and J_y , so that it would no longer be appropriate to dismiss interactions between spins on the same sublattice.

These results suggest that magnetic interactions are quite different in $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, in spite of their structural similarity. The magnetic phase diagrams of these compounds, from which many of these exchange parameters were derived, show these differences in a graphic way.

B. Comparison of thermal-expansion and specific-heat experiments

The theoretical relationship between the specific-heat and the thermal-expansion coefficient has been considered in terms of a microscopic theory by Callen and Callen,¹⁰ using statistical mechanics,^{11,12} and by means of thermodynamic treatments.¹³⁻¹⁵ A simple phenomenological model used by Argyle *et al.*¹⁵ for EuO furnished an approximate relationship between the specific heat at constant volume C_v and the volume thermal expansion coefficient

$\beta: \beta = (\gamma_m/BV)C_v$, where V is the volume, B is the isothermal bulk modulus of the composite (magnetic plus lattice) system, and $\gamma_m = -d \ln J / d \ln V$ is the magnetic Grüneisen parameter. Since $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ possess monoclinic symmetry, the thermal-expansion coefficients measured along three perpendicular axes will be different. Thus Philp *et al.*^{17,18} used the results of Janovec¹⁴ to relate the linear-expansion coefficients to the specific heat.

TABLE I. Exchange constants for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$. The J_i and K_i are defined by Eq. (1) and all values are given in units of 10^{-17} erg.

Material	Source	J_x	J_y	K_x	K_y	$J_z - K_z$
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	Ref. 3	9.0	8.5	0	-1.4	...
	Ref. 5	8.1	8.7	0.8	-1.6	10.6
	Ref. 6	8.0	8.0	1.0	-0.9	9.6
	Ref. 7	7.9	7.5	1.1	-0.6	9.3
$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$	Ref. 8	10.0	7.5	-1.1	-6.3	18.5

They found that the proportionality constant between the singular parts of the linear expansion coefficient α_i and the specific heat C_m gives the stress dependence of the Néel temperature.

Philp *et al.* measured the linear expansion coefficients along the a , b , and c' axes in both $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, making a careful determination of the singular part. In the case of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, these results were compared to the high-resolution specific-heat measurements of Dixon and Rives,¹⁶ allowing a determination of the stress dependence of the transition temperature. Combining results for the three mutually perpendicular axes, one obtains the pressure dependence of T_N . The values obtained by Philp *et al.* for both $T > T_N$ and $T < T_N$ are shown in Table II. We see that there is good agreement with our values of $d \ln T_N / dP$ obtained for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$. Dixon and Rives also compared their C_P data to the thermal-expansion measurements and obtained slightly different values for $d \ln J / dP$ (which we assume equal to $d \ln T_N / dP$) which are shown also in Table II.

In the case of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$, Philp *et al.* found all of the α_i to be *negative*. This result together with the necessarily positive specific-heat singularity, would suggest that the pressure coefficient of T_N is negative: $dT_N/dP < 0$. Our measurements show, in fact, that the opposite is true, that is, that $dT_N/dP > 0$. This suggests that the simple relation between the thermal-expansion coefficient and the specific heat must not be valid in the present case.

To understand the source of this problem we consider the microscopic theory of Callen and Callen.¹⁰ For cubic materials these authors obtained tensor relationships between the microscopic strains and three forms of the spin-correlation functions. Both the thermal-expansion coefficients and the specific heat are linear combinations of the same variables, the temperature derivatives of the spin correlation functions. We cannot apply the Callen and Callen theory

directly since it would require more information than is available for our materials. However, we may illustrate the qualitative predictions with the results of a model used by Argyle *et al.*¹⁵ for EuO . Considering a Heisenberg model with isotropic exchange interactions A_n between the n th neighbors, with A_n depending only on volume, these authors obtained

$$\beta = \left(\frac{N}{BV} \right) \left[z_1 A_1 \gamma_1 \left(\frac{\partial \langle \bar{S} \cdot \bar{S}' \rangle_1}{\partial T} \right)_V + z_2 A_2 \gamma_2 \left(\frac{\partial \langle \bar{S} \cdot \bar{S}' \rangle_2}{\partial T} \right)_V + \dots \right], \quad (2)$$

$$C_m = N \left[z_1 A_1 \left(\frac{\partial \langle \bar{S} \cdot \bar{S}' \rangle_1}{\partial T} \right)_V + z_2 A_2 \left(\frac{\partial \langle \bar{S} \cdot \bar{S}' \rangle_2}{\partial T} \right)_V + \dots \right]. \quad (3)$$

In these expressions z_n is the number of n th neighbors, γ_n are the magnetic Grüneisen constants for the A_n , and $\partial \langle \bar{S} \cdot \bar{S}' \rangle_n / \partial T$ are the temperature derivatives of the correlation functions between the n th neighbors. Assuming only A_1 and A_2 different from zero, we see that β and C_m will be proportional when the second terms of the right-hand sides of Eqs. (2) and (3) are negligible compared to the first terms. Alternatively, when $\partial \langle \bar{S} \cdot \bar{S}' \rangle_1 / \partial T$ and $\partial \langle \bar{S} \cdot \bar{S}' \rangle_2 / \partial T$ are proportional, then β and C_m will also be proportional. It is reasonable to assume that similar considerations are applicable to materials with lower symmetries and where the exchange interactions are anisotropic.

In the case under consideration, that of the $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$, the corresponding expression for the specific-heat and the thermal-expansion coefficients are more complicated due to the low symmetry of the lattice, involving in addition, other

TABLE II. Pressure dependence of T_N for $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$.

Material	Source	$d \ln T_N / dP$ ($10^{-3}/\text{kbar}$)	Comment
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	Ref. 18	11.5	$T < T_N$
		10.5	$T > T_N$
	Ref. 16	9.1	$T < T_N$
		9.2	$T > T_N$
$\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$	This work	10 ± 1	
$\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$	This work	13 ± 1	

correlation functions. However, our previous discussion of exchange interactions in these compounds allows us to make qualitative comments about the relationship between C_m and the α_i . We saw previously that, in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, the nearest-neighbor exchange interactions are nearly an order of magnitude larger than those between next-nearest neighbors. This suggests that it would be reasonable, in the expressions for the specific heat and the linear thermal-expansion coefficients, to neglect all terms other than those involving the J_i . If the resultant simplification is equivalent to that which occurs for cubic materials, we might expect to observe a proportionality between C_m and α_i which would furnish the stress dependence of T_N . This seems to be the case for $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ because the sign and magnitude of $d \ln T_N / dP$, determined indirectly, are in agreement with our values for $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{Br}_{0.74}\text{Cl}_{0.26})_2 \cdot 4\text{H}_2\text{O}$. On the other hand, it is clearly not possible to make such a simplification in the case of $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$ because K_y is comparable to J_y and J_x . Thus it is probably necessary to maintain in the expressions for the α_i and C_m terms involving nearest and next-nearest neighbors. If the correlation functions involved have different temperature dependences, this might explain why the forced proportionality between α_i and C_m does not, in this case, furnish the stress dependence of T_N . If this interpretation is correct, then the present results suggest that in general a certain caution must be exercised in comparing the specific-heat to thermal-expansion coefficients to obtain the stress

dependence of the Néel temperature.

Finally, we note that Westphal and Becerra⁹ studied the dependence of T_N on the relative concentration of Cl and Br in the compounds $\text{Mn}(\text{Br}_{1-x}\text{Cl}_x)_2 \cdot 4\text{H}_2\text{O}$. These authors observed a linear dependence of T_N on x , between the values 1.62 and 2.12 K of the chloride and bromide, respectively. The substitution of Cl in place of Br reduces the Mn-Mn separation and results in a decrease in the value of T_N . On the other hand, since dT_N/dP is positive here, it is evident that a reduction in the lattice parameter due to pressure does not cause the same changes as those associated with reducing the lattice parameter by changing the halogen. Thus any *a priori* prediction of the sign of dT_N/dP based solely on the distances between magnetic ions should be regarded with a certain reserve.

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