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Nature of the Antiferromagnetic-Paramagnetic Transition in $MnCl_2 \cdot 4H_2O$†

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The heat capacity and magnetization at constant field versus temperature, as well as the adiabatic variation of temperature with magnetic field, have been determined in fields directed along the c axis of a large spherical single crystal of $MnCl_2 \cdot 4H_2O$ to virtually the limits of resolution of the dc methods used. In this study of the behavior of these quantities in the neighborhood of the antiferromagnetic-paramagnetic transition, one specific goal was to observe the (near) singularity in $(\partial M/\partial T)_H$ at $T_N(H)$. In addition, we sought to test the predictions that isentropes cross the phase boundary (defined as the locus of maxima in C_H) tangentially, and that this crossing point should prove to be the point of inflection of the isentropes provided C_H does not diverge too strongly. A test for determining the existence of a divergence without the necessity of measuring infinitely high values is outlined. The fact that the maximum in the zero-field adiabatic susceptibility occurs at a temperature $T_{max} > T_N(0)$ has been found to be reflected in the persistence of a minimum in plots of the isentropic variation of T versus H up to $T = T_{max}$. This curious behavior has led us to speculate on a larger coexistence region of somewhat different character than has heretofore seemed reasonable.

The bulk magnetothermodynamic properties of antiferromagnetic substances have for some time been the subject of intensive study. It has been the practice of those performing these experiments to summarize the salient features of the resultant data in a graphical display known as the phase diagram in the H-T plane. For a uniaxial antiferromagnet of weak anisotropy with the field applied along this axis, the resultant diagram will be similar to that shown in Fig. 1. The letters a, p, and b will be used to denote the antiferromagnetic, paramagnetic, and spin-flopped regions. Unfortunately, the phase diagrams derived from different types of measured data are not always congruent.

The heat capacities of these materials typically exhibit λ-shape anomalies. In analogy with the work of Buckingham and Fairbank on He, [1] the maxima in these curves are usually taken as the Néel temperature $[T_N(H)]$. The available data on the in-field heat capacities of oriented single-crystal antiferromagnets are sparse,[2-5] but that available data agree well with the estimates of $T_N(H)$ derived from optical[6] and radio-frequency[7] spectroscopic measurements although more comment is also necessary even here. Large discrepancies appear, however, in attempts at correlations with magnetization data where the maxima in the observed M versus T isoersteds have been used as a measure of $T_N(H)$.

The antiferromagnetic-paramagnetic (ap) transition in antiferromagnets is often referred to as being of second order. Using the Ehrenfest criteria, this implies that the second derivatives of the Gibbs function with respect to its intensive variables are discontinuous. Thus we might expect the trio

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_H = C_H, \quad \left(\frac{\partial^2 G}{\partial H^2}\right)_T = \chi_T, \quad \left(\frac{\partial^2 G}{\partial H \partial T}\right) = \left(\frac{\partial M}{\partial T}\right)_H$$

to exhibit discontinuities if this scheme were applicable. Cooperative phenomena display, rather, a divergence of these Ehrenfest derivatives to hypothetically infinite values where the physical

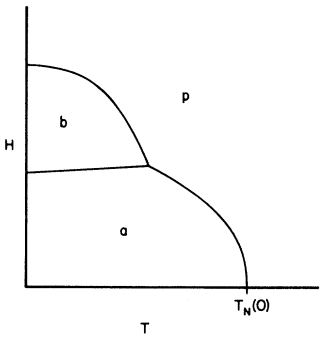

FIG. 1. Schematic phase diagram for a uniaxial antiferromagnet with field direction coincident with axis of maximum anisotropy.

meaning of a discontinuity is not clear. Experimental evidence that C_H exhibits the anomaly characteristic of the continuous phase transition is readily available. The singular nature of χ_T has been viewed in $CoCl_2 \cdot 6H_2O$ by Schmidt and Friedberg[8] and in $MnCl_2 \cdot 4H_2O$ by Rives[9]; however the divergence in $(\partial M/\partial T)_H$ has not been similarly appreciated. Fisher[10,11] has found this behavior in his two-dimensional superexchange model and also as a general characteristic of antiferromagnets. Schelleng and Friedberg[3] report a (near) singularity in the slope of the temperature-susceptibility curve at fields near zero in $MnBr_2 \cdot 4H_2O$, while Sawatzky and Bloom[12] have made similar inferences for $CoCl_2 \cdot 6H_2O$

SAMPLE PREPARATION

The growth of this sample has been described by Reichert and Giauque[2] and will not be presented here. The sample was machined into a 0.925-in.-diam sphere and then mounted in a special goniometer whereby the crystal axes were located by x-ray diffraction. The c crystal axis was marked by drilling 1-mm-diam × 5-mm-long holes in both sides of the crystal. The sample thus prepared was found to weigh 13.6118 g (0.068 780 moles). The sample holder consisted of two 1.125-in.-diam gold-plated copper hemispheres into which the sample was inserted under a He^4 atmosphere. The sample was supported and aligned by insertion of gold-plated copper pins and the entire assembly bonded with a 50% by weight mixture of Shell Epon 828 resin and Shell Versamide 140 hardener.

APPARATUS

The apparatus used in this study has been described elsewhere,[13] however, a few remarks are perhaps in order at this time.

The magnetization measurements were obtained by hand control of the pumping rate to maintain a constant sample thermometer resistance value. This was found to be superior to automatic control of the cooling chamber He vapor pressure by servo control of current to the sample heater. The manual control restricted the temperature deviation over a measurement to less than 50 μdeg while the automatic system fluctuated as much as 200 μdeg.

The heat-capacity data were obtained using a fully automatic measurement and data-acquisition system which allowed the thermometer circuit to be monitored continuously. The method was the standard dc potentiometric method with an integrating digital voltmeter replacing the potentiometer. The data thus obtained were automatically punched on cards and were later reduced by computer.

The same automatic data-acquisition system was used to obtain the temperature and magnetic field data upon adiabatic magnetization and demagnetization of the sample. This method resulted in a T-H definition which greatly exceeds any previously reported. This is shown in Table I which gives the data for series 21 of the adiabats. The adia-

TABLE I. Adiabatic demagnetization temperature as a function of applied magnetic field (series 21).

H (G)	T (°K)	H (G)	T (°K)	H (G)	T (°K)	H (G)	T (°K)
9982.7	2.093	7593.7	1.763	5142.8	1.618	2649.0	1.607
9824.0	2.075	7396.5	1.744	4966.7	1.615	2463.2	1.609
9642.6	2.044	7206.8	1.726	4773.3	1.611	2279.4	1.610
9459.4	2.014	7016.1	1.711	4579.8	1.609	2089.7	1.612
9284.7	1.984	6828.2	1.696	4389.0	1.607	1897.8	1.613
9139.5	1.959	6633.6	1.683	4197.1	1.605	1702.5	1.615
8951.5	1.933	6449.4	1.671	3999.3	1.604	1503.6	1.616
8760.7	1.905	6266.0	1.661	3799.4	1.604	1305.1	1.617
8568.8	1.878	6085.4	1.651	3596.7	1.604	1115.6	1.619
8381.3	1.853	5914.7	1.643	3398.9	1.604	939.7	1.620
8188.0	1.829	5722.4	1.637	3203.7	1.604	773.7	1.623
7992.3	1.806	5525.1	1.630	3015.8	1.605		
7793.9	1.784	5328.2	1.624	2833.7	1.606		

bats were spaced as closely as the heat leak (60 ergs/sec) would permit. No unexplained thermal losses were observed in the adiabats. Therefore, we shall use the terms adiabatic and isentropic interchangeably.

The carbon thermometer was calibrated against the vapor pressure of He^4 using the 1958 temperature scale.

Adiabatic data below 300 G have not been reported as the results were erratic in this region. The exact cause of this is as yet undetermined. However, superconducting solenoids are known to produce nonuniform field profiles at very low fields and this may be the source of the difficulty. Studies are now in progress to evaluate this possibility.

DISCUSSION

Given the shape of a typical trace of the adiabatic variation of temperature with magnetic field for fields directed along the axis of maximum anisotropy, it is apparent why the magnetization maximum was ever considered as a means of some sort of phase delineation. Reference to any of the lower curves of our data for the adiabatic demagnetization of $MnCl_2 \cdot 4H_2O$ which is given in Fig. 2 shows clearly that as the field is lowered, the temperature decreases approximately quadratically passing through a clearly rounded minimum and thence through a point of inflection so that zero field is approached with downward concavity. Given the fact that C_H possesses at least a near singularity and the magnetocaloric equation

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H ,$$

the assumption that magnetization, heat-capacity, and isentrope extrema all coincide seems most reasonable. In fact, if C_H max does not coincide with $(\partial M/\partial T)_H = 0$, the absence of another minimum in T versus H requires that $(\partial M/\partial T)_H$ must diverge near T_N in a manner similar to C_H.

The heat capacity (Fig. 3) and isoerstedic magnetization have been determined for a spherical single crystal of $MnCl_2 \cdot 4H_2O$ with applied magnetic fields of 3, 5, and 6 kG directed along the c crystallographic axis. A low-resolution plot of M versus T is presented in Fig. 4. The positions of the corresponding heat-capacity maxima are marked by arrows. The uncertainty in the position of the heat-capacity maxima is 2 m°K. Clearly in each case M increases with temperature above $T_{\max C_H}$.

We shall now examine the behavior of $(\partial M/\partial T)_H$ near $T_N(H)$. Applying the identity

$$\left(\frac{\partial W}{\partial X}\right)_Y = \left(\frac{\partial W}{\partial X}\right)_Z - \left(\frac{\partial W}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Z$$

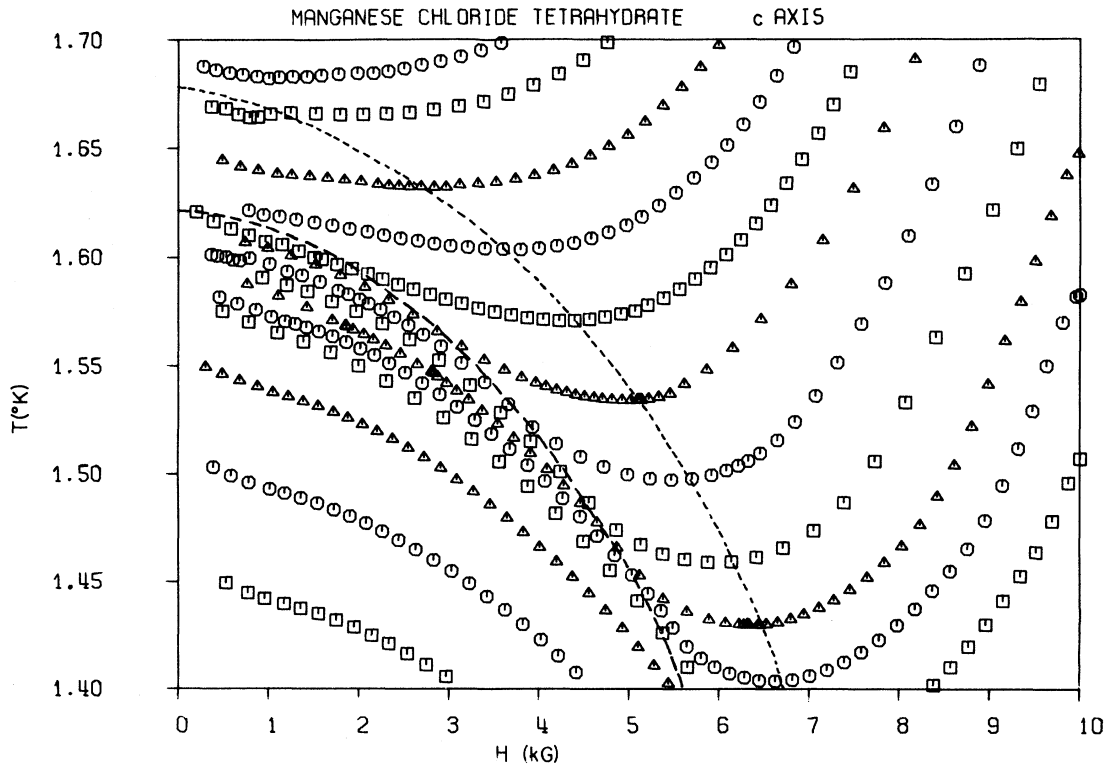

FIG. 2. Isentropic variation of temperature with the applied magnetic field parallel to c axis.

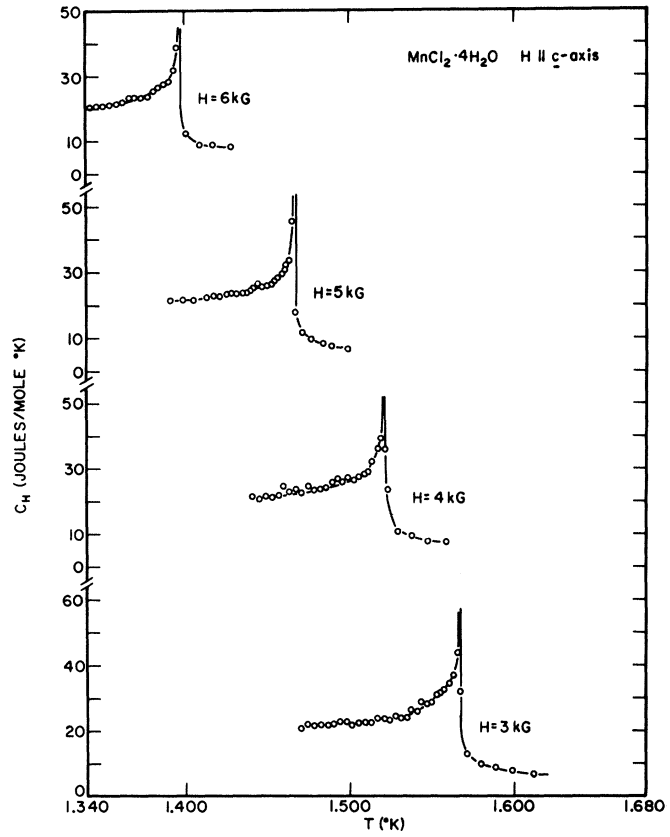

FIG. 3. Heat capacity versus temperature at constant applied magnetic field.

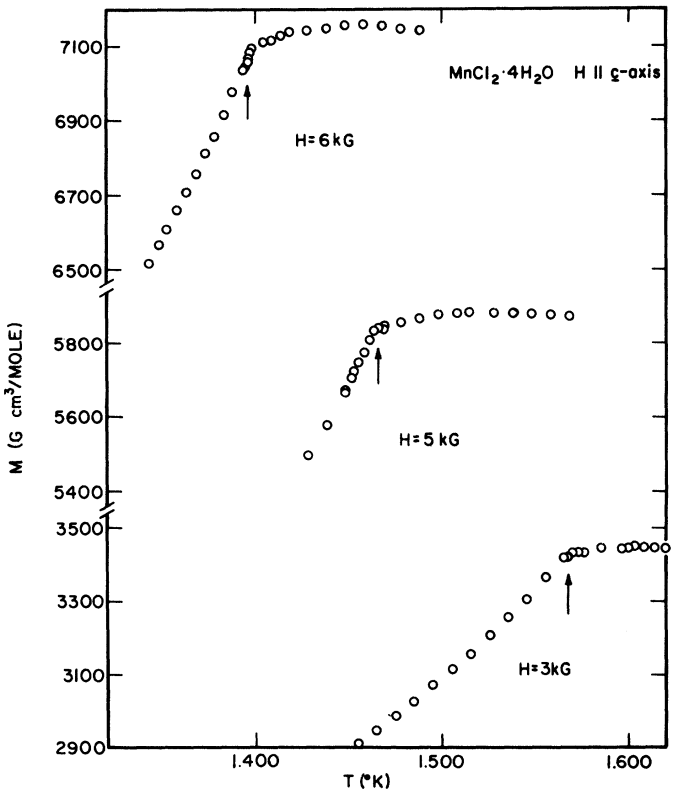

FIG. 4. Low-resolution magnetization versus temperature at constant applied magnetic field.

to S and incorporating the device of the neighborhood temperature,[1] $t = |T - T_N|$, we obtain

$$\left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial S}{\partial T}\right)_t - \left(\frac{\partial S}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_t .$$

However, $(\partial H/\partial T)_t$ is just the slope of a line parallel to the locus of C_H maxima, thus

$$\frac{C_H}{T} = \left(\frac{\partial S}{\partial T}\right)_t - \left(\frac{\partial M}{\partial T}\right)_H \left(\frac{dH}{dT_N}\right). \quad (1)$$

Buckingham and Fairbank[1] have shown the first term to vary slowly as $t \to 0$ for a broad class of systems so that at finite fields we may neglect this term for small t. Here it is clear that dH/dT_N is not infinite, as only for $H = 0$ does that possibility arise for most substances thus far investigated. It should be noted for future reference that Eq. (1) implies a linear relationship between C_H and $(\partial M/\partial T)_H$.

Sawatzky and Bloom[12] have shown that a similar relationship exists between the specific heat and $(\partial M/\partial H)_T$, namely,

$$\frac{C_H}{T} = \left(\frac{dH}{dT_N}\right)^2 \left(\frac{\partial M}{\partial H}\right)_T + \text{slowly varying terms}$$

and have verified this relationship, at least for $T < T_N$, using the heat capacity and the adiabatic susceptibility for $CoCl_2 \cdot 6H_2O$. Of course, the linear relationships demand that all three quantities C_H, $(\partial M/\partial T)_H$, and $(\partial M/\partial H)_T$ diverge with identical exponents.

Fisher[14] has obtained expressions for the variation of $\chi_\parallel(T)$ of the form $\chi_\parallel \propto t^{1-\alpha}$ for $H = 0$ in both two- and three-dimensional antiferromagnets. This would appear to conflict with the results of Sawatzky and Bloom.[10] Skalyo *et al.*[15] corroborate the Fisher relation in $CoCl_2 \cdot 6H_2O$ and, in addition, the zero-field functional form has been tested by Wolf and Wyatt[16] on DAG with quite good agreement both above and below $T_N(0)$. For a two-dimensional superexchange antiferromagnet, however, Fisher finds just the anticipated divergence in nonzero field $\chi_\parallel(H, T) \propto t^{-\alpha}$.

The abrupt behavior in $(\partial M/\partial T)_H$ has been observed for $MnCl_2 \cdot 4H_2O$ at 6000 G as a (near) discontinuity in M versus T. These data are presented in Fig. 5. The experiment is extremely difficult and only at this field were results of sufficient stability obtained. A direct measurement of $(\partial M/\partial T)_H$ is much to be preferred and preparations are under way for this determination using the standard moment measuring configuration and sampling the induced voltage of the bucked coil pair while the sample is heated at a constant rate.

Skalyo *et al.*[15] have given a theoretical argument stating that isentropes cross the phase

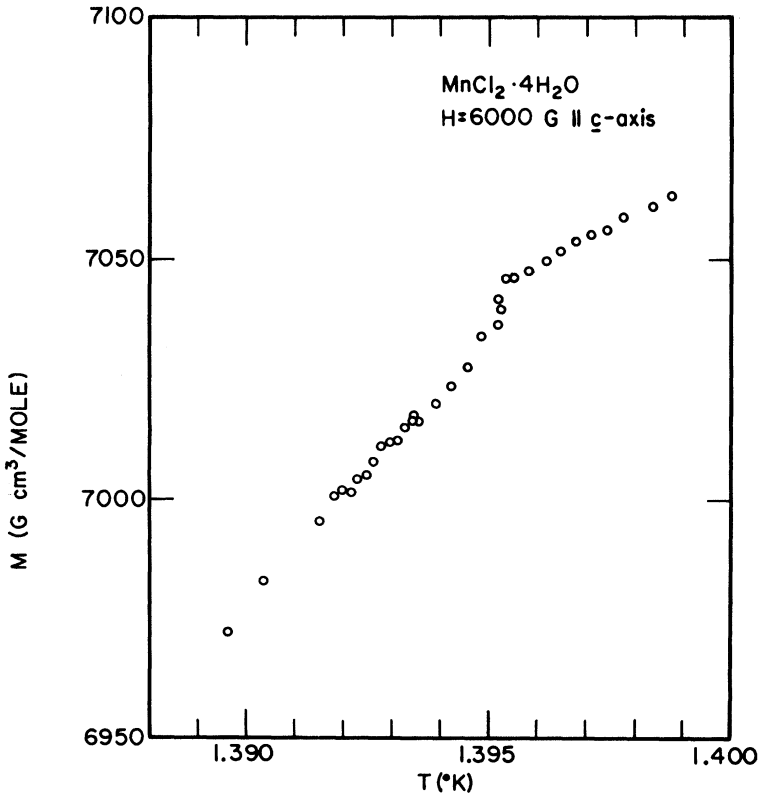

FIG. 5. High-resolution magnetization versus temperature at an applied field of 6 kG.

boundary tangentially and Griffiths[17] has shown, in addition, that this crossing is the point of inflection of these adiabats provided that C_H diverges as $t^{-\alpha}$ where α is $<\frac{1}{2}$. Both of these features have been detected in isentropes of $MnBr_2 \cdot 4H_2O$ by Schelleng and Friedberg.[3,4] It has recently been put forth that the heat-capacity anomaly becomes less abrupt for antiferromagnets with increasing field. One of us[18] has shown that an analysis of the heat capacity of $MnCl_2 \cdot 4H_2O$ using the scaling law formalism yields a uniform decrease in α from a value of ~0.3 in zero field so that these predictions are applicable to this salt.

This tangential crossing further requires $(\partial M/\partial T)_H$ to diverge like C_H. The only other alternative being that neither of these quantities [and by extension $(\partial M/\partial H)_T$] diverges even for a perfect crystalline antiferromagnet for $H \neq 0$, but rather they attain some finite value. Thus it is not required that an infinitely high value of these quantities be measured to assert that divergences occur (or would but for the rounding due to imperfections and such), but it is sufficient to demonstrate simply that at least two of these quantities approach the transition with identical governing exponents.

Figure 6 is a plot of $(\partial T/\partial H)_S$ versus T at constant external field. The derivatives were obtained numerically from the point by point isentropic data of Fig. 2. Each curve in Fig. 6 is a vertical cut across the isentropes. The cusp to larger negative values of $(\partial T/\partial H)_s$ may be seen to appear precisely at the temperatures of the maxima in C_H. This is also the temperature of the point of inflection of the adiabats themselves, $(\partial^2 T/\partial H^2)_S \to \pm\infty$. The locus of these points of inflection is presented as a dashed line in Fig. 2. The constant-temperature view of this quantity is presented in Fig. 7. Fisher[10] has shown the parabolic H-T curve to be characteristic of the two-dimensional superexchange model, while Bienenstock[19] has suggested the form $T_N(H) = T_N(0) \times [1 - (H/H_c)^2]^{\xi}$ from a study of Ising lattices which reduces to a parabolic form for H small compared

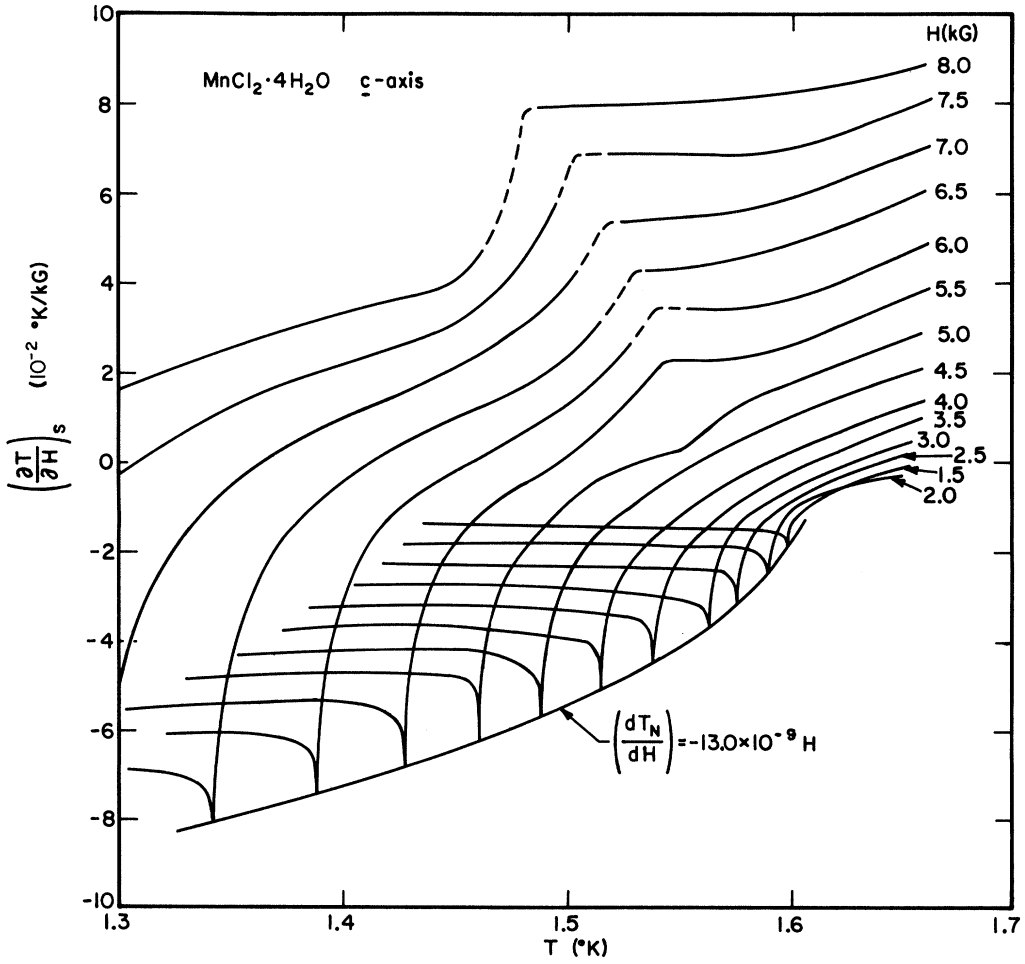

FIG. 6. $(\partial T/\partial H)_S$ versus T at constant applied fields.

to H_c. Experimentally both $MnBr_2 \cdot 4H_2O$ [4] and $CoCl_2 \cdot 6H_2O$ [15] also appear to possess quadratic H-T curves. Thus fortified, it is no surprise to find that the curve is nearly exactly described by $T_N(H) = T_N(0) - AH^2$, where $A = (6.5 \times 10^{-9})\ ^\circ K/G^2$. (dT_N/dH) is then just $-2AH$. The solid line in Fig. 6 outlining the cusp envelope gives the values of (dT_N/dH) thus calculated and allows a comparison with the cusp heights as derived from the slope analysis of the isentropic data. Although our data do not allow very careful definitions of these cusps, it is clear that the slopes of the isentropes passing through the phase boundary are a good estimate of the slope of the critical curve as predicted by Skalyo *et al.* [15]

The introduction of the phase boundary in Fig. 2 produces, however, several distressing asides. It may be seen that several complete adiabats which lie wholly above the dashed line possess distinct minima. Thus, we have a nominal paramagnet both cooling and heating as the field is changed in only one direction. Putting aside for a moment the discussion of this curious "phase," the question of the behavior of $(\partial T/\partial H)_S$ as H approaches zero must now be considered. Unfortunately measurements below 300 G cannot be reported due to the effect of the superconducting magnet.

The usual observation that $(\partial M/\partial T)_H$ is identically zero at zero field, and from the magnetocaloric equation, that $(\partial T/\partial H)_S$ is also everywhere zero, is duly noted. However, the locus of C_H maxima has been identified with the locus of points of inflection in T versus H, and the former terminates on the H axis at $T_N(0) = 1.620\ ^\circ K$. Since the arguments of Skalyo *et al.* [15] and Griffiths[17] do not break down as $H \to 0$ [indeed at $H = 0$ they no longer require the divergence of C_H if $(dT_N/dH) = 0$], there is no reason to suppose the coincidence ends.

If the locus of C_H maxima is indeed parabolic, the requirements of tangential crossing at the point of inflection would dictate that the three features, in the in-field minimum, the point of inflection, and any maximum inside the critical curve, would coalesce at zero field. Griffiths

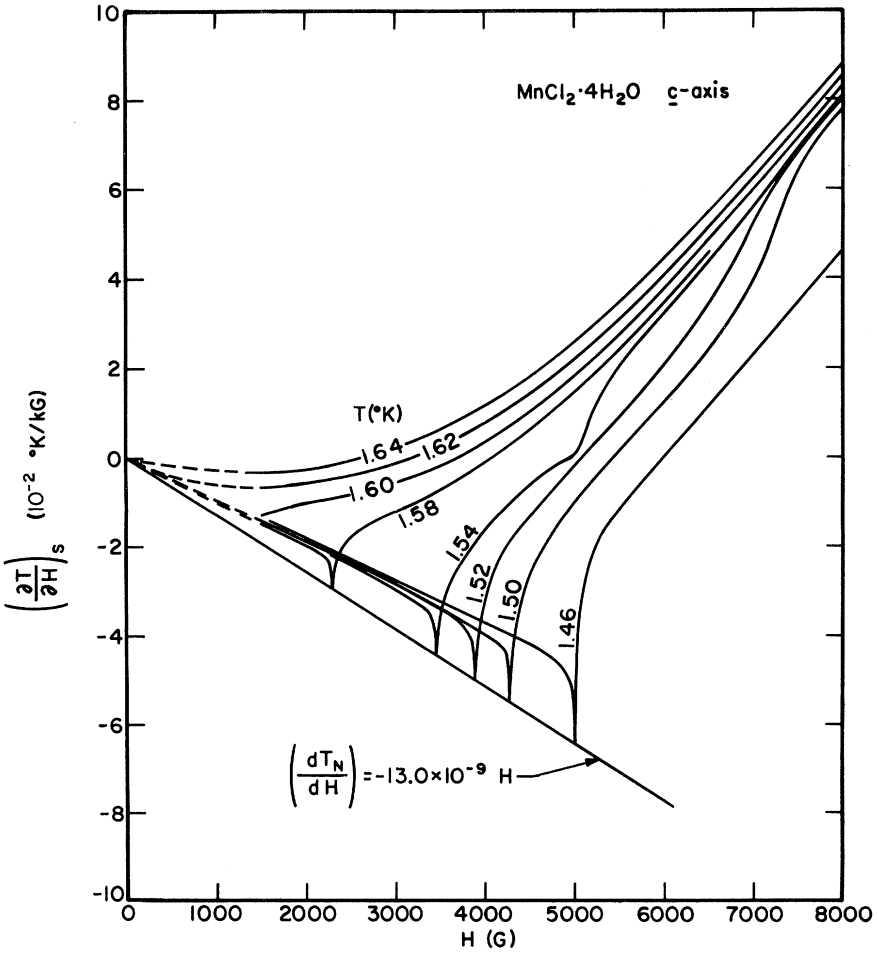

FIG. 7. $(\partial T/\partial H)_S$ versus H_{appl} at constant temperature.

has stated that for $\alpha > \frac{1}{2}$, the curvatures of the isentropes and the phase boundary would coincide at the crossing point. From the Maxwell relation $(\partial M/\partial T)_H = (\partial S/\partial H)_T$, the latter quantity is zero at $H=0$. The parabolic boundary requires further $(\partial S/\partial H)_t$ and the change in entropy along the boundary $S_b'(H)$ to be zero at $H=0$. Reference to Griffiths's expression for the curvature of the isentropes,

$$\left(\frac{\partial^2 T}{\partial H^2}\right)_S = \left(\frac{\partial^2 T}{\partial H^2}\right)_s - S_b''(H)\left(\frac{\partial T}{\partial S}\right)_H - 2S_b'(H)\left\{\frac{\partial(\partial T/\partial S)_H}{\partial H}\right\}_s + S_b'(H)^2\left(\frac{\partial^2 T}{\partial S^2}\right)_H$$

(where s denotes the neighborhood entropy), shows that the curvature of the two curves coincides at zero field for all $\alpha > 0$.

Again following Skalyo *et al.*,[15]

$$\left(\frac{\partial^2 T}{\partial H^2}\right)_S = -\frac{T}{C_H}\frac{\partial \chi_S}{\partial T_H}, \quad \text{where } \chi_S = \left(\frac{\partial M}{\partial H}\right)_S .$$

The adiabatic susceptibility has not been measured for this salt, but Lasheen *et al.*[20] in an attempt to measure the isothermal susceptibility note that their relaxation measurements show a relaxation only at frequencies lower than that used in their susceptibility experiments. Their measurements thus might well be χ_S or are probably at best some mixture of the two. For our purpose here, the difference is of no concern. We shall make reference only to their zero-field data. It may be seen therein (Fig. 2 of Ref. 20) that at temperatures below T_N, the slope of χ_s versus T is positive so that the concavity of our isentropes below the dotted line should be downward at $H=0$. In the region immediately above T_N, $(\partial \chi_S/\partial T)_H$ is still positive so that we would again expect a maximum in T versus H at zero field up to the temperature of the maximum in χ_S where the approach to zero field smoothly goes over into the maximum expected of a paramagnet.

Series 21 is the first isentrope (Fig. 2) which lies wholly above the H-T boundary. The curvature estimates obtained from three-point polynomial fits and appropriate differentiation show that $(\partial^2 T/\partial H^2)_S$ goes through zero at approximately 1500 G. Higher numbered series show an inflection point at higher fields.

Referring to Griffiths's[17] equation for the slope of such an isentrope,

$$\left(\frac{\partial T}{\partial H}\right)_S = \left(\frac{\partial T}{\partial H}\right)_s - S_b'(H)\left(\frac{\partial T}{\partial S}\right)_H , \tag{2}$$

where $s = |S - S_b|$ is the neighborhood entropy. This may be rewritten

$$\left(\frac{\partial T}{\partial H}\right)_S = -2AH + 2aH\frac{T}{C_H} , \tag{3}$$

where we have used the field dependency of the H-T and S-H boundaries. The latter is also empirically determined to be quadratic in H, fitting an expression of the form

$$S_b(H) = S_b(0) - aH^2 , \tag{4}$$

where $a = 6.3\times10^{-9}$ gibbs/mole G^2. The calculated curve compares well ($\pm 0.5\%$) with values of the entropy at the boundary obtained by picking off the field of a tangential crossing, noting the temperature at which the same isentrope crosses 5 kG, and using the table of Reichert and Giauque[2] to establish the absolute entropy at the tangential crossing field.

C_H near the boundary has the form $Kt^{-\alpha} + K'$. If we ignore the possible reduction in amplitude and scaling index with field, the variation of C_H with field may be approximated by

$$C_H = K_1(t_0 + K_2H^2)^{-\alpha} + K' , \tag{5}$$

where $t_0 = |T - T_N(0)|$. Thus for high fields,

$$\left(\frac{\partial T}{\partial H}\right)_S \approx -2AH + \frac{2aT}{K_1K_2^{-\alpha}}H^{1+2\alpha} , \tag{6}$$

while at low fields

$$\left(\frac{\partial T}{\partial H}\right)_S \approx -2AH + \frac{2aT}{K_1t_0^{-\alpha} + K'}H . \tag{7}$$

With increasing field then, $(\partial T/\partial H)_S$ starts at zero at zero field, goes negative led by the linear term, and then through a minimum as the higher power term asserts itself. As t_0 becomes large, the second term in Eq. (3) approaches a linear variation in H (C_H is nearly constant with field). The coefficient of this term increases with T (C_H also decreases in value) and the minimum disappears. We can assert that the boundary entropy has the form of Eq. (4), at least for low fields, on the following basis:

(a) $S_b'(0) = 0$ so that no term $H^\delta (\delta \leq 1)$ may be incorporated.

(b) The eventual disappearance of the in-field minimum in T versus H with increasing temperature depends upon the exponent of the second term in Eq. (6) becoming < 1. Thus values of $\delta > 2$ are excluded in the expression for $S_b(H)$. This leaves $1 < \delta \leq 2$.

Two further observations are of interest here. The locus of minima in $(\partial T/\partial H)_S$ is a parabola displaced from the locus of points of inflection a distance of $0.057 + 6.0\times10^{-10}H^2 (\pm 0.004)$ °K (dotted line in Fig. 2). Extrapolation of this line below 2 kG was accomplished using Eqs. (3) and (5). The two constants, K_1 and K' were taken

from a linear interpolation of the values of Reichert[18] at 0 and 5 kG. The agreement with the observed values of the minima is well within the experimental error for all fields > 2 kG. The H intercept of this curve corresponds to the maximum in $\chi_s(T)$. Unfortunately, the data of Lasheen *et al.*[20] do not permit close comparison though the value obtained here [(1.677 ± 0.004) °K] is quite reasonable.

The striking series of anomalies (Fig. 6) which develop at fields > 5.5 kG and at temperatures well above the extrema in T versus H and M versus T are a complete mystery. These curves are derived from constant field cuts across the adiabat plot of Fig. 2. Thus, the shapes are a result of points from several adiabats and so would appear to be real. The effect is completely lost in the more usual plot of $(\partial T/\partial H)_S$ versus H along the isentrope itself. In that case, only a single deviant point appears on each curve which could easily be dismissed as scatter. Evidently a corresponding disturbance will occur in both M and C_H.

Having established that the isentropes above but near the H-T boundary go through an in-field minimum, we would like to address a few comments to the nature of the material in this region. A thermally isolated paramagnet in an applied external magnetic field cools as the field is lowered because the degree of order in the spin system decreases as the field is lowered. In systems in which the degree of order increases as the field is lowered, i.e., an initial field application tends to break up the extant order, the substance warms.

There are, of course, spin systems without spontaneous ordering in which adiabats with well-defined in-field minima may be observed. The origin of the effect here is the convergence and crossing of levels which are split in zero field due to single-ion anisotropy effects. Indeed, such an effect might be anticipated in this substance since the 90-kG heat capacity is exactly described by a Schottky function of six unequally spaced levels from which we would infer an effective splitting in zero applied field of 2.16 cal for the $m_S = \pm\frac{5}{2}$ level and 0.88 cal for the $m_s = \pm\frac{3}{2}$ level, both above the $m_s = \pm\frac{1}{2}$ level. This, of course, presupposes no further interaction between the Mn^{++} ions.

Assuming the lattice heat capacity is of the form $A \cdot T^3$ and is not anomalous, this modified Schottky expression for the heat capacity produces only a very low-temperature minimum in the adiabats (about 0.6 °K for the initial temperature-field coordinates of run 21). Adjustment of the splitting size does not significantly affect the disagreement with the observed adiabats.

It is clear then that $MnCl_2 \cdot 4H_2O$ is still ordered in some sense above 1.62 °K in zero external field and that this ordering is antiferromagnetic. The observed persistence in several antiferromagnets of NMR lines of paramagnetic origin[21] down into the antiferromagnetic region and the similar extension of antiferromagnetic lines well into the paramagnetic region[22,23] would seem to hint at a coexistence or overlap of the two "phases."

Marshall and Lowde[24] in their recent review of magnetic correlations point out the lack of qualitative difference in correlation in the two regions. The correlation between nearest neighbors at T_N is only $\sim \frac{1}{2}$, and it would appear that the clusters of short-range order are capable of supporting constructions similar to spin waves – an inherently long-range concept. Neutron scattering experiments too show a tendency in both regions to "anticipate" the behavior encountered on the other side of T_N.

These transition lines are often described as a line of critical points. A critical point is, to most of us, the end of a line of first-order phase transitions. These first-order transitions in antiferromagnets have been conceptualized by Fisher[25] as a discontinuous change in atomic moment orientation (sublattice magnetization) as an applied "staggered" magnetic field passes through zero to negative values. The real world, of course, coincides to the plane wherein $H_{\text{staggered}} = 0$. This is closely analogous to the first-order line in a liquid-gas phase diagram so that we might expect that for an antiferromagnet at any temperature and real applied field below the line of critical points, the different staggered phases must be in mutual equilibrium. Thus, the antiferromagnetic "phase" is better envisioned as a mixture of at least two staggered phases.[26] At the critical point, it is the difference between these staggered phases that disappears.

Returning to the liquid-gas analog again, we might note that P-V isotherms depart from their ideal hyperbolic form at a considerable distance from the critical point; that point being merely the coordinate of the first horizontal inflection point in the isotherm sequence. The paramagnetic "phase" is no more a distinct phase than a fluid immediately above its critical point is a phase distinct from either the gas or liquid phases.

The old name for these changes put forward by Landau[27] was "continuous transitions." It would appear that a view of these anomalies as such, with the lines of phase diagrams taken as merely the site of the maximum rate of change, or if you prefer, an infinite gradient in the pair correlation function (single-particle correlation function in the case of He) would be more in line with the available evidence.

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