the maximum separation of the fine lines, which is $30|a| - 2A^2/g\beta H_0$, has a value between A and $2A$. This is the value required to produce the disappearance of the hyperfine lines. Using this value, a half-width of about 20 G for the fine lines can be inferred from the spectra at the angle of minimum separation, $\theta = 31°$. This line width cannot be accounted for by the effects of spin-spin interactions at concentrations of $10^{17}/cm^3$. Since, as mentioned earlier, the spin-lattice interactions contribute negligibly to the linewidth, it is suggested that the unusual width of the lines results from the hyperfine interactions with nearest-neighbor As atoms[6] and next-nearest-neighbor Ga atoms, all isotopes of which have a nuclear spin of 3/2.

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[6] M. Tinkham, Proc. Roy. Soc. (London) A236, 549 (1956).

III. CONCLUSIONS

The paramagnetic resonance spectra of manganese in GaAs have been observed at 77°K. The measured g and A are isotropic with values of 2.004 and 56 G, respectively. The spin Hamiltonian describing manganese in GaAs is expressed by Eq. (1). The angular variation of the fine structure lines obtained from this expression accounts for the unusual angular dependence of the spectrum. Finally, a maximum value of 3.5 G is estimated for the cubic anisotropy constant.

ACKNOWLEDGMENTS

Specific Heat of Single-Crystal MnCl₂ in Applied Magnetic Fields

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The specific heat of a single-crystal sample of MnCl₂ has been measured, in the liquid-helium temperature region, in applied magnetic fields extending up to 7.26 kOe. In all cases the magnetic field was applied parallel to an a axis of the hexagonal cell. The two specific heat maxima, which have been previously reported at 1.81 and 1.96°K in zero field, are associated with antiferromagnetic transitions. Both transition temperatures are found to be field dependent. The upper transition temperature increases with applied field while the lower transition temperature decreases. These results are correlated with neutron diffraction studies of the magnetic structure transitions.

INTRODUCTION

THE magnetic and thermal properties of MnCl₂ in the liquid-helium temperature region have been reported previously.[1-3] Briefly stated, MnCl₂ is paramagnetic at temperatures greater than 1.96°K, at which temperature a transition to an antiferromagnetic state occurs. At a slightly lower temperature, 1.81°K, the spin moments reorient to a different structure, and the magnetic system undergoes another phase transition to the low-temperature antiferromagnetic state. A well-defined λ-type anomaly in the specific heat is observed at each of these critical temperatures. The complex order of the Mn⁺⁺ spin system in both the high-temperature and low-temperature antiferromagnetic state has been studied by the methods of neutron diffraction, as reported by Wilkinson, Cable, Wollan, and

Koehler.[3] Interpretation of the neutron diffraction results is based, in a large part, on diffraction patterns from oriented single crystals, especially in an external magnetic field. In this regard, it is of considerable interest to examine the dependence of the transition temperatures on an external field which is applied along a known direction of a single crystal. For this purpose a series of specific-heat measurements in various applied fields has been performed. The two transition temperatures are identified by sharp λ-type maxima in the specific heat, and both are found to be a function of the magnetic field. In all measurements reported here, the external field was applied parallel to an a axis of the hexagonal cell.

EXPERIMENTAL PROCEDURE

A large crystal was grown from anhydrous MnCl₂ powder by the Stockbarger-Bridgman method in a quartz crucible. A final dehydration was performed by heating in vacuum immediately prior to crystal growth. A cylindrical crystal was machined from a section of the ingot which was optically clear and free from visible flaws. The final cylinder was 7.8 mm in diameter by

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* Oak Ridge National Laboratory is operated by Union Carbide Corporation for the United States Atomic Energy Commission.
[1] R. B. Murray and L. D. Roberts, Phys. Rev. 100, 1067 (1955).
[2] R. B. Murray, Phys. Rev. 100, 1071 (1955).
[3] M. K. Wilkinson, J. W. Cable, E. O. Wollan, and W. C. Koehler, Oak Ridge National Laboratory Report ORNL-2501, 1958 (unpublished), p. 37. Also, Oak Ridge National Laboratory Report ORNL-2430, 1958 (unpublished), p. 65.

9.7 mm long, and weighed 1.292 g (1.027×10^{-2} mole). The sample was machined with the ingot in an orientation such that the axis of the cylinder would be parallel to a crystalline a axis. The orientation of the resulting cylinder was checked by neutron diffraction and it was found that the axis of the cylinder was inclined to an a axis of the hexagonal cell by $2°$. This angular deviation is insignificant for present purposes. Following the completion of all specific-heat measurements, the crystal was removed from its container and re-examined by neutron diffraction. It was found that the reflections were still sharp and single, from which it is concluded that the crystal had not deteriorated during the course of the experiment.

The sample assembly is shown schematically in Fig. 1. The crystal X was snugly contained within a silver cup A which was soldered at the top to an insert on the bottom of a long copper tube C. Helium exchange gas at $\frac{1}{4}$ atm pressure was admitted to the interior of the cup and the copper tube was then pinched and soldered at the top. A heater coil H of 0.003-in. enamel coated manganin wire was wrapped around the exterior of the cup and secured with GE 7031 cement. A carbon resitance thermometer R, whose exterior coating had been ground off, was bonded to the assembly with cement. Superconducting leads S of tinned copper led from the heater and thermometer to bath temperature. The assembly was suspended by light nylon threads T. Thermal contact between the assembly and bath temperature was achieved by a mechanical thermal switch whose jaws J are indicated in Fig. 1. With the use of
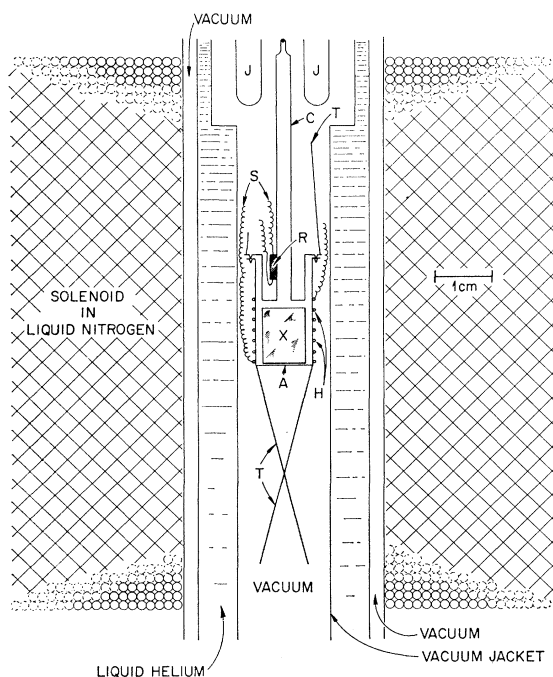

FIG. 2. Molar specific heat of $MnCl_2$ in various magnetic fields applied along a crystalline a axis.

FIG. 1. Schematic diagram of sample assembly. The crystalline a axis is vertical.

this thermal switch it was possible to cool the sample assembly to $1.3°K$ without the use of helium heat-exchange gas. Exchange gas was used during thermometer calibrations in order to insure thermal equilibrium with bath temperature.

Magnetic fields were generated by a solenoid of copper wire contained in the liquid-nitrogen bath. Magnet current was derived from a motor-generator set and was monitored with a precision potentiometer. The magnet calibration (145 Oe per A) had been previously determined by a ballistic method using a standard mutual inductance as reference. The $MnCl_2$ crystal was carefully positioned at the center of the solenoid. In an auxiliary measurement the magnetic field was found to be uniform within about 0.6% over the length of the crystal.

The procedures for thermometer calibration and for recording specific heat warmup curves were very similar to those reported previously[2] and need not be described further. Care was taken during various thermometer

calibrations to look for a dependence of the thermometer resistance on applied field. The dependence was found to be very weak; the maximum increase in resistance with applied field occurred at the lowest temperature and amounted to less than 0.2% for the largest applied field. This small resistance change corresponded to a calibration change of less than one millidegree and is negligible. The liquid-helium temperature scale used in the thermometer calibration is the 55E scale.[4]

RESULTS AND DISCUSSION

The results of all experiments are shown in Fig. 2, where the molar specific heat is shown as a function of temperature for the various external fields. All data points have been corrected for the small specific heat of the calorimeter cup, copper tube, etc. The ordinate represents *total* specific heat of the sample and includes both the magnetic and lattice specific heats. The lattice specific heat, however, is only a small fraction of the total. Recent measurements by Chisholm and Stout[5] indicate that the lattice specific heat amounts to about 2.5% of the total specific heat at 4.0°K. The lattice contribution decreases rapidly at lower temperatures and is completely negligible near 2°K.

It is seen in Fig. 2 that the transition temperatures are a function of the applied field. The dependence is given explicitly in Fig. 3. The error limits on each point in Fig. 3 are subjective estimates of the uncertainty of the temperature corresponding to the specific-heat maximum. The transition temperatures in zero field are found to be 1.81 and 1.96°K with an uncertainty of ±0.01°K, in exact agreement with preceding measurements on polycrystalline material.[2] It is seen in Fig. 3 that the dependence of the two transition points on applied field is quite different: the high-temperature
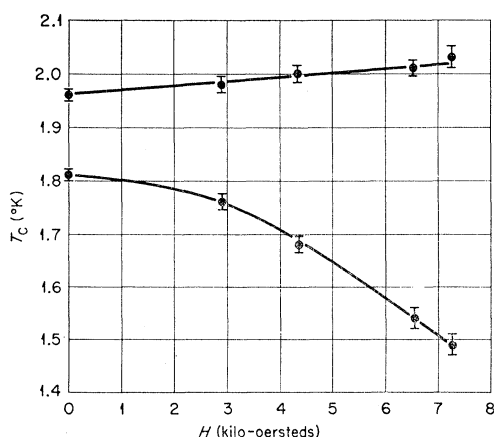

FIG. 3. Transition temperatures as a function of magnetic field applied along a crystalline *a* axis.

anomaly moves to higher temperature while the low-temperature transition moves to lower temperature. Thus the application of a magnetic field along the *a* axis has the effect of stabilizing the high-temperature antiferromagnetic state. This observation is in accord with results of the neutron diffraction studies by Wilkinson *et al.*[3]

The upper specific-heat anomaly is associated with the transition from paramagnetism to the antiferromagnetic state which is stable only to about 1.81°K (in zero field). This is the "high-temperature" antiferromagnetic configuration, referred to hereafter as state I. At the lower transition point, the spin system reorients to antiferromagnetic state II. The structures of the spin system in these two states are very complicated, and have been found in the neutron diffraction studies[3] to consist of bands of ferromagnetism which alternate in the direction of magnetization. These bands are inclined at an angle of about 58° to the crystalline *c* axis. A major feature of the magnetic structure, which was revealed by neutron diffraction, is the existence of antiferromagnetic domains in both states I and II. The difference in structure between the two ordered states is subtle, and involves principally changes in the domain structure and the size of the magnetic unit cell, accompanied by a slight change in the direction of magnetization with respect to the crystalline axes. In the antiferromagnetic state I the magnetic structure is apparently one in which the magnetic moments are parallel to the basal plane and are oriented perpendicular to the hexagonal *a* axis. In zero external field this configuration appears in three equally populated domains along the three hexagonal *a* axes, as illustrated in Fig. 4. An external magnetic field which is applied parallel to a hexagonal *a* axis, as in the present experiments, is thus initially (at small H) oriented perpendicular to the magnetization axis for $\frac{1}{3}$ of the spin system and is oriented at 30° to the magnetization axis for $\frac{2}{3}$ of the spins. With increasing H, the "perpendicular" domain (domain A of Fig. 4) grows at the expense of the other domains and appears to deplete the other two domains completely at an applied field of about 5 kOe at $T=1.85°$K.[3]

Referring to Fig. 3 it may be noted again that the high-temperature anomaly increases in temperature with applied field. An *increase* in this paramagnetic-antiferromagnetic transition temperature is in direct contrast with the behavior of other antiferromagnetic compounds whose H-T phase diagram has been studied. For example, the transition temperature *decreases* with applied field in $MnBr_2$,[6] $MnCl_2 \cdot 4H_2O$,[7,8] $MnBr_2 \cdot 4H_2O$,[8] $CuCl_2 \cdot 2H_2O$,[9] and $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$.[10] The ob-

[4] J. R. Clement, J. K. Logan, and J. Gaffney, Phys. Rev. **100**, 743 (1955); see their note added in proof.
[5] R. C. Chisholm and J. W. Stout, J. Chem. Phys. **36**, 972 (1962).

[6] E. O. Wollan, W. C. Koehler, and M. K. Wilkinson, Phys. Rev. **110**, 638 (1958).
[7] W. H. M. Voorhoeve and Z. Dokoupil, Physica **27**, 777 (1961).
[8] W. E. Henry, Phys. Rev. **94**, 1146 (1954)
[9] N. J. Poulis and G. E. G. Hardeman, Physica **18**, 429 (1952).
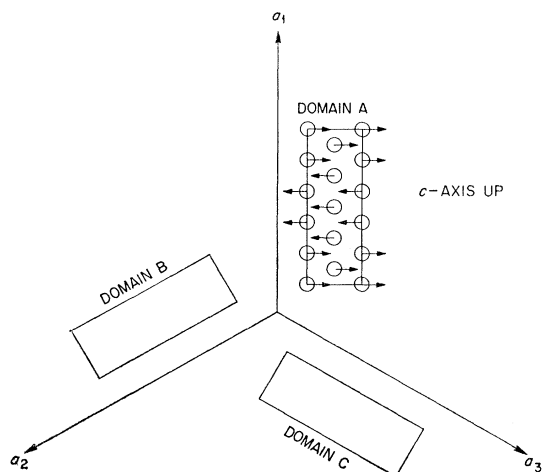[10] C. G. B. Garrett, Proc. Roy. Soc. (London) **A206**, 243 (1951).

FIG. 4. Magnetic order and domain pattern for state I as determined by neutron diffraction. Axes labeled a_1, a_2, a_3 are equivalent a axes of the hexagonal cell. From Wilkinson *et al.*, reference 3.

served increase in the transition point in the present case is also in contrast with theoretical predictions.[11] The anomalous dependence of this transition temperature on the external field may well be a property of the domain structure and the growth of the preferred domain with applied field. On the other hand, the magnetic ordering in state I is that of ferromagnetic bands, so that the applied field may have the effect of stabilizing the ferromagnetic coupling and hence raise the transition point. It does not seem possible to resolve this point on the basis of existing information.

It may be noted that a similar increase in transition temperature with applied field has been observed over a limited region of the phase boundary of $CoCl_2 \cdot 6H_2O$.[12]

The lower temperature anomaly, as previously indicated, corresponds to the transition between antiferromagnetic states I and II. The dependence of this transition temperature on external field is determined by the details of the magnetic coupling, crystalline anisotropies, and the domain pattern. In view of the complex magnetic structures involved here, it does not appear possible to predict the dependence of this transition point on the applied field.

It is appropriate to comment briefly on the order of the two transitions in view of existing measurements of the specific heat and magnetic susceptibility. It is clear that neither transition is of first order as there is no evidence of an infinity in the specific heat; both the entropy (see Fig. 5) and the magnetic susceptibility[1] are continuous throughout the transition region. In a second-order transition both the specific heat and

$(\partial \chi / \partial T)_H$ undergo a discontinuity.[13] It is very difficult to assess the specific-heat data in the neighborhood of a transition point to determine whether there is, in fact, a discontinuity. Examination of the data in Fig. 2 and previous specific heat data in zero field[2] indicates that the specific heat is probably continuous through both transitions. A plot of $(\partial \chi / \partial T)_{H=0}$, from previous measurements,[1] appears to be continuous throughout the transition region. Thus, the conditions for a second-order transition are not met. In a third-order transition both $(\partial C / \partial T)_H$ and $(\partial^2 \chi / \partial T^2)_H$ are discontinuous. It appears from Fig. 2 that $(\partial C / \partial T)_H$ is discontinuous at both transition points. A plot of $(\partial \chi / \partial T)_{H=0}$ reveals that $(\partial^2 \chi / \partial T^2)_{H=0}$ is probably discontinuous near 1.8°K; at 1.96°K, $(\partial^2 \chi / \partial T^2)_{H=0}$ is nearly zero and it is not possible to determine whether it undergoes a discontinuity or not. It is thus concluded, on the basis of existing data, that the conditions for a third-order transition are satisfied by the lower temperature anomaly, and may be satisfied by the 1.96°K transition. For a third-order transition, the magnetic analog of the Clapeyron equation can be written

$$\frac{dT_c}{dH} = -HT\frac{\Delta(\partial^2 \chi / \partial T^2)_H}{\Delta(\partial C / \partial T)_H}, \qquad (1)$$

where T_c is the transition temperature and Δ represents the change in the function across the phase boundary. For the lower temperature transition, both Δ's are apparently nonzero and are of the same sign, so that
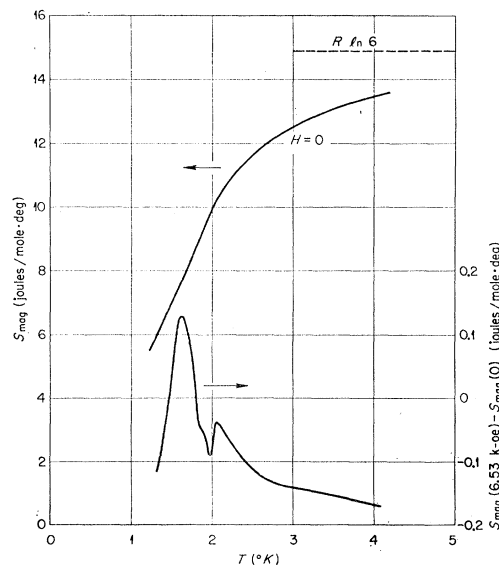

FIG. 5. Magnetic entropy of MnCl₂ as derived from the measured specific heat. The upper curve is the magnetic entropy in zero applied field. The lower curve is the magnetic entropy in an external field of 6.53 kOe minus the magnetic entropy in zero field.

[11] See, for example, K. P. Belov, *Magnetic Transitions* (translation by W. H. Furry, Consultants Bureau Enterprises, Inc., New York, 1961); p. 129. Also T. Nagamiya, K. Yosida, and R. Kubo, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

[12] W. van der Lugt and N. J. Poulis, Physica **26**, 917 (1960).

[13] See A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, New York, 1960), Chap. 9.

dT_c/dH should be negative and approach zero as $H \to 0$. This condition is fulfilled by the data of Fig. 3. It is probably not appropriate to apply the Clapeyron equation for $H>0$, since the magnetic system exhibits hysteresis effects associated with domain growth.[3] Furthermore, we do not know $(\partial^2\chi/\partial T^2)_H$ for $H>0$.

Considerations in the foregoing paragraph are due largely to correspondence with J. W. Stout of the University of Chicago.

CALCULATION OF MAGNETIC ENTROPY

In the absence of specific-heat data in the region below 1.3–1.4°K, one cannot evaluate the magnetic entropy directly by integration of C_{mag}/T from 0°K. It is possible, however, to calculate the magnetic entropy from the present specific-heat data by utilizing the fact that the total entropy of the spin system to be achieved at a high temperature is $R \ln(2S+1) = R \ln 6$, since the Mn^{++} ion is in a $^6S_{5/2}$ state. Recent measurements of the specific heat of $MnCl_2$ at higher temperatures, by Chisholm and Stout,[5] have made possible an estimate of the lattice specific heat at liquid-helium temperatures which is undoubtedly much more accurate than that available previously.[2] With this improved estimate of the lattice contribution, Chisholm and Stout were able to re-evaluate the magnetic specific heat in the temperature region above the transition point. They conclude that in the region above 3.2°K, C_{mag} is given by

$$C_{mag} = 55.2/T^2 - 54.8/T^3 \text{ J/mole-deg.} \tag{2}$$

On this basis, the magnetic entropy at 4°K (in zero field) is given by

$$S(4) = R \ln 6 - \int_4^\infty (55.2/T^3 - 54.8/T^4) dT. \tag{3}$$

The magnetic entropy between 1.3 and 4°K is then obtained by numerical integration of the (zero-field) specific-heat data. The entropy for the $H=0$ case is shown as the upper curve in Fig. 5. This curve is almost identical with that given previously,[2] being shifted downward very slightly by the re-evaluation of the lattice specific heat.[14]

Evaluation of the magnetic entropy in the presence of an external field may be obtained similarly, noting

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[14] A misprint occurred in the final equation of the previous report on the specific heat (reference 2): A factor $1/T$ should appear in the integrand. This was a printing error only; the entropy was correctly calculated.

that

$$(\partial S/\partial H)_T = (\partial I/\partial T)_H \tag{4}$$

from the thermodynamic Maxwell equations, where I is the magnetic moment per mole. Writing $I = \chi H$ and integrating Eq. (4), one obtains

$$S(H,T) - S(0,T) = \int_0^H \left(\frac{\partial\chi}{\partial T}\right)_H H dH. \tag{5}$$

In the case of $MnCl_2$ previous measurements of the magnetic susceptibility[1] have indicated that χ is independent of H for applied fields up to 2.4 kOe. At 4°K it is probably a good approximation to take χ, and $(\partial\chi/\partial T)_H$, as field independent over the range of H available in the present experiments, so that Eq. (5) can be written

$$S(H,4^0) - S(0,4^0) \approx \tfrac{1}{2}(\partial\chi/\partial T)_H H^2. \tag{6}$$

From previous measurements[1] of χ, we obtain $(\partial\chi/\partial T)_H = -8\times10^{-2}$ erg/mole-G²-deg at 4°K. Having established the entropy scale in this manner, the entropy curve is obtained by numerical integration of the specific-heat data. Specific-heat measurements were carried up to 4°K in only two values of the applied field, $H = 2.90$ and 6.53 kOe. In both cases the magnetic entropy curves are very nearly the same as the curve in zero field and are virtually indistinguishable when plotted on the same scale. In order to illustrate the entropy in the 6.53 kOe case, the difference curve $S(6.53 \text{ kOe}) - S(0)$,is shown in the lower part of Fig. 5. It should be understood that the exact position of this curve with respect to the entropy scale is based on the assumption that $(\partial\chi/\partial T)_H$ is field independent at 4°K.