

larger decrease in H_{c1} . The magnitude of the decrease is more than twice that of the increase. This asymmetrical spread resembles the behavior expected from mechanism *A*. For the completely aligned state, each mechanism predicts $H_{c1} \approx 0$, but for mechanism *A*, $H_{c11} \approx \bar{H}_c$, as compared to the predictions for mechanisms *B* and *C* of $H_{c11} \approx 2\bar{H}_c$.

An additional comparison between theory and experiment may be made with the relation between random coercive force and median elongation ratio. Data have been collected^{18,22} for samples ranging in median elongation ratio (by frequency) from 1.3 to 4.6, with particle diameters lying between 140 Å and 180 Å. For the models, we assume that the median elongation adequately characterizes the behavior, and we determine the random coercive force of a sample of uniformly elongated particles (neglecting magnetocrystalline anisotropy). Figure 8 presents the comparison of experiment with mechanisms *A*, *A'*, *B*, and *C*. Mechanism *C* is ruled out at high elongation, as noted earlier. The failure of models *A*, *A'*, and *B* at low elongation is also as expected. The general trend of predictions *A*, *A'*, and *B* is in fair agreement with the experimental results at higher elongations. In particular, despite the

crudeness of the assumptions, there is apparent support for the fanning mechanism *A'* in this correlation.

SUMMARY

We have re-examined the predictions of magnetic behavior arising from shape anisotropy in single-domain particles. Several approximate models have been suggested which may exist in certain experimental situations. Detailed calculations have been carried out for a "chain-of-spheres" model. Comparison with recent results on certain elongated iron particles favors the chain-of-spheres model as a suitable description of their magnetic behavior. A successful calculation has been made of the coercive force of material prepared by several earlier workers. A comparison of the new models with the older ones indicates a direction for experimental advance.

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Magnetic and Thermal Properties of MnCl_2 at Liquid Helium Temperatures. I. Magnetic Susceptibility*

R. B. MURRAY† AND L. D. ROBERTS
Oak Ridge National Laboratory, Oak Ridge, Tennessee
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Measurements of the magnetic susceptibility of polycrystalline and single-crystal samples of anhydrous MnCl_2 have been carried out from 1.1° to 4.2°K with an ac mutual-inductance bridge. The susceptibility was found to be essentially independent of an applied magnetic field up to 2400 oersteds throughout this region, and displayed anomalous behavior near 2°K indicating a magnetic ordering transition. In view of the observed susceptibility behavior this transition is interpreted as one of an antiferromagnetic nature, although the susceptibilities of both the single-crystal and polycrystalline samples were found to rise slowly with decreasing temperature below the transition region. This interpretation is supported by preliminary neutron diffraction studies below 2°K. A calculation of the magnetic anisotropy is in reasonable agreement with that observed at 4.2°K.

INTRODUCTION

ANHYDROUS MnCl_2 is a member of the series of iron-group anhydrous chlorides. The magnetic and thermal properties of these compounds have been previously investigated at a number of laboratories from liquid hydrogen temperatures to room temperature and above. An extensive study of the magnetic susceptibilities of the members of this group has been

carried out by Starr, Bitter, and Kaufmann¹ (SBK); references to earlier work may be found in their paper. This series of compounds is of interest because of the high density of magnetic ions which leads to strong magnetic interactions, and hence to magnetic ordering transitions at relatively high temperatures. Many of these compounds are crystallographically isomorphous, having a hexagonal layer structure, so that their magnetic properties may be compared directly. Magnetic susceptibility measurements have shown well defined maxima in the susceptibilities of several compounds of this series, characteristic of an antiferromagnetic

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† Graduate Fellow of the Oak Ridge Institute of Nuclear Studies from the University of Tennessee. This work was included in a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Tennessee.

¹ Starr, Bitter, and Kaufmann, *Phys. Rev.* **58**, 977 (1940).

transition. The unusual low-temperature magnetic properties of these latter compounds have earned them the name "metamagnetic"; these metamagnetic properties have recently been interpreted by Néel² as arising from an antiferromagnetic structure. Measurements of the specific heats of CrCl₃, FeCl₂, CoCl₂, and NiCl₂ by Trapeznikowa *et al.* (see reference 1) have revealed sharp λ -type anomalies at temperatures close to the corresponding susceptibility maxima, in the range 20° to 50°K.

MnCl₂, however, retains its normal, paramagnetic behavior down to 14°K, the magnetic susceptibility χ following a Curie-Weiss law, $\chi = C/(T + \theta)$, where T is the absolute temperature, C the Curie constant, and θ the Weiss constant. The measured Curie constant is approximately that expected for a free spin moment of 5/2, corresponding to the ⁶S_{5/2} ground state of the Mn²⁺ ion. SBK found the Weiss constant to be 3.3°K; earlier workers measured somewhat different values of the Weiss constant, all of which, however, were quite small (see reference 1). The specific heat of MnCl₂ was measured from 14° to 130°K by Trapeznikowa and Miljutin³; later measurements by Kelley and Moore⁴ covered the region between 50° and 300°K. No evidence of a co-operative transition was found between 14° and 300°K.

In view of the absence of a magnetic transition in MnCl₂ above 14°K, it is of interest to extend a study of its magnetic and thermal properties to lower temperatures in a search for a transition to a state of magnetic order. The fact that the Weiss constant is found to be several degrees Kelvin suggests that such a transition might occur at liquid helium temperatures. The purpose of the investigation reported here is to determine whether or not such a transition occurs at liquid helium temperatures by a study of the magnetic susceptibility and specific heat, and to gain as much information as possible concerning the nature of the low-temperature magnetic state of MnCl₂ from these measurements.

SUSCEPTIBILITY MEASUREMENTS

The magnetic susceptibility of MnCl₂ was measured from 1.1° to 4.2°K by using a cryostat and an ac mutual inductance bridge which was constructed and described by Erickson, Roberts, and Dabbs.⁵ The susceptibility measured by this technique is the differential magnetic susceptibility, and is determined with an oscillating (500 cycles/sec) measuring field of about two-oersteds strength. Susceptibility measurements were carried out on both a polycrystalline and a single-crystal sample of MnCl₂. Sample temperatures were determined from the measured vapor pressure of the liquid helium bath

employing the 1948 temperature scale⁶ with the corrections to this scale as given by Erickson and Roberts.⁷ The measured vapor pressures were corrected for the hydrostatic pressure of the liquid helium above the sample level, and measured pressures were normalized to standard gravity and temperature (20°C). The relative susceptibilities read on the bridge were converted to absolute susceptibilities by a previous bridge calibration,⁵ assuming the validity of the Curie-Weiss law for MnCl₂ at 77°K.

SAMPLE PREPARATION

The polycrystalline sample of MnCl₂ studied was part of the sample used in the specific heat measurements, to be described in the accompanying paper, Part II.⁸ The anhydrous material was obtained by the dehydration of reagent grade MnCl₂·4H₂O in an atmosphere of dry HCl gas. During the dehydration the temperature was raised to about 400°C over a period of several hours until no more water was given off. The dehydrated powder was then melted in an HCl atmosphere, cooled over a period of about one hour to room temperature, and the fused solid was broken into particles of average size 1 to 4 mm. In order to prevent chemical reactions or contamination, the sample was contained in a platinum boat throughout the dehydration and melting procedures. This coarse powder (0.03690 mole) was then loosely packed in a flat bottomed glass tube which was sealed off in an atmosphere of helium gas at room temperature. This helium gas served as a heat exchange medium to insure thermal equilibrium between the particles of MnCl₂ and their surroundings. The polycrystalline specimen occupied a cylindrical volume of radius 5 mm and height 25 mm. The anhydrous material was handled at all times in an inert, dry atmosphere to prevent any exposure to water vapor.

In the preparation of the single-crystal specimen of MnCl₂, the anhydrous powder, contained in a cylindrical quartz tube of 2 inch diameter, was melted in a furnace. The quartz tube containing the liquid MnCl₂ was then slowly withdrawn, over a period of days, from the furnace, allowing the growth of the single crystal from the liquid state. Susceptibility measurements were carried out on a sphere of 1/2 inch diameter which was machined from the large single crystal ingot. Precautions were taken to prevent exposure to water vapor in the preparation and handling of the single crystal. The authors are indebted to D. E. Lavalley for all preparations of anhydrous MnCl₂ and to J. Schenck for growing the single crystal.

² L. Néel, Brussels Conference, September, 1954 (unpublished).

³ O. Trapeznikowa and G. Miljutin, *Physik. Z. Sowjetunion* **11**, 55 (1937).

⁴ K. K. Kelley and G. E. Moore, *J. Am. Chem. Soc.* **65**, 1264 (1943).

⁵ Erickson, Roberts, and Dabbs, *Rev. Sci. Instr.* **25**, 1178 (1954).

⁶ H. Van Dijk and D. Shoenberg, *Nature* **164**, 151 (1949).

⁷ R. A. Erickson and L. D. Roberts, *Phys. Rev.* **93**, 957 (1954). These corrections are in accord with the temperature scale revisions adopted at the 1955 Paris Low Temperature Conference.

⁸ R. B. Murray, following paper [*Phys. Rev.* **100**, 1071 (1955)].

SINGLE-CRYSTAL SUSCEPTIBILITIES

The crystal structure of $MnCl_2$ is a hexagonal layer structure of the $CdCl_2$ type.⁹ The Mn^{++} ions assume a hexagonal structure in sheets; each sheet of Mn^{++} ions is sandwiched between two sheets of Cl^- ions. The crystalline c -axis is perpendicular to these layers of Mn^{++} and Cl^- ions, while the a - and b -axes are contained in the layers. Susceptibility measurements were performed on the crystalline specimen so as to measure, first, the susceptibility along the c -axis (χ_c). The crystal was then reoriented with respect to the cryostat so that the measuring field was parallel to the crystallographic ab planes; the susceptibility measured in this orientation is denoted χ_{ab} . The orientation of the c -axis of the spherical crystal was determined by neutron diffraction from the (003) and (006) planes (indexed in terms of a hexagonal system). The (006) reflections were found to be sharp and single, indicating an unique c -axis in the spherical specimen studied.

The results of the measurements of χ_c and χ_{ab} are shown in Fig. 1. The ordinate in Fig. 1 represents the reactive component of the susceptibility only, the resistive component being negligibly small and temperature independent.

In order to examine the field dependence of both χ_c and χ_{ab} , external fields from an air-core solenoid up to 2400 oersteds were applied to the sample parallel to the oscillating measuring field. This was done over the entire temperature range for χ_c and at 1.13°K for χ_{ab} . No evidence of field dependence was found.

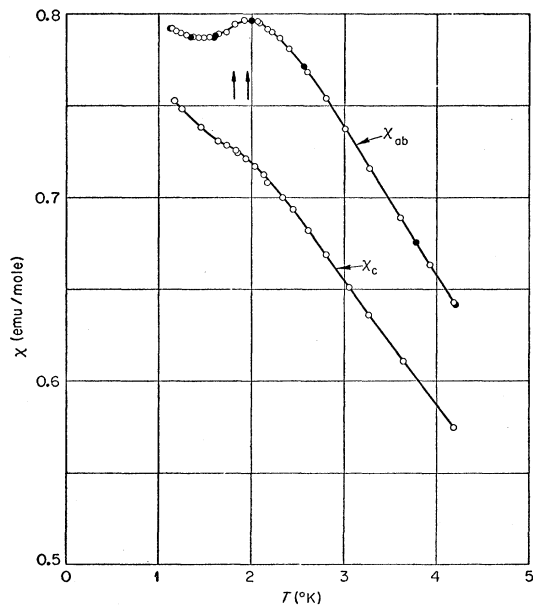


FIG. 1. Magnetic susceptibility of $MnCl_2$ (spherical crystal) as a function of temperature. The arrows locate specific heat maxima (see reference 8). Open and closed circles represent different experiments.

⁹ L. Pauling and J. L. Hoard, *Z. Krist.* **74**, 546 (1930).

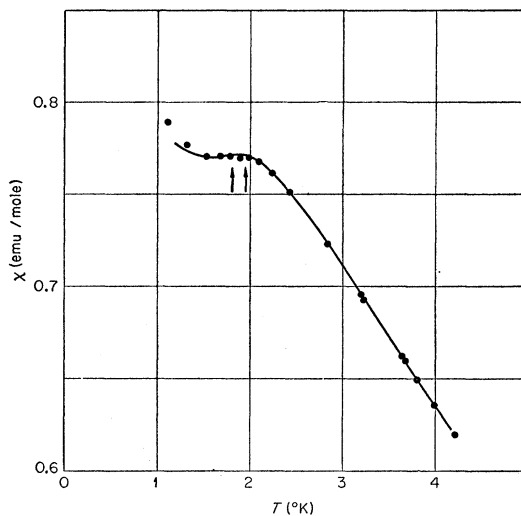


FIG. 2. Magnetic susceptibility of $MnCl_2$ (powder sample) as a function of temperature. The arrows locate specific heat maxima (see reference 8).

These measurements were carried out in collaboration with Dr. R. A. Erickson.

POWDER SUSCEPTIBILITY

The techniques used in measuring the susceptibility of the polycrystalline sample were the same as those applied in the single crystal measurements. The data points, shown in Fig. 2, were obtained from the bridge readings by applying a small, approximate shape correction and normalizing to the powder average (χ_p) of the single-crystal susceptibilities, Fig. 1, at 4.2°K. By virtue of the symmetry of the $MnCl_2$ lattice, χ_p is taken to be

$$\chi_p = \frac{2}{3}\chi_{ab} + \frac{1}{3}\chi_c.$$

The curve in Fig. 2 is this average; it is seen to be in good agreement with the data points for the polycrystalline sample. This good agreement is taken as evidence that the single-crystal material was not contaminated in the process of crystal growing and machining to a spherical shape. As before, the ordinate of Fig. 2 is the reactive component of the susceptibility only, the resistive component being negligible.

DISCUSSION

The irregular behavior of the susceptibility observed in both the single crystal and polycrystalline samples near 1.9°K, Figs. 1 and 2, suggests either a Schottky-type effect due to electric field splittings, or a cooperative magnetic ordering transition. In that the over-all splitting of the spin multiplet of an S -state ion (Mn^{++}) due to crystalline electric fields¹⁰ may reasonably be expected to be quite small compared with 2°K, we dismiss the possibility that this transition is due

¹⁰ M. H. L. Pryce, *Phys. Rev.* **80**, 1107 (1950).

primarily to electric field effects. The sharp specific heat anomalies near 2°K (see Part II⁸) indicate, rather, that the effects observed here are of a co-operative ordering type. The possibility that this transition is ferromagnetic in character can reasonably be ruled out on the basis of the susceptibility measurements since (1) the susceptibility was found to be virtually field independent, (2) no evidence of magnetic hysteresis was observed, and (3) the susceptibility near 2°K was found to be small compared to that predicted by the Curie law, $\chi=C/T$.

In view of the above, we are led to the conclusion that the observed susceptibility anomaly is the result of a transition from the paramagnetic to an antiferromagnetic state. This antiferromagnetic transition, however, must be of an unusual nature in that neither the powder susceptibility nor either component of the single-crystal susceptibility demonstrates the usual maximum in the transition region. In particular, the fact that χ_c does not decrease with falling temperature below the Néel point indicates that the antiferromagnetic state is not one in which the spin moments are aligned along the crystalline *c*-axis. In view of the unusual behavior of the susceptibility below the Néel point, it does not seem possible to derive the magnetic structure from these measurements. In this connection, it is interesting to note a recent calculation by Anderson¹¹ showing that a falling susceptibility is not a necessary property of certain types of antiferromagnetic order.

It is to be noted, that, although Mn²⁺ has the largest spin moment ($S=5/2$) of the isomorphous group MnCl₂, FeCl₂, CoCl₂, and NiCl₂, it nevertheless has a Néel temperature which is an order of magnitude lower than that of the others.

In connection with this investigation, a neutron diffraction study of MnCl₂ at liquid helium temperatures (1.4°–4.2°K) has been initiated at this laboratory by M. K. Wilkinson and C. G. Shull. Preliminary results demonstrate magnetic superstructure lines which first appear near 1.9°K, confirming the above interpretation of the observed susceptibility anomaly as due to an antiferromagnetic transition near 1.9°K. No evidence of ferromagnetism was found.

MAGNETIC ANISOTROPY

The observed magnetic anisotropy in the single-crystal susceptibilities, Fig. 1, may arise from (1) both long- and short-range order in the spin system, (2) magnetic dipole interactions, and (3) crystalline electric fields. At 4.2°K the entropy has achieved approximately 90% of its saturation value $R \ln 6$, so that the cooperative ordering is largely dissipated at that tem-

perature (Part II⁸). Within this assumption, the observed anisotropy should be accounted for mainly in terms of magnetic dipole interactions and crystalline electric field effects. We consider first the effect of magnetic dipole interactions.

Keffer¹² has shown that the contribution to the magnetic anisotropy of a single crystal arising from dipole interactions is given approximately by

$$\chi_{\parallel} - \chi_{\perp} = (\chi_{\parallel} \cdot \chi_{\perp})(\Phi_c - \Phi_a), \quad (1)$$

where Φ_c and Φ_a are dipole sums taken over the neighbors of a Mn²⁺ ion, χ_{\parallel} is the susceptibility measured parallel to the crystalline symmetry axis (χ_c), and χ_{\perp} that measured perpendicular to the symmetry axis (χ_{ab}). The dipole sums Φ_c and Φ_a , whose values are determined by the crystalline symmetry and lattice parameters, were evaluated numerically in this case by the Oak Ridge digital computer, the ORACLE. The sums were performed over neighbors contained within a sphere, and were evaluated out to 5×10^8 neighbors. The numerical value of these sums converge rapidly as a function of the number of neighbors counted. The results of the calculation give $\Phi_c = -0.163$, $\Phi_a = 0.081$. Inserting these values into Eq. (1), along with the values of χ_c and χ_{ab} measured at 4.2°K, we obtain $\chi_c - \chi_{ab} = -0.090$. This is to be compared with the observed anisotropy of -0.068 .

We turn next to the contribution from crystalline electric fields. Pryce¹⁰ has shown that the predominant term in the spin Hamiltonian of a Mn²⁺ ion, arising from the interaction of the Mn²⁺ charge distribution with the tetragonal component of the crystalline field, is of the form DS_z^2 , where D is a constant and S_z is the *z*-component of the spin angular momentum operator. The magnetic anisotropy due to such an interaction has been calculated by Yosida,¹³

$$\chi_{\parallel} - \chi_{\perp} = \chi_p(-D/kT)[0.4S(S+1) - 0.3], \quad (2)$$

where S is the spin quantum number, equal to 5/2. The calculation of the coefficient D in Eq. (2) can be carried out only to an order of magnitude. A rough estimate, similar to that given by Keffer, indicates that, for MnCl₂, D is negative and of the order of hundredths of a wave number. We note that exact agreement with the observed anisotropy requires $D \approx -0.06 \text{ cm}^{-1}$, which is within reason. It should be noted that the precautions taken in orienting the crystal with respect to the cryostat were not elaborate, so that the observed anisotropy is considered to be known only to $\pm 20\%$. In view of this, and the approximate nature of the calculation of the anisotropy, it is considered that the agreement is satisfactory.

¹² F. Keffer, Phys. Rev. **87**, 608 (1952).

¹³ K. Yosida, Progr. Theoret. Phys. (Japan) **6**, 691 (1951).

¹¹ P. W. Anderson, Phys. Rev. **79**, 705 (1950).