

$n^{1/6}r_{\text{eff}}$ . It is likely, however, that in the glassy materials used the nearby proton environments of all the hydrogen atoms were not the same. Hence an interpretation of  $r_{\text{eff}}$  in terms of actual distances would depend upon the assumed nature of the distribution. It should be noted that the satellite intensity, being proportional to  $1/r^6$ , is relatively insensitive to all but the nearest protons. If observations were made with a spectrometer of sufficient sensitivity, a second set of satellites ( $1/r^{12}$  intensity dependence) could be observed corresponding to two neighboring protons concurrently changing state. Such observations would give additional information on the nature of this proton distribution.

Satellite lines have been seen in systems other than those containing atomic hydrogen. In gamma-irradiated materials at low temperatures, the paramagnetic-resonance lines are often sufficiently sharp that the

satellites from environmental protons are completely resolved at 8000 gauss, but they are often weak compared to the central line. At 3000 gauss they are much stronger because of the  $1/H^2$  dependence, but are often not clearly resolved. For the cases discussed here an intermediate field would be optimum. The transition probabilities can be appreciable for distances out to, say, 3 Å. The satellite intensity does not depend upon the magnetic moment of the neighbor nucleus, but if the moment is small the satellites may not be resolved. They will however contribute to the width of the main absorption line. Van Vleck<sup>4</sup> purposely discarded terms giving rise to satellites in his second-moment development, and accordingly, if a moment analysis of a paramagnetic-resonance line is made, care should be taken to exclude the effect of satellite lines.

<sup>4</sup> J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

## Magnetic Susceptibility of a Sintered Rod of $\alpha\text{MnS}\dagger$

ROBERT LINDSAY, *Trinity College, Hartford, Connecticut*

AND

JOHN J. BANEWICZ, *Southern Methodist University, Dallas, Texas*

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The magnetic susceptibility of a sintered sample of  $\alpha\text{MnS}$  was measured from 90°K to 550°K by an absolute Gouy method. The extrapolated susceptibility at 0°K was approximately equal to 7/10 the maximum susceptibility at the Néel point (154°K). It was not possible to fit the data above the Néel point with a unique set of Weiss-Curie constants, probably due to the persistence of short-range ordering effects above the Néel temperature. Upon using the recent Wojtowicz application of the Ising-Bethe theory, a unique set of constants,  $\tilde{J}/k = -100.5^\circ\text{K}$  and  $C_M = 3.57$ , fitted the data satisfactorily between 175°K and 550°K. A diamagnetic correction of  $58 \times 10^{-6}$  per mole was applied to the data before calculating the above values. Above the Néel point the susceptibility of the sintered specimen was less than the susceptibility of a powder sample by a factor which was too large to be explained in terms of the standard correction for powders or by differences in geometry. Multiple maxima in the susceptibility which were outside the range of experimental error were noted at 144°K, 151°K, 157°K, and 167°K. When considered in conjunction with the specific heat anomalies previously detected at 139°K and 147°K, it is suggested that a change in either spin ordering or crystal structure occurs in this temperature region and is responsible for the irregular susceptibility behavior.

### INTRODUCTION

THE magnetic susceptibility of  $\alpha\text{MnS}$  powder has previously been reported by the authors.<sup>1</sup> These data showed a Néel temperature of 154°K and a rather broad plateau of susceptibility between 154°K and 170°K, and indicated that a single set of Weiss-Curie constants would not fit the curve up to 800°K. It was felt that there might be some interest in a study of the sintered type of sample with the same composition and structure.

<sup>†</sup> Assisted by a Frederick Gardner Cottrell grant from the Research Corporation.

<sup>1</sup> J. J. Banewicz and R. Lindsay, Phys. Rev. 104, 318 (1956).

### EXPERIMENTAL

The  $\alpha\text{MnS}$  powder<sup>1</sup> was prepared for sintering by being mixed with distilled water and then extruded as a paste into a long cylindrical rod. After initial drying at 100°C, the rod was sintered in a vacuum of about  $10^{-4}$  mm for two hours at 1150°C. The result was a hard green-grey specimen with a slight metallic luster. Chemical analysis indicated the final composition to be better than 99% MnS. X-ray analysis showed the structure to be NaCl type with a lattice constant of 5.20 Å, the same as the powder sample. The sample had an average diameter of 0.41 cm and a length of 10.0 cm. Its measured density was 2.6 g/cm<sup>3</sup> which is 65% of the crystalline density of 3.99 g/cm<sup>3</sup>. The

density of the original powder in reference 1 was  $\sim 1.2$  g/cm<sup>3</sup>. Magnetic susceptibility measurements were made by a Gouy method over a temperature range from 90°K to 550°K with the apparatus previously described.<sup>1</sup>

### RESULTS

Figure 1 shows the gross appearance of the data taken over the whole temperature range. The data obtained earlier on the powder sample are also shown for comparison. The general patterns are similar except that the sintered susceptibility is about 5% lower in magnitude at temperatures above the Néel point and becomes more than 10% lower at 90°K. Because of small irregularities in the geometry of the sintered sample, the comparison of absolute values is probably uncertain by about 1%. The values of  $\chi_M$  and  $1/\chi_M$ , where  $\chi_M$  is the molar susceptibility, are tabulated in Table I.  $\chi_M$  includes a diamagnetic correction of  $58 \times 10^{-6}$  per mole.<sup>1</sup> The position of the Néel point is the same as for the powder sample, i.e., 154°K.

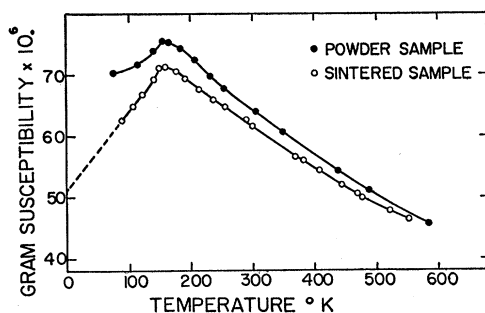


FIG. 1. The magnetic susceptibility of  $\alpha$ MnS, powder and sintered. The points were taken at  $H = 1080, 1545,$  and  $1980$  oe.

Figure 2 shows some typical data when the behavior in the immediate vicinity of the Néel temperature is studied in detail. Examining first the dashed line which represents the cooling curve, we see that the main peak now appears to be split into four peaks, something which was not readily discernible in the same temperature region for the powdered sample. The estimated precision of relative measurement in this region is  $\pm 0.25\%$  or about  $\pm 0.10$  susceptibility units. We feel that these maxima are representative of the sintered sample and not the result of uncertainties in measurement. The solid curve is the warming curve taken after the sample had been kept at 90°K for about four hours following its initial cooling. There is evidence of thermal hysteresis here, since the third and fourth peaks occur at about the same temperatures as on the cooling curve, but are slightly higher in magnitude. This was the only warming run on which such hysteresis was observed.

Figure 3 shows a composite curve with points based on the average of three cooling runs and one warming run (not the warming run in Fig. 2). The mean deviation

TABLE I. Values of  $\chi_M$  (molar susceptibility) and  $1/\chi_M$  as functions of absolute temperature. A diamagnetic correction of  $58 \times 10^{-6}$  per mole has been applied to  $\chi_M$ .

$T^\circ\text{K}$	$\chi_M \times 10^6$	$1/\chi_M$	$T^\circ\text{K}$	$\chi_M \times 10^6$	$1/\chi_M$
175	6189	161.6	248	5728	174.6
180	6156	162.4	254	5686	175.9
185	6131	163.1	290	5502	181.7
191	6078	164.5	300	5401	185.2
194	6032	165.8	368	4973	201.0
204	5994	166.8	381	4922	203.2
210	5966	167.6	406	4805	209.7
214	5936	168.5	442	4577	218.5
218	5901	169.5	467	4463	225.0
232	5829	171.6	476	4401	227.3
237	5795	172.6	520	4201	238.0
241	5763	173.5	551	4093	244.3

in the data for each plotted point is  $\pm 0.17$  unit. The maxima, although smoothed out by the averaging, still appear distinctive. It is also noted that the peak at 157°K is split. This leads us to suspect that there may actually be more than four peaks, some perhaps occurring very close together.

Table II gives a best estimate of the positions and magnitudes of the four peaks based on the available data.

### DISCUSSION

The observed fact that the susceptibility of the sintered sample becomes increasingly lower below the Néel temperature than the corresponding value for the powdered sample is possibly subject to interpretation in the light of a suggestion made by Bizette and Tsai.<sup>2</sup> The susceptibility of a rigid antiferromagnetic structure below the Néel temperature should be lower than that of a finely powdered form at the same field strength because there can be no twisting of microcrystalline grains so that their axes of magnetization are aligned in the preferred planes perpendicular to the external

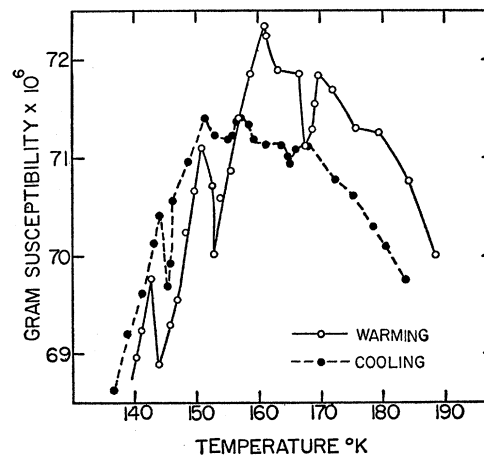


FIG. 2. The magnetic susceptibility of sintered  $\alpha$ MnS on a cooling and warming cycle in the Néel region.  $H = 1980$  oe.

<sup>2</sup> H. Bizette and B. Tsai, *Compt. rend.* **238**, 1575 (1954).

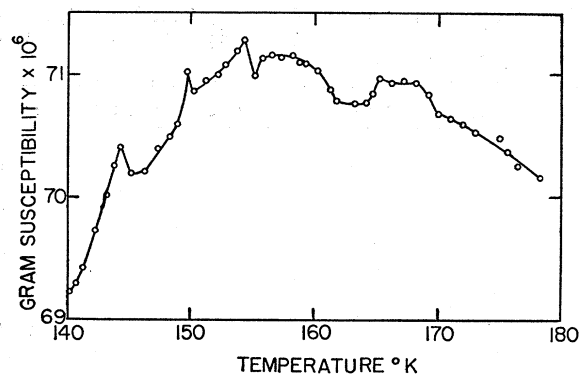


FIG. 3. The magnetic susceptibility based on the average of points taken on three cooling runs and one warming run in the Néel region.  $H=1080, 1545, \text{ and } 1980 \text{ oe}$ .

field. In the powdered form, where such twisting may be mechanically feasible, the contribution from  $\chi_1$  will become greater than that to be expected on the assumption of a random distribution of antiferromagnetic axes, thus leading to an over-all increase in the average value of  $\chi$ . If a random distribution does prevail, the average susceptibility is given by:  $\chi = \frac{1}{3}\chi_{11} + \frac{2}{3}\chi_1$ , and at  $0^\circ\text{K}$   $\chi$  should approach  $\frac{2}{3}\chi_{\text{max}}$  as the contribution from  $\chi_{11}$  vanishes. When the susceptibility curve for the sintered sample in Fig. 1 is roughly extrapolated to  $0^\circ\text{K}$ , a value of about  $0.71\chi_{\text{max}}$  is obtained. Hence these data seem to be consistent qualitatively with the implications of the above suggestions.

An attempt was made to fit the data in Table I to the Weiss-Curie law  $\chi_M = C_M/(T+\theta)$ , but it was impossible to determine a unique set of constants over the entire temperature range. As in our previous work on the powder, we feel this implies the persistence of short-range ordering effects to temperatures well above the Néel point. On the basis of a study of high-temperature power series, Danielian and Stevens<sup>3</sup> have concluded that it is necessary to use experimental data obtained at temperatures at least ten times the Néel temperature to calculate a proper  $\theta$  by the extrapolation method ( $1/\chi_M$  vs  $T$ ). Very recently, Wojtowicz<sup>4</sup> has applied the Ising-Bethe theory to derive an expression in closed form for the susceptibility above the Néel point, and has shown that it is possible to fit the data of reference 1 with a single set of constants up to  $800^\circ\text{K}$ .

TABLE II. Positions of susceptibility maxima.

Peak	$T^\circ\text{K}$	$\chi \times 10^6$ (per gram)
1	$144 \pm 1$	$70.28 \pm 0.20$
2	$151 \pm 1$	$71.22 \pm 0.20$
3	$157 \pm 2^a$	$71.37 \pm 0.08$
4	$167 \pm 2$	$71.17 \pm 0.05$

<sup>a</sup> Possibly split.

<sup>3</sup> A. Danielian and K. W. H. Stevens, Proc. Phys. Soc. (London) **B70**, 326 (1957).

<sup>4</sup> P. J. Wojtowicz, Phys. Rev. **107**, 429 (1957).

His formulation does take into account short-range order, and at very high temperatures his expression reduces to the Weiss-Curie law. His equation has the form

$$\chi_M = \frac{C_M}{T} \left\{ 1 - \frac{n}{2} \left[ 1 - \exp\left(\frac{-\tilde{J}}{kt}\right) \right] \right\}^{-1}, \quad (1)$$

where  $C_M$  is the molar Curie constant,  $T$  is the absolute temperature,  $k$  is Boltzmann's constant,  $n$  is the number of interacting neighbors with a given central ion, and  $\tilde{J} = 4S^2J$ .  $S$  is the spin per magnetic ion and  $J$  the exchange energy of interaction between neighboring ions. From the data for the sintered sample and with  $n=6$ , values of the constants  $\tilde{J}/k$  and  $C_M$  in Eq. (1) were calculated. A value of  $\theta$  can be calculated from the limiting high-temperature relation,  $\theta = -n\tilde{J}/2k$ , as noted in reference 4. These values and their comparison with results on the powdered sample are shown in Table III. The values of  $\tilde{J}/k$  and  $C_M$  reproduce the data with a root-mean-square deviation of 0.6% and maximum deviation of 1.2%. Therefore the Wojtowicz application of the Ising-Bethe theory is capable of

TABLE III. Ising-Bethe constants.

	Powdered <sup>a</sup>	Sintered
$\tilde{J}/k(^\circ\text{K})$	-97.0	-100.5
$C_M$	3.645	3.57
$\theta(^\circ\text{K})$	291	300
Temperature range ( $^\circ\text{K}$ )	170-829	165-550

<sup>a</sup> As calculated in reference 4.

reproducing the sintered data equally as well as the powdered data.

The results of Table III indicate close agreement between the constants for the powdered and sintered data. Hence, even though the sintered particle aggregation possesses a bulk susceptibility different from the powdered aggregation, the Wojtowicz constants do not appear to be significantly affected by this difference. One would expect that the constants  $C_M$  and  $\tilde{J}/k$  should reflect intrinsic properties of the compound and not be sensitive to differences in type of bulk aggregation. It is to be noted in Fig. 1 that at higher temperatures the powder and sintered data show signs of converging. It is also of interest to note that the values of  $C_M$  obtained by the above procedure are considerably lower than the theoretical value of 4.379 which an  $\text{Mn}^{++}$  ion with a spin of  $\frac{5}{2}$  and  $g=2$  should possess.

The difference between the  $\chi$  values for the powder and sintered samples poses the question whether the actual average magnetization itself is a function of the particle size or whether the accurate determination of this magnetization is affected by the particle size. Corrections to the powder data based on the filling factor and demagnetizing factor of the container<sup>5</sup>

<sup>5</sup> B. Bleaney and R. A. Hull, Proc. Roy. Soc. (London) **A178**, 86 (1941).

proved negligible. The data of Richardson and Milligan<sup>6</sup> on NiO indicate that the susceptibility values of an antiferromagnet at and below the Néel temperature can be affected by particle size, and they suggest that the magnetic environment is altered in terms of average number of next nearest neighbors as the particle size is changed. It is conceivable that such effects persist above the Néel temperature as long as some degree of short-range ordering exists.

We do make the somewhat qualified suggestion that the experimental absolute susceptibility associated with the sintered sample is more nearly representative of polycrystalline  $\alpha$ MnS above the Néel point than the corresponding powder data. This statement is based on the intuitive assumption that the sintered sample is probably characterized by a greater homogeneity and continuity of its magnetic environment and the observed fact that its density is closer to that of the single crystal than is the powder specimen.

The apparent presence of multiple maxima in the Néel region is an unorthodox feature of these data. The specific heat data by Anderson<sup>7</sup> indicated two anomalies in this same region, one at 139°K and the other at 147°K. These are quite close to the two lowest maxima observed in this investigation and have about the same separation. One possibility which suggests itself is that perhaps MnS is really characterized by two states of antiferromagnetic spin orientation, somewhat similar to the situation which has been established as existing in  $\alpha$ Fe<sub>2</sub>O<sub>3</sub>.<sup>8</sup> Neutron diffraction studies on  $\alpha$ MnS at 4°K<sup>9</sup> indicate that the spins are aligned alternately parallel and antiparallel in the (111) planes, with the moments in a given plane being ferromagnetically aligned in what is called ordering of the second kind. It is suggested that on heating, somewhere around 140°K at least a portion of the substance undergoes a

change in spin orientation. This might then be expected to show up as an anomaly on the specific heat curve. The eventual breakdown of the antiferromagnetic coupling of this new state would then show up on the specific heat curve as a second anomaly. The fluctuations in the susceptibility at higher temperatures might then appear as a result of fluctuations in the short-range ordering of the two states. Another possibility which cannot be ruled out is that of an actual crystal structure change in this region. The cubic  $\beta$  and hexagonal  $\beta$  forms of MnS both have susceptibilities considerably lower than that of the  $\alpha$  type.<sup>9</sup> Rooksby and Tombs<sup>10</sup> in their x-ray diffraction studies noted no change from the normal  $\alpha$  structure at 200°K, although rhombohedral deformation was noted at 90°K. These hypotheses with regard to the existence of more than one spin state or crystalline form are capable of experimental check.

The multiple maxima effects described place  $\alpha$ MnS in the category of antiferromagnetic substances which display some degree of irregular behavior in the vicinity of the Néel point. These include MnTe,<sup>11</sup> which as a broad uneven transition region as well as some thermal hysteresis; MnCl<sub>2</sub>,<sup>12</sup> which has a double peak on its specific heat curve; UI<sub>3</sub>,<sup>13</sup> which has a double peak on its susceptibility curve; and MnSe,<sup>14</sup> which shows a pronounced thermal hysteresis.

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<sup>6</sup> J. T. Richardson and W. O. Milligan, *Phys. Rev.* **102**, 1289 (1956).

<sup>7</sup> C. T. Anderson, *J. Am. Chem. Soc.* **53**, 476 (1931). (His sample apparently consisted of particles of varying sizes with individual densities of 3.93 g/cm<sup>3</sup>.)

<sup>8</sup> Shull, Strauser, and Wollen, *Phys. Rev.* **83**, 333 (1951).

<sup>9</sup> Corliss, Elliott, and Hastings, *Phys. Rev.* **104**, 924 (1956).

<sup>10</sup> H. P. Rooksby and N. C. Tombs, *Nature* **167**, 364 (1951).

<sup>11</sup> Uchida, Kondoh, and Fukuoka, *J. Phys. Soc. Japan* **11**, 27 (1956).

<sup>12</sup> R. B. Murray and L. D. Roberts, *Phys. Rev.* **100**, 1067 (1955).

<sup>13</sup> L. D. Roberts and R. B. Murray, *Phys. Rev.* **100**, 650 (1955).

<sup>14</sup> R. Lindsay, *Phys. Rev.* **84**, 569 (1951).