

# High-Temperature Magnetic Susceptibility of Sintered $\alpha$ MnS†

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(Received August 20, 1959)

The magnetic susceptibility of sintered  $\alpha$ MnS was measured by a Faraday method at temperatures from 300°K to 1244°K. When the data were fitted by a least squares method to the Weiss-Curie law,  $\chi_M = C_M/(T + \theta)$ , using only points above 675°K, values of  $C_M = 3.94 \pm 0.02$  and  $\theta = 397 \pm 6^\circ\text{K}$  were obtained. Even in this range the  $1/\chi$  vs  $T$  curve was very slightly inflected towards the  $1/\chi$  axis so the above values are considered only as establishing upper limits on the constants. It is suggested that the deviation of  $C_M$  from the theoretical spin only value of 4.379 be interpreted in terms of a reduced ionic character of the MnS bond.

THE magnetic susceptibility of a sintered rod of  $\alpha$ MnS up to 550°K has previously been reported by these authors.<sup>1</sup> In this temperature range the data did not exactly fit a Weiss-Curie law  $\chi_M = C_M/(T + \theta)$  where  $\chi_M$  = molar susceptibility. This was indicated by the fact that the plot of  $1/\chi_M$  vs  $T$  showed a slight concave curvature towards the  $1/\chi_M$  axis. This defect was attributed to the persistence of short range order above the Néel point. Hence the data were fitted to the Wojtowicz application of the Ising-Bethe method, a treatment which does take into account short range ordering effects. It has been since pointed out to us that

TABLE I. Values of  $1/\chi_M$ , where  $\chi_M$  = molar susceptibility, as functions of absolute temperature  $T$ . A diamagnetic correction of  $58 \times 10^{-6}$  per mole has been applied to  $\chi_M$ .  $H = 815$  oe.

Point	Run A T°K	$1/\chi_M$	Point	Run B T°K	$1/\chi_M$
Sample No. 1. Mass 95.8 mg					
1	299	177.6	1	300	182.0
2	393	201.5	2	496	230.0
3	472	222.8	3	720	284.0
4	585	252.0	4	723	282.5
5	688	278.5	5	841	315.0
6	796	305.0	6	934	337.0
7	532	240.5	7	1023	360.0
8	298	177.3	8	1092	377.3
9	416	208.4	9	1219	409.0
10	689	279.3	10	1224	412.5
11	795	303.7	11	979	350.0
12	920	336.6	12	499	228.7
13	996	356.3	13	301	185.0
14	1063	373.5			
Sample No. 2. Mass 129.4 mg					
1	301	182.7	1	300	182.0
2	447	216.5	2	486	225.0
3	550	242.7	3	692	276.8
4	675	273.0	4	837	310.5
5	825	310.0	5	958	340.5
6	1006	357.0	6	1080	371.0
7	1104	382.5	7	1244	417.0
8	1173	400.0	8	946	338.0
9	802	305.5	9	706	278.5
			10	301	183.3

† Assisted by grants from the Research Corporation and the National Science Foundation.

<sup>1</sup> R. Lindsay and J. J. Banewicz, *Phys. Rev.* **110**, 634 (1958).

the equation to which the data were fitted, Equation (2) in the paper by Wojtowicz,<sup>2</sup> was in error.<sup>3,4</sup> Therefore the calculated values of the constants  $\bar{J}/K$ ,  $C_M$ , and  $\theta$  in reference 1 are not valid.

We have extended the susceptibility measurements on sintered  $\alpha$ MnS to 1244°K in an effort to locate a region where the Weiss-Curie equation  $\chi_M = C_M/(T + \theta)$  might be applicable thus enabling representative values of  $C_M$  and  $\theta$  to be directly obtained.

The Faraday method was used to measure the susceptibility of two spherical samples with masses of 95.8 and 129.4 mg. The samples were taken from the sintered rod of reference 1. The force due to the inhomogeneous field was measured with a Sartorius balance in a helium atmosphere. The data obtained on four different runs are shown in Table I. A diamagnetic correction of  $58 \times 10^{-6}$  per mole has been applied.<sup>5</sup>

These data have been fitted to  $\chi_M = C_M/(T + \theta)$  by the least squares method. Only points above 675°K were used. The 675°K cutoff point was rather arbitrarily chosen. Including data below this temperature worsened the fit to the straight line. With higher cutoff temperatures the number of data points became too few for good averaging. The results of this treatment are shown in Table II as well as the root mean square percentage deviation and the maximum percentage deviation of the calculated values of  $1/\chi_M$  from the experimental values of  $1/\chi_M$ . It was evident from this analysis that  $1/\chi_M$  vs  $T$  was still slightly inflected towards the  $1/\chi_M$  axis even in the temperature range above 1000°K. However it is assumed that the values  $C_M = 3.94$  and  $\theta = 397^\circ\text{K}$  do establish upper limits on  $C_M$  and  $\theta$  even though they are not necessarily exactly representative of the limiting values as  $T \rightarrow \infty$ .

The value of  $C_M = 3.94$  is significantly smaller than the theoretical value of  $C_M = 4.379$  which is calculated under the assumption that  $g = 2$  and the  $\text{Mn}^{++}$  ion is in an  $S$  state with five unpaired electrons. One possible explanation for the discrepancy might be that the  $g$

<sup>2</sup> P. J. Wojtowicz, *Phys. Rev.* **107**, 429 (1957).

<sup>3</sup> P. J. Wojtowicz (private communication).

<sup>4</sup> A. Danielian (private communication).

<sup>5</sup> J. J. Banewicz and R. Lindsay, *Phys. Rev.* **104**, 318 (1956).

value in this case is less than the electron spin resonance value of 2.00. Measurements<sup>6</sup> in the temperature range from the Néel point ( $\sim 155^\circ\text{K}$ ) to  $300^\circ\text{K}$  indicate that  $g=2.01$ , so this explanation seems unlikely.

Another possibility is that the ionic model of  $\text{Mn}^{++}$  no longer completely holds and the electronic structure is correspondingly affected. The electronegativity model of Pauling implies that the ionic character of MnS should be somewhat less than that of MnO, and should decrease further with MnSe and MnTe. Existing susceptibility data on  $\text{MnO}$ <sup>7,8</sup> indicate values of  $C_M$  between 4.27 and 4.37 at temperatures up to about  $500^\circ\text{K}$ . The values of  $C_M$  (see Table III) found for the other compounds in this series are less than the MnO value, and, except for MnSe, decrease as the ionic character decreases. Hence, very crudely, the decrease in  $C_M$  is correlated with a decrease in the ionic character of the bond. It might also be noted that the experimental

TABLE II. The Weiss-Curie constants  $C_M$  and  $\theta$  calculated from data in Table I above  $675^\circ\text{K}$ .

Run	Temp. range ( $^\circ\text{K}$ )	$C_M$	$\theta$	$\delta_{\text{rms}}^a$	$\delta_{\text{max}}^b$
A	688-1063	3.95	409	0.5	1.0
B	720-1224	3.93	394	0.3	0.5
C	675-1175	3.91	392	0.2	0.3
D	692-1244	3.95	393	0.5	0.8

$C_M(\text{Av}) = 3.94 \pm 0.02$   
 $\theta(\text{Av}) = 397 \pm 6^\circ\text{K}$

<sup>a</sup>  $\delta_{\text{rms}}$  = Root mean square of percent deviation of fitted line from experimental points.

<sup>b</sup>  $\delta_{\text{max}}$  = Maximum percent deviation of fitted line from experimental points.

MnO bond distance is only 0.03 Å less than that calculated by the addition of ionic radii, while for MnS and MnSe the difference increases to about 0.10 Å.

Since the covalent complexes which the  $\text{Mn}^{++}$  ions form would have only one unpaired electron, the increase in covalent character seems to change the magnetic properties in the right direction.<sup>9</sup> However, the bonds existing between the  $\text{Mn}^{++}$  and the negative ions cannot be thought of as intermediate forms resonating between the extreme ionic and covalent types because resonance is not possible between structures with different numbers of unpaired electrons.

<sup>6</sup> L. R. Maxwell and T. R. McGuire, *Revs. Modern Phys.* **25**, 279 (1953).

<sup>7</sup> Bhatnagar, Cameron, Harbord, Kapur, King, and Prakash, *J. Chem. Soc. (London)*, Part II, 1433, (1939).

<sup>8</sup> W. D. Johnston and R. R. Heikes, *J. Am. Chem. Soc.* **78**, 3255 (1956).

<sup>9</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1945), Chap. III.

TABLE III. Approximate high-temperature Weiss-Curie constants for four manganese chalcogenides.

Compound	$C_M$
MnO <sup>a</sup>	4.32
MnS	3.94
MnSe <sup>b</sup>	4.0 <sup>d</sup>
MnTe <sup>c</sup>	3.24

<sup>a</sup> See references 7 and 8.

<sup>b</sup> A. Serres, *J. phys. radium* **8**, 146 (1947).

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

<sup>d</sup> The  $1/\chi$  vs  $T$  curve shows signs of requiring a value somewhat lower than this at higher temperatures.

It is perhaps of interest to point out that susceptibility measurements on dilute alloys of copper with manganese have indicated moments of the  $\text{Mn}^{++}$  ion there to be less than the spin only value.<sup>10</sup> In this case the bonding is metallic and there are conduction electrons available from the host metal which can possibly go into the partially filled  $3d$  shells of the  $\text{Mn}^{++}$  ions, and suppress the moment.

It might be possible to explain a decrease in the magnetic moment in terms of a theory presented by Zener and Heikes concerning  $d$ -shells vs  $d$ -band models.<sup>11</sup> According to this view the electronic structure of the transition element chalcogenides can be represented in terms of both a shell model and a band model. Above the Néel temperature the shell model is internally consistent only if the width of the energy band  $\Delta E$ , composed of pairs of magnetic ions  $\text{T}^+$  and  $\text{T}^{++}$ , is less than twice the activation energy  $E_i$  required to create such a pair. As the chalcogenide ion changes from  $\text{O}^{--}$  to  $\text{S}^{--}$  to  $\text{Se}^{--}$  it becomes more polarizable, hence decreasing the necessary activation energy  $E_i$ . When the consistency condition for the shell model breaks down a band model becomes more appropriate. In the extreme case the band model is characterized by a decoupling of the  $3d$  electron spins normally associated with each magnetic ion. On this picture MnS with its reduced magnetic moment per ion might represent the first tendency towards this decoupling. Accordingly the suggestion is made that an analysis of the limiting values of Weiss-Curie constants of the transition element chalcogenides might throw additional light on the general problem of the electronic structure models of these compounds.

<sup>10</sup> Owen, Browne, Arp, and Kip, *J. Phys. Chem. Solids* **2**, 85 (1957).

<sup>11</sup> C. Zener and R. R. Heikes, Westinghouse Research Laboratories Scientific Paper 8-0628-P9 (unpublished).