Application of the Ising-Bethe Theory to the Susceptibilities of the Polymorphic Forms of MnS

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(Received April 11, 1957)

With the aid of the Ising-Bethe theory it has been shown that the susceptibilities of the three polymorphic forms of MnS can be correlated with the same indirect exchange mechanism as that required to explain the observed magnetic structures. It has also been possible to obtain certain semiquantitative information concerning the Mn−S−Mn indirect exchange interaction. In view of the results reported in this paper, it is recommended that greater use be made of the Ising-Bethe or Bethe-Weiss-Li theories in the interpretation of susceptibility data obtained at temperatures not too far above the Néel temperature.

INTRODUCTION

THE magnetic properties of the three polymorphic forms of manganous sulfide have recently been investigated. Banewicz and Lindsay[1] have measured the susceptibility of αMnS (NaCl structure), while Carter and Stevens[2] have measured the susceptibilities of the two β modifications (zincblende and wurtzite structures). Corliss, Elliott, and Hastings[3] have not only measured the susceptibilities of all three forms, but have also determined the magnetic ordering structures below the Néel temperature.

The magnetic ordering structures have been explained[3] on the basis of an indirect exchange mechanism which (a) in αMnS favors magnetic coupling between next-nearest Mn ions through six octahedrally located 180° Mn−S−Mn bonds, and (b) in the β forms favors magnetic coupling between nearest Mn ions through twelve tetrahedral Mn−S−Mn bonds. A discussion of the high-temperature susceptibilities in terms of this coupling scheme has not been given, however. It is the purpose of this note to show that with the aid of the Ising-Bethe theory the susceptibilities of all three forms can be correlated with the same indirect exchange mechanism as that required to understand the magnetic structures. In addition, it has been possible to obtain some semiquantitative information on the Mn−S−Mn indirect exchange interaction.

ISING-BETHE THEORY

The principal contributions to the Ising-Bethe theory for magnetism have been made by Peierls,[4] Firgau,[5] Weiss,[6] and Ziman.[7] The main features of the theory are the use of the Ising form of Hamiltonian and the Bethe[8] cluster method of solution. A given ion and the immediate neighbors with which it interacts are considered in detail, while the interaction of this cluster with the remainder of the system is treated in an approximate but self-consistent manner. The Hamiltonian of the cluster is given by:

$$\mathcal{3C}_c = -2JS_{0z}S_{1z} - g\beta S_{0z}H_0 - g\beta S_{1z}H_1, \qquad (1)$$

where J is the exchange interaction between neighboring ions, and S_{0z} and S_{1z} are the z components of the spins of the central ion and combined shell of neighbors, respectively. The external field (in the z direction) is H_0, while H_1 is an effective field combining the interaction of the shell of neighbors with the external field and the remainder of the crystal. Above the Néel temperature H_1 is eliminated by the consistency condition, $m_0 = m_1$: the moments of the central and neighbor ions are equal in magnitude and in the direction of H_0. The partition function can be evaluated exactly in the Ising approximation, and unlike the quantum-mechanical theory[6,9] the susceptibility above the Néel point is obtained in closed form:

$$\chi = \frac{C}{T}\left\{1 - \frac{n}{2}\left[1 - \exp\left(\frac{-\tilde{J}}{kT}\right)\right]\right\}^{-1}, \qquad (2)$$

where C is the molar Curie constant, n is the number of neighbors with which the central ion interacts, and $\tilde{J} = 4S^2J$. T is the thermodynamic temperature, k is Boltzmann's constant, and S is the spin per magnetic ion. At very high temperatures Eq. (2) reduces to the familiar Curie-Weiss law:

$$\chi = C/(T+\theta), \quad \theta = -n\tilde{J}/2k. \qquad (3)$$

The departure of Eq. (2) from the Curie-Weiss law at lower temperatures is a manifestation of the persistence of short-range magnetic ordering above the Néel temperature.

NUMERICAL CALCULATIONS AND DISCUSSION

The high-temperature reciprocal susceptibilities reported in references 1 and 3 were examined from the point of view of Eq. (2). According to the magnetic coupling scheme advanced by Corliss et al.,[3] n is set equal to six for αMnS, while $n = 12$ for the β forms. The

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TABLE I. Results obtained on fitting experimental data
to the Ising-Bethe susceptibility equation.

Form	αMnS[a]	αMnS[b]	β-cubic[b]	β-hexag.[b]
$\tilde{J}/k$ (°K)	−97.0	−87.7	−86.8	−89.9
C	3.645	3.379	3.169	3.525
Δ_{rms}	0.900	0.635	2.070	1.638
μ_B	5.42	5.22	5.06	5.33
θ (°K)	291	263	521	539
Temperature range (°K)	170–829	167–405	195–440	195–471

[a] Data of reference 1.
[b] Data of reference 3.

constants C and $\tilde{J}$ were then determined for each set of data by the method of least squares on an IBM-650 calculator. The results of this calculation are presented in Table I. Included with the Curie constants C and the effective exchange interactions $\tilde{J}$ are the root-mean-squared deviations (Δ_{rms}) in χ^{-1} obtained, the number (μ_B) of Bohr magnetons per Mn^{++} ion, the effective Curie-Weiss θ as given by the second of Eq. (3), and the temperature ranges over which the data were fit to Eq. (2).

The Ising-Bethe theory is found to be capable of reproducing the data of reference 1 over a temperature range of 660°K with a root-mean-squared deviation of about $\frac{1}{2}\%$ and a maximum deviation of only 2% using a *single* set of constants C and $\tilde{J}$ (a single Curie-Weiss law fitted to the high-temperature data gives deviations of 10% near the Néel point). The results obtained for the data of reference 3 are about as good, having root-mean-square deviations of the order of 1%. The persistence of short-range order mentioned by Banewicz and Lindsay[1] and discussed in detail by Wangsness[10] is therefore very well accounted for by this theory.

The constants C and $\tilde{J}$ are found to be almost the same for the three polymorphs as measured by Corliss and co-workers[3] (the difference in $\tilde{J}$ for αMnS is the result of a basic disagreement in the data between references 1 and 3). That the $\tilde{J}$ do have approximately the same values for all three polymorphs, and that the agreement between theory and experiment is so good, indicate that our choice of interacting neighbors is a correct one, and that the susceptibilities can indeed be correlated with the same indirect exchange mechanism which explains the magnetic structures.

The Ising-Bethe theory is also capable of giving some semiquantitative results concerning the properties of the Mn−S−Mn indirect exchange interaction. Table II summarizes the available information on Mn−S−Mn bond distances and angles[2,3] together with the $\tilde{J}$ values computed here. Assuming that exchange interactions decrease with increasing separation, the $\tilde{J}$ for the β forms should be larger in magnitude than that for αMnS. The values are found to be approximately the same however. This suggests an angular dependence which decreases the magnitude of the interaction upon increasing the deviation of the Mn−S−Mn angle from 180°. The superexchange model proposed by Anderson[11] contains such a directional property.

Also of interest are the values of θ obtained from the $\tilde{J}$ by the use of Eq. (3). These are equivalent to those

TABLE II. Characteristics of the Mn−S−Mn bonds
in the manganous sulfides.

Form	αMnS	β-cubic	β-hexag.
MnS distance (A)	2.606	2.425	2.427
Mn−S−Mn angle	180°	109.5°	109.5°
$\tilde{J}/k$ (°K)	$\begin{cases} -97.0^{a} \\ -87.7^{b} \end{cases}$	−86.8[b]	−89.9[b]

[a] From data of reference 1.
[b] From data of reference 3.

which would be obtained by fitting the Curie-Weiss law to very-*high*-temperature susceptibility data. The values obtained by this method are lower than those reported in references 1 to 3 by almost a factor of two. Thus the problem of having exceptionally large θ values as discussed by Carter and Stevens[2] does not arise when the Ising-Bethe theory is used. Danielian and Stevens[12] have recently come to an equivalent conclusion: to obtain the correct θ by linear extrapolation of $(\chi^{-1}-T)$ curves it is necessary to use data obtained at temperatures at least ten times the Néel temperature.

In view of the results reported in this paper, it is recommended that investigators consider interpreting experimental data with the aid of the Ising-Bethe or Bethe-Weiss-Li[6,9] theories in which the concepts of discrete near-neighbor interaction structure and short-range order are explicitly included.

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