Characterization of the magnetic phase transition in cubic β-MnS

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The magnetic phase transition in the cubic form of β-MnS has been found to be first order. This result is discussed in relation to proposed magnetic structures as well as to theoretical considerations based on symmetry and on renormalization-group calculations.

I. INTRODUCTION

MnS exists in three allotropic modifications: the rocksalt or α structure, the zinc-blende or cubic β structure, and the wurzite or hexagonal β structure. The magnetic structures of all three forms were determined[1] a number of years ago by powder neutron diffraction, proceeding from the assumption that the spins were collinear. In the case of the cubic β form, this analysis led to a spin arrangement forecast by Anderson[2] for an fcc array of cations, and now called type III ordering. This structure, which is associated with a wave vector $\vec{k}=(2\pi/a)(\frac{1}{2},1,0)$, where a is the lattice constant of the chemical unit cell, is shown in Fig. 1. The spin axis lies in the yz plane at an undetermined angle to the y axis. If the requirement of collinearity is relaxed in the structure determination, the conclusions are unchanged, except that the spins in the planes at $x=\frac{1}{4}$ and $\frac{3}{4}$ can be rotated an arbitrary but equal amount with respect to those in the planes at $x=0$ and $\frac{1}{2}$. It should be noted that the indeterminacy of spin orientation would not be removed by the use of single crystals (if one could be grown!) unless it could be made single domain.

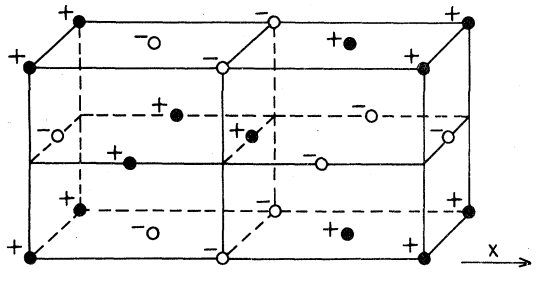

FIG. 1. Magnetic ordering scheme deduced from diffraction studies. Spins lie in the yz plane but the direction within this plane is not completely determined. Collinear as well as noncollinear possibilities are discussed in the text.

Keffer and O'Sullivan[3] pointed out a serious difficulty with the proposed structure in that the magnetic dipolar energy is minimized by placing all spins parallel to the x axis. In a later paper[4] Keffer showed that the Moriya-Dzyaloshinskii interaction is allowed by the structure and might be of sufficient magnitude to outweigh the magnetic dipole interaction among the spins. By trial and error he selected a simple noncollinear spin arrangement which he judged very likely to have lowest energy, and showed that it gave the same powder diffraction pattern as the collinear case. In the proposed model, the spins are still confined to the yz plane, but those at $x=\frac{1}{4}$ (and $\frac{3}{4}$) are rotated 90° about the x axis relative to those at $x=0$ (and $\frac{1}{2}$).

Both the collinear and the Keffer models have been considered as bases for the description of the magnetic ordering transition. Bak and Mukamel[5] showed that the appropriate order parameter for the type III antiferromagnet has 12 components. The group representation to which it belongs was found to be reducible, and, according to Landau theory,[6] the transition is expected to be first order. By contrast, it has been shown[7] that the Keffer model is described by a six-component order parameter which transforms according to a single irreducible representation of the paramagnetic symmetry group. The corresponding Landau-Ginzburg-Wilson (LGW) Hamiltonian yields a stable fixed point and therefore, the transition associated with this representation *may* be second order.

We undertook a powder neutron study of the ordering transition because of its intrinsic interest and in the hope of determining critical indices for comparison with renormalization-group predictions, if it proved to be second order. In addition, it was realized that a determination of the order of the transition could, in principle, help decide between competing spin models. We have also analyzed the renormalization-group transformations associated with the $n=6$-component LGW model. We find that if the magnetic structure in the vicinity of T_N is the

one proposed by Keffer, the stable fixed point is *inaccessible,* and the transition is expected to be first order. Therefore, observation of a second-order transition would rule out both the collinear model and the Keffer ordering. The magnetic structure in this case would have to be one for which the stable fixed point of the $n=6$ model is accessible. A first-order transition would be consistent with both the collinear and the Keffer models.

II. SAMPLE PREPARATION

The stable form of MnS at room temperature and above is the rocksalt modification, and it forms readily. Synthesis of the thermodynamically unstable cubic β form is less straightforward and was carried out in the following way: To a freshly prepared saturated solution of reagent-grade manganous acetate [$Mn(CH_3COO)_2 \cdot 4H_2O$] sufficient reagent-grade sodium acetate [$Na(CH_3COO) \cdot 3H_2O$] was added to make the molar ratio of manganous acetate to sodium acetate 19:1. In the process, sufficient water was added, as needed, to prevent any precipitation of the acetates. This solution was then acidified with glacial acetic acid until it registered just on the acid side of neutral on a pH paper test strip (i.e., $7 > p\mathrm{H} >> 6$). A second saturated solution was then prepared containing the stoichiometrically equivalent amount of sodium sulfide ($Na_2S \cdot 9H_2O$). This solution was filtered and used soon after preparation.

The precipitation of the β-MnS was accomplished by dropwise addition of the sulfide solution to the rapidly stirred acetate solution. The resulting solution, containing precipitate, was allowed to "digest" overnight, with a cover to exclude air. The β-MnS was removed by filtration and washed successively with water, methanol, and finally chloroform. Excess chloroform was removed from the final product by vacuum pumping. The yield was almost 100%.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The polycrystalline sample was sealed in a cylindrical aluminum cell containing He exchange gas to provide good thermal contact, and placed in a variable-temperature cryostat whose temperature, in the vicinity of the transition, could be controlled with a precision of 1 mK. The temperature dependence of the order parameter was followed by monitoring the intensity of the principal antiferromagnetic reflection, which indexes as (110) in the magnetic cell shown in Fig. 1. After each change in temperature, to ensure satisfactory thermal equilibration, the peak intensity was followed for a period of hours until the individual points were found to fluctuate randomly about the average value with deviations consistent with their

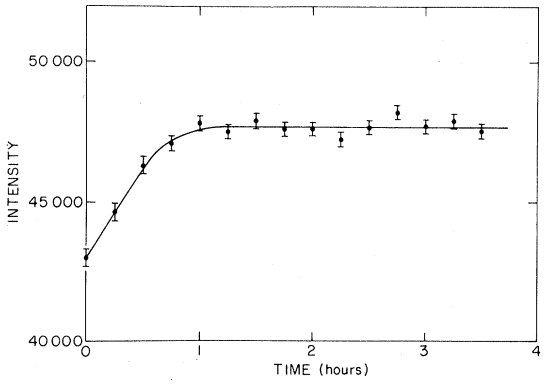

FIG. 2. Typical behavior of peak intensity as a function of time following a change in cryostat temperature.

statistical uncertainties. A typical run is shown in Fig. 2. (In this case the run was actually continued overnight and no further change was observed.)

In the vicinity of 98 K the intensity changes abruptly, suggesting a first-order transition. This is shown in Fig. 3, where the solid line, representing the square of the Brillouin function for spin $\frac{5}{2}$, has been fitted to three lowest temperatures to indicate qualitatively the temperature dependence expected for a second-order transition.

Proof of the first-order character of the transition was provided by the observation of hysteresis as shown in Fig. 4. Here the arrows indicate the direction of temperature change; runs with decreasing temperatures were started after long equilibration at about 110 K and those with increasing temperature, after soaking at 78 K. The numbers attached to the points represent the time sequence in the four traverses of the transition region. The hysteresis is approximately 0.13 K and, although small, is

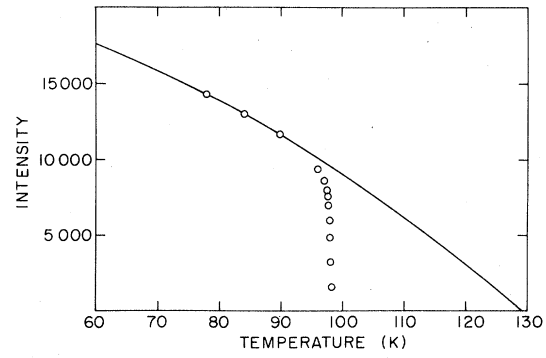

FIG. 3. Temperature dependence of magnetic peak intensity. The solid line is the square of the Brillouin function for spin $\frac{5}{2}$ fitted to the three lowest-temperature points, and is intended to provide a qualitative indication of the deviation from second-order behavior.

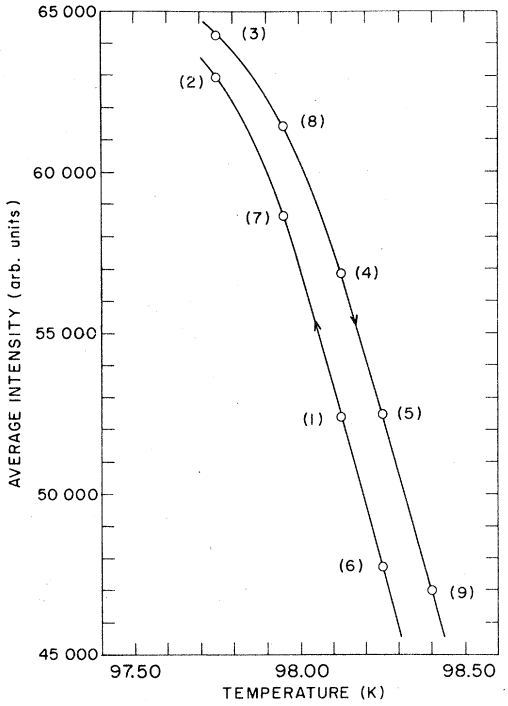

FIG. 4. Hysteresis of the magnetic transition. Arrows indicate direction of temperature change between the end points of 78 and 110 K, and numbers in parentheses give the time sequence of the measurements.

nevertheless large compared to the errors in the individual points. To see this, let us examine points 6 and 9 of Fig. 4. The errors arising from the uncertainty in the intensities can be converted with sufficient accuracy to errors in temperature by using the measured slope for the average intensity, which is approximately 36 000 counts/K. The errors in the two points arising from counting statistics of the total counts thus become 0.002 and 0.003 K, respectively, giving a combined error of 0.0036 K, which is only about 3% of the observed hysteresis.

IV. RENORMALIZATION-GROUP CONSIDERATIONS

Let $(\phi_i, \bar{\phi}_i)$ $i=1,2,3$ be the six-component order parameter associated with the antiferromagnetic ordering proposed by Keffer. The order parameters ϕ_i and $\bar{\phi}_i$ correspond to the magnetic structures in which the nonprimitive unit cell is doubled in the i direction, $i=1,2,3$ for x,y,z, respectively (for details see Ref. 7). The LGW Hamiltonian takes the form:

$$\mathcal{H}=-\tfrac{1}{2}\sum_{i=1}^{3}[r(\phi_i^2+\bar{\phi}_1^2)+(\nabla\phi_i)^2+(\nabla\bar{\phi}_i)^2]$$
$$-u\left(\sum_{i=1}^{3}\phi_i^2+\bar{\phi}_i^2\right)^2-v\sum_{i=1}^{3}(\phi_i^2+\bar{\phi}_i^2)^2-W\sum_{i=1}^{3}\phi_i^2\bar{\phi}_i^2 \quad . \tag{1}$$

This model has a stable fixed point satisfying $w^*=0$, $u^*>0$, and $v^*<0$. At this fixed point the quartic anisotropy favors an ordering along some $[\alpha\beta\alpha\beta\alpha\beta]$ direction in the $(\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3)$ space, where α and β are determined by the initial value of the parameters u, v, and w. Such a magnetic structure involves doubling of the nonprimitive unit cell in *all three directions.* The ordered structure reached in a second-order transition is governed by the stable fixed point. In this case the magnetic structure in the vicinity of T_N is therefore expected to be of the $[\alpha\beta\alpha\beta\alpha\beta]$ type. However, the structure suggested by Keffer is an $[\alpha\beta0000]$ ordering with doubling in only one direction. The transition to this structure is not governed by the stable fixed point, and is expected to be first order. One may argue, however, that the $[\alpha\beta0000]$ ordering is favored only at low temperatures and is not present at T_N. The reason why this might be so is that in the $[\alpha\beta\alpha\beta\alpha\beta]$ case the sublattice magnetization has different magnitude on different sublattices. This is an energetically unfavored ordering at low T. However, if the magnetic structure near T_N is of the $[\alpha\beta\alpha\beta\alpha\beta]$ type, one would expect a spin-flop transition at a lower temperature associated with $[\alpha\beta0000]$ ordering. Such a transition has not been observed experimentally.

We therefore conclude that the experimentally observed first-order transition is consistent with both the collinear and the Keffer orderings.

ACKNOWLEDGMENTS

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