Critical behavior in the Ising antiferromagnet $MnTe_2$

J. M. Hastings, L. M. Corliss, and W. Kunnmann
Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

D. Mukamel
Department of Physics, The Weizmann Institute of Science, Rehovot, Israel

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Symmetry considerations indicate that although $MnTe_2$ has cubic symmetry, the antiferromagnetic transition in this compound is Ising-like. Critical properties of $MnTe_2$ have been studied in the reduced temperature range $5\times10^{-4}\leq|t|=|(T-T_N)/T_N|\leq1\times10^{-1}$ by neutron scattering techniques. It is found that the critical exponent $\beta=0.431\pm0.009$ is anomalously large, while the value of $\nu=0.635\pm0.014$ is in reasonable agreement with the expected theoretical estimates. The exponents can be reconciled with the theoretical values by application of corrections to scaling. However, the size of some of the corrections and the increased uncertainties in the exponents produced by the introduction of additional fitting parameters, make it difficult to be sure the analysis is justified.

I. INTRODUCTION

The Ising model with nearest-neighbor interactions describes the critical behavior of a large variety of physical systems. These include liquid-gas critical points,[1–4] phase transitions in binary fluid mixtures,[3–5] certain transitions in binary alloys[3,6] and a variety of magnetic systems.[3,6] Extensive experimental studies of the critical behavior of many fluids (either at the liquid-gas point or in binary mixtures) have been carried out and detailed comparisons with the theoretically expected behavior have been made in the last two decades. It is now generally accepted that the critical behavior of these systems is well described by the $d=3$ dimensional Ising model, and that, for example, the critical exponent β is very close to the expected value[7] $\beta\simeq0.325$ of the Ising model. For reviews on critical behavior of fluids see, e.g., Refs. 1–5. In magnetic systems, on the other hand, the situation is less clear. First, the number of physical systems corresponding to the Ising model is much smaller than in fluids. Moreover, while many experiments in fluids were performed at reduced temperatures as small as $|t|=|(T-T_c)/T_c|\simeq10^{-5}$, in magnetic systems, due to inhomogenieties in crystals, it is usually difficult to get that close to T_c. Most experiments in magnetic systems were therefore performed at reduced temperatures $|t|\gtrsim10^{-4}$–10^{-3}, and the exponents obtained are in some cases substantially different from the theoretical predictions. The critical exponent β of some Ising-like magnetic systems, together with the reduced temperature range over which the experiments were performed are given in Table I.

In this paper we report the results of a neutron diffraction study of the critical behavior of $MnTe_2$. This is a cubic crystal which undergoes an antiferromagnetic transition at $T_N\simeq86.55$ K. Usually one expects such transitions in cubic crystals to be described by an $n\geq3$ component vector model. However, in the case of $MnTe_2$ (as in the case of DyAlG) the order parameter which describes the transition has a single component, and the transition is expected to be Ising-like. It is thus of interest to study the critical behavior of $MnTe_2$ and compare it to other Ising-like systems. In order to determine the dimen-

TABLE I. Critical exponent β of some Ising-like magnetic systems.

Compound	β	Range of t	Reference
$FeCl_2$	0.29 ±0.01	10^{-4}–10^{-1}	8
MnF_2	0.335±0.005	5×10^{-5}–2×10^{-1}	3,9
FeF_2	0.325±0.01	5×10^{-4}–10^{-1}	3,10
DyAlG (powder)	0.33 ±0.01	2×10^{-4}–10^{-1}	11
DyAlG (single crystal)	0.26 ±0.02	5×10^{-4}–2×10^{-2}	12
$MnCl_2\cdot4H_2O$	0.297±0.003		13
$GdAlO_3$	0.31 ±0.01	6×10^{-5}–1×10^{-2}	14
Cr_2O_3	0.35 ±0.01	3×10^{-5}–3×10^{-2}	15
$DyAlO_3$	0.311±0.005	5×10^{-3}–4×10^{-2}	16
$GdVO_4$	0.50 ±0.05	1×10^{-3}–2×10^{-2}	17
$DyPO_4$	0.314	1×10^{-4}–3×10^{-2}	18
$HoPO_4$	0.315±0.01	7×10^{-3}–7×10^{-2}	19

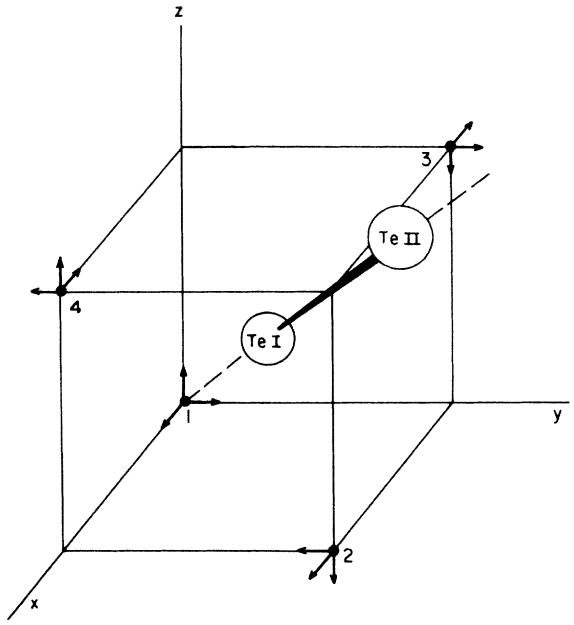

FIG. 1. One octant of the $MnTe_2$ unit cell. Arrows represent spin components of manganese atoms. Te_2 groups centered at the unoccupied corners in the above diagram have been omitted.

sionality of the order parameter, we note that the paramagnetic symmetry group of $MnTe_2$ is Pa3. Each unit cell contains four molecules and the positions of the Mn ions are (1) (000), (2) $(\frac{1}{2}\frac{1}{2}0)$, (3) $(0\frac{1}{2}\frac{1}{2})$, and (4) $(\frac{1}{2}0\frac{1}{2})$, respectively. The site symmetry of these ions is $\bar{3}$. The magnetic structure has been studied[20–22] by Mössbauer and neutron diffraction techniques. It has been found that each of the four magnetic ions in the unit cell points along a different body diagonal direction (see Fig. 1). Let $\mathbf{S}_i \equiv (S_{ix}, S_{iy}, S_{iz})$, $i = 1, \ldots, 4$ be the spin vector at site i. In the antiferromagnetic phase one has $\mathbf{S}_1 = S(111)$, $\mathbf{S}_2 = S(1\bar{1}\bar{1})$, $\mathbf{S}_3 = S(\bar{1}1\bar{1})$, and $\mathbf{S}_4 = S(\bar{1}\bar{1}1)$, where S determines the magnitude of the magnetic moment. Note that the magnetic moment at each site points along the threefold axis of that site and it is not free to choose any of the other three-body diagonal axes at that site. By applying the symmetry elements of the space group Pa3, it is found that the magnetic structure is invariant under the group. The symmetry element which is lost at the transition is time reversal. Thus, the order parameter associated with the transition has only one component ϕ given by

$$\phi = S_{1x} + S_{1y} + S_{1z} + S_{2x} - S_{2y} - S_{2z} - S_{3x} + S_{3y} - S_{3z} - S_{4x} - S_{4y} + S_{4z} .$$

The transition is therefore expected to be Ising like.

II. EXPERIMENTAL METHOD AND SAMPLE PREPARATION

Neutron scattering data were obtained with a two-crystal spectrometer utilizing a germanium monochromator, 20-min in-pile collimation, and appropriate masks to decrease background scattering. The sample was a cleaved crystal with dimensions $3 \times 3 \times 0.5$ mm, grown by vapor transport using iodine as the carrier. The powdered materials used for transport were synthesized from spectrographic grade elemental manganese and tellurium by solid-state reaction in an evacuated sealed tube. The transport was carried out in a tube 6 in. long and 1 in. in diameter, fitted with a porous silica plug at its center. The charge, consisting of an intimately ground mixture of 90% $MnTe_2$ and 10% MnTe, was placed on one side of the plug together with a 0.2 mm^3 crystallite of iodine, and the air rapidly evacuated. The tube was placed in a furnace with the charged end maintained at 690 °C and the other at 660 °C for a period of several days, in which time suitable crystals were obtained.

III. DATA COLLECTION AND ANALYSIS

An approximate value of the Néel temperature, T_N, was obtained by determining the temperature dependence of the intensity of the diffuse scattering at a fixed angular position displaced 0.35° from the magnetic Bragg (010) peak position. The size of the displacement required to avoid the Bragg peak was determined by measuring the Bragg profile at low temperature where the diffuse scattering is absent. The results, shown in Fig. 2, yield an estimate for T_N of 86.55 ± 0.05 K.

The angular dependence of the critical scattering was obtained at a series of temperatures close to and above T_N, and was corrected for small second-order nuclear Bragg contributions by subtracting scans taken at temperatures well above the transition. The inverse range pa-

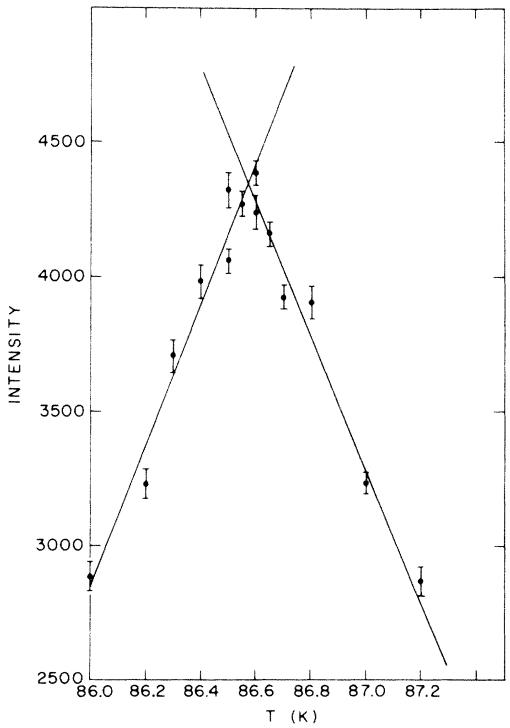

FIG. 2. Intensity of critical scattering at a fixed angular setting of the crystal, displaced 0.35 degrees from the magnetic Bragg (010) peak position. From the position of the maximum, T_N is estimated to be 86.55 ± 0.05 K.

rameter, κ, was obtained by least-squares analysis of the angular variation of intensity, using as a fitting function, a Lorentzian cross section convoluted with the instrumental resolution function.

Integrated intensities of the magnetic Bragg peak were collected by rotating the crystal with the counter held fixed. The data were corrected for second-order scattering, as noted above. Close to T_N, critical scattering corrections to the integrated intensities were made by determining κ from the scattering in the wings and calculating the contribution at the center.

IV. DETERMINATION OF β AND ν

It is well known that if data are restricted to a small region close to T_N, the values of critical indices obtained from power-law fits are strongly correlated with T_N itself. While an independent value of T_N can be obtained from the temperature variation of the critical scattering, as indicated above, the method generally lacks the sensitivity required in the determination of exponents because data must be collected relatively far from the magnetic reciprocal-lattice point. However, the exponents ν and β, determined from power-law fits above and below T_N, respectively, change in opposite directions in response to a change in T_N, and fits to the individual power laws exhibit variances which, as a function of T_N, are unsymmetrical about their minima, but in opposite senses. Greater sensitivity in determining T_N can therefore be achieved by minimizing the combined error of the two fits.

As a measure of the agreement between calculated and observed quantities we have used the weighted R factor commonly employed in least-squares analysis:

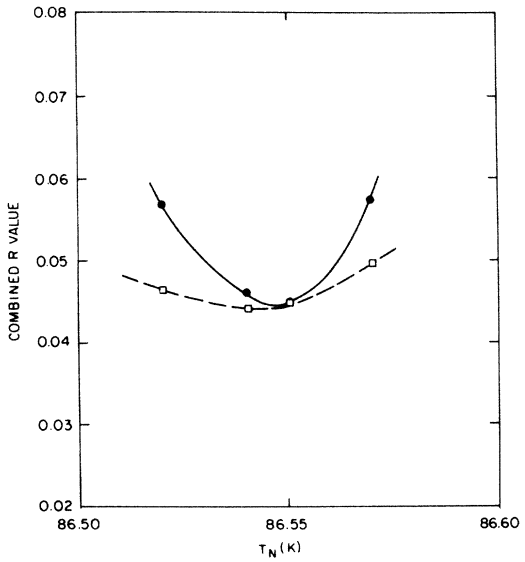

FIG. 3. Dependence on T_N of the combined R factor for fits to the temperature dependence of the order parameter and inverse-range parameter. Solid and dashed lines refer to the uncorrected and corrected power laws, respectively.

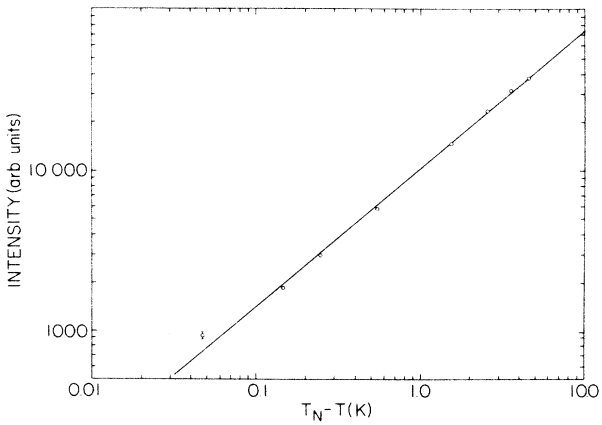

FIG. 4. Power-law fit of the temperature dependence of the magnetic Bragg intensity.

$$R=\left[\frac{\sum_i w_i(Y_i^{\rm calc}-Y_i^{\rm obs})^2}{\sum_i w_i(Y_i^{\rm obs})^2}\right]^{1/2}, \quad w_i=\text{weights}.$$

For a series of assumed values of T_N, the combined R value of the least-squares fits of power laws to the temperature dependence of the inverse range parameter, κ, and the order parameter, M, was determined. The value of T_N corresponding to minimum R was then taken to be the correct value. The dependence of R on T_N is shown in Fig. 3, where it is seen that the minimum occurs at $T=86.547$. This may be compared to the qualitative estimate of 86.55 ± 0.05 obtained from the maximum in the critical scattering at fixed angular setting. With the more refined value of T_N the critical exponents are found to be

$$\beta=0.431\pm0.009\,,$$

$$\nu=0.635\pm0.014\,.$$

The least-squares fits to the data are shown in Figs. 4 and 5. Whereas ν agrees very well with the theoretical estimate of 0.634, the value of β is far from the expected value of 0.325, and the scaling law $(d-2+\eta)\nu=2\beta$, with $\eta\simeq0$, is violated.

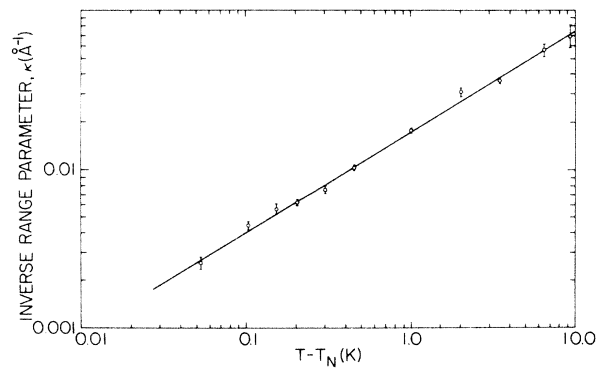

FIG. 5. Power-law fit of the temperature dependence of the inverse-range parameter κ.

V. POSSIBLE SOURCES OF ERROR IN β

In the treatment of the data, it is tacitly assumed that the only process contributing to the increase in magnetic Bragg intensity with decreasing temperature in the critical region is the growth of the order parameter. One might be led to question this assumption because of the unusual magnetic structure of $MnTe_2$. According to the model, individual spins have components of equal magnitude with respect to the three cubic axes, and are directed along the four [111] axes. The x, y, and z components contribute individually to the (110), (100), and (010) reflections, respectively. The measurements reported above refer only to the z component but should be adequate as long as the original configuration is maintained. However, considering the errors assigned in the Mössbauer experiments, it is conceivable that the high value of β could have been produced by a small rotation of the spins which would increase the z component progressively as the temperature was lowered. This, of course, would have decreased the x and y components correspondingly and would have resulted in an anomalously low value of β for these components. Note that such a rotation involves an extra phase transition at some temperature below T_N. To test this idea, the exponents were checked for the x and y components, using the (110) and (100) reflections. The results were found to be essentially the same as for the more carefully studied z component, and clearly eliminate this possible explanation.

Some error in β can be expected to arise from extinction in highly perfect crystals. These errors are in general quite small because extinction is itself a function of intensity and vanishes as $T \rightarrow T_N$. Furthermore, extinction, if present, would decrease β and could not be invoked to explain the observed anomaly. Nevertheless, an investigation of extinction in the nuclear peaks demonstrated that such effects, in the intensity range used for the determination of β, were quite negligible.

VI. CORRECTIONS TO SCALING

An attempt was made to reconcile the data with the theoretical values for the exponents by applying corrections to scaling. Fitting functions for the order parameter and the inverse range parameter were taken to be

$$M = A(\Delta T)^{\beta}[1 + C(\Delta T)^{\Delta_1}] ,$$

$$\kappa = B(\Delta T)^{\nu}[1 + D(\Delta T)^{\Delta_1}] ,$$

where Δ_1, the correction-to-scaling exponent, is held fixed at the value 0.5 given by mean field and renormalization-group calculations.[7]

The combined R value of the two fits exhibits a shallow minimum as a function of T_N and is shown in Fig. 3. The minimum is slightly displaced from that obtained without corrections to scaling and has been taken to be 86.54 K. Corresponding to this value of T_N the parameter values were found to be

$$\beta = 0.353 \pm 0.042 ,$$

$$\nu = 0.673 \pm 0.041 ,$$

with $C = 0.174$ and $D = -0.060$. In the case of the order parameter the range of ΔT covered was 0.04 to 4.5 K, giving a correction at the highest ΔT of 0.37. For κ, ΔT varied from 0.06 to 9.46 K, giving a maximum correction of -0.18.

Introduction of the correction terms increases the uncertainty in β and ν. The overall R value is improved slightly, but probably not significantly. A significance test of the weighted R-factor ratio[23] based on R(uncorrected)/R(corrected) equal to 1.0199 and 1.0010 for ν and β, respectively, indicate that the power laws without correction to scaling cannot be rejected even at the 50% level of significance. Under the circumstances one can say that the results are consistent with corrections to scaling, but that the justification for these corrections has not been clearly established.

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