Critical behavior of the principal magnetoelectric susceptibilities of $GdAlO_3$

R. M. Hornreich*
Department of Electronics, The Weizmann Institute of Science, Rehovot, Israel

Hans J. Scheel
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

B. Sharon*
Department of Electronics, The Weizmann Institute of Science, Rehovot, Israel

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The three independent magnetoelectric susceptibilities of $GdAlO_3$ have been measured in the critical region $6\times10^{-5} < \Delta T/T_N < 1\times10^{-2}$. For all three elements, we find power-law behavior with the same critical exponent $\beta_a = 0.31 \pm 0.01$. Although Gd^{3+} is an S-state ion and the dominant interaction is isotropic Heisenberg exchange, this exponent is Ising-like. This is interpreted as being due to the strong uniaxial character of the magnetic order. Our results are compared with those for other magnetoelectric materials.

I. INTRODUCTION

The compound $GdAlO_3$ crystallizes in an orthorhombically distorted perovskite structure (space group $Pbnm$) with four formula units per unit cell.[1] Below $T_N = 3.9$ K, it exhibits an antiferromagnetic spin structure.[2,3] The magnetic behavior of $GdAlO_3$ has been extensively investigated.[2-16] The reason for this interest is that $GdAlO_3$ is an excellent system for studying the properties of uniaxial antiferromagnets with dominant Heisenberg exchange interaction between nearest-neighbor spins and comparing the results with predictions based upon various theoretical models.

Interestingly, in view of the above, the antiferromagnetic mode characterizing the ordered Gd^{3+} spin system was not, until recently, entirely clear. Magnetic studies[3,7,8] had indicated that the spins were aligned with the b crystallographic axis and both optical[4] and magnetic[7] studies had implied that the configuration was one in which the spins of all the nearest neighbors of a given Gd^{3+} spin were aligned antiparallel to it. Thus, in the notation of Bertaut,[17] the spin mode was expected to be G_y. However, following the suggestion of Tenenbaum,[18] Mercier and Velleaud[19] had carried out magnetoelectric measurements which showed unambiguously that the spins order in a G_xA_y mode. This disagreement was resolved in two recent studies[20,21] which pointed out that the antiferromagnetic axis is in fact parallel to the a rather than the b axis, and that G_x is therefore the correct designation for the Gd^{3+} spin structure.

In addition to the general studies cited above, there have been a limited number of investigations of critical behavior in $GdAlO_3$. In particular, Rohrer[22,23] has studied the properties of $GdAlO_3$ near the bicritical point.[24] In addition, Cashion *et al.*[8,25] have carried out an analysis of the singularity in the specific heat near the critical point. They reported a logarithmic divergence below T_N and a power-law divergence above T_N with α, the specific-heat critical exponent, equal to 0.29. The $T > T_N$ data have, however, been recently reanalyzed by Guttman.[26] He obtained $\alpha = 0.14 \pm 0.03$.

Here, we report[27] on a study of the critical behavior of the magnetoelectric (ME) susceptibility of $GdAlO_3$. This study is, we believe, particularly interesting for two reasons: One, $GdAlO_3$ is the first simple two-sublattice Heisenberg antiferromagnet whose critical behavior has been intensively studied by means of ME measurements, and two, results are given, for the first time, for the critical exponent of more than one element of a ME susceptibility tensor.

In Sec. II, we summarize our experimental procedure and present the results of our measurements. In Sec. III, we discuss the implications of our study and compare our findings with those carried out on other ME materials and with the predictions of theoretical models of critical behavior.

II. EXPERIMENTAL

A. Crystal preparation

Our measurements were performed on flux-grown $GdAlO_3$ crystals. Earlier attempts to grow this promising laser host from the melt[28] produced crystals with cracks and twin domains. A destructive transition to a rhombohedral or cubic perovskite phase at temperatures above 1600 °C was postulated. It could not be verified due to experimental limitations. In order to evaluate the possibility of melt growth, a flux-grown $GdAlO_3$ crystal was heated to 1800 °C; after cooling at

about 100°/h to room temperature twins and cracks were observed in the formerly untwinned crystal. Therefore, crystals were grown at relatively low temperatures from high-temperature solutions.[29]

A PbO-PbF_2-B_2O_3 solvent was used as crystals grown from the solvents based on Bi_2O_3 (see Ref. 30) contained a few percent Bi (Ref. 29, p. 89). High-purity chemicals (264 g Gd_2O_3, 120 g Al_2O_3, 840 g PbO, 840 g PbF_2, 48 g B_2O_3, and 12 g PbO_2) in a sealed 500-cm^3 platinum crucible were heated at 1300 °C for 15 h. After temperature cycling[31] a cooling rate of 0.3°/h was applied down to 960 °C, where the remaining solution was decanted. Flux remanents were dissolved in hot diluted nitric acid. By using the accelerated crucible-rotation technique[32,33] in combination with localized cooling, the number of nuclei was drastically reduced and a faster stable-growth rate[31] achieved so that several crystals with inclusion-free regions of 1–2 cm^3 could be produced. The cube-shaped crystals obtained were colorless to yellow and frequently showed a brown zone around the central dendritic region. Crystals smaller than about 5–10 mm were free of inclusions. Such crystals contained 400–450 ppm Pb and less than 10 ppm F as shown by chemical analyses.

B. Procedure and results

For the ME measurements, an oriented crystal was cut into the form of a rectangular parallelepiped with its edges parallel to the orthorhombic crystallographic axes. The crystal dimensions were 2×2×3 mm with the latter parallel to the c axis. In a series of experiments, silver electrodes were painted successively onto each pair of opposing faces of the crystal. It was then cooled to below T_N in the presence of parallel electric (~5 kV/cm) and magnetic (~9 kOe) fields so as to introduce a ME remanent state in the antiferromagnetic material.[34] The magnetic moment induced in the material by applying an alternating voltage (650 V at 2 kHz) was measured using apparatus previously described.[35] Three nonzero elements of the ME susceptibility tensor α_{11}, α_{22}, and α_{33} were found. The observed temperature dependence of all three susceptibilities was similar to that reported by Mercier and Velleaud.[19] We thus confirm that the antiferromagnetic mode is G_xA_y and that the antiferromagnetic axis is along a.[20,21]

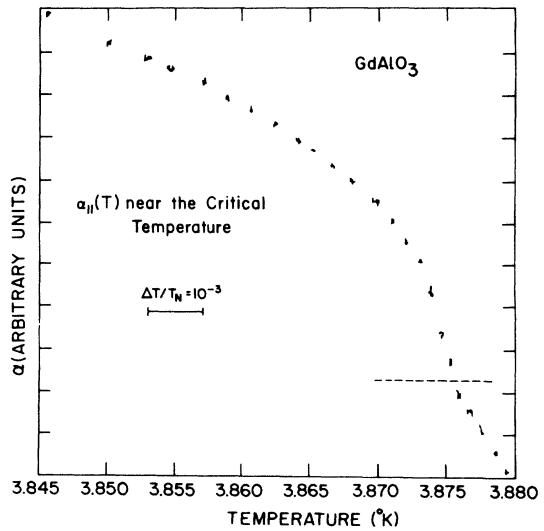

FIG. 1. Temperature dependence of the magnetoelectric susceptibility matrix element α_{11} near T_N. When fitting this data to a power law in $(1-T/T_N)$ data points below the dashed line were ignored (see text).

In the critical region, all data were recorded point by point at fixed temperatures. The temperature was sensed by means of an Allen-Bradley 100-Ω 0.1-W resistor placed immediately behind one of the electrodes. At each point the temperature was determined by a measurement of the vapor pressure of the helium gas. The crystal-resistor assembly was immersed directly in the liquid helium. This served to essentially eliminate temperature gradients and also to reduce the time required to establish a new thermal equilibrium following a change in vapor pressure to approximately 15 min. During each measurement, the pressure was kept constant to within ±0.2 Torr (equivalent to a relative accuracy of $\pm 4\times10^{-4}$ K) by means of a Cartesian manostat. The absolute temperature accuracy was 2×10^{-3} K. Each data point was recorded over a 2 min period with the time constant of the lock-in amplifier set at 1 sec. A typical set of data is shown in Fig. 1. The variation of each measurement in both amplitude and temperature is clear from the figure.

Two independent sets of data were recorded for α_{11}, α_{22}, and α_{33}. In order to check that the "rounding-off" of the data in the immediate vicinity of T_N (see Fig. 1) was not due to temperature inhomogeneities, α_{11} measurements were also taken on a 1×1×1 mm sample. Essentially identical results were obtained, the only difference being the larger relative variation in α_{11} at each point due to the signal-to-noise ratio being an order of magnitude smaller. The rounding-off effect was again present. It is thus probably due to inhomogeneities and local strain in the crystal. Our ability to approach T_N was limited by this effect rather than by the apparatus employed.

In the critical region the ME susceptibility is expected to exhibit asymptotic power-law behav-

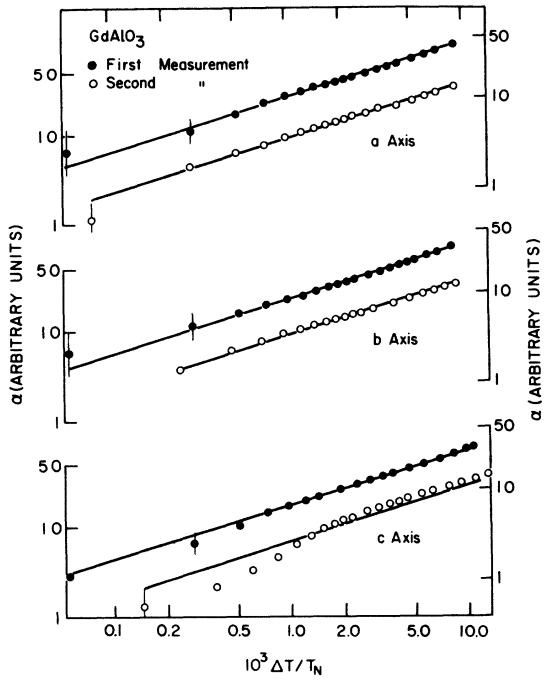

FIG. 2. Log-log plots of the magnetoelectric susceptibility matrix elements α_{11}, α_{22}, and α_{33} vs temperature difference from T_N. The ordinate of the first (second) measurement is on the right- (left-) hand side of the figure. The theoretical fits to the data are given by the solid lines.

ior[36] of the form

$$\alpha = D(1 - T/T_N)^{\beta_\alpha}. \quad (1)$$

We therefore fitted each of our six sets of data to an expression of this form under the following conditions: (i) Data points in the rounded-off region above $T = 3.875$ K (see Fig. 1) are neglected. (ii) The critical temperature T_N is the same for all sets of data. (iii) The ME critical exponent β_α is the same for at least the pair of data sets corresponding to a given element of the susceptibility tensor. (Least-squares fits carried out without this restriction gave essentially identical results.) (iv) Since the magnitude of a given α may vary slightly from measurement to measurement due to small differences in the degree of ME anneal,[37] a different value for D is allowed for each data set.

The fit was carried out by computer using a best least-squares-fit criterion. The critical exponents obtained were $(\beta_\alpha)_a = 0.318 \pm 0.01$, $(\beta_\alpha)_b = 0.310 \pm 0.01$, and $(\beta_\alpha)_c = 0.306 \pm 0.01$. The errors quoted are statistical and refer to two standard deviations in the given parameter with the other parameters fixed at their optimal values.

Since all three exponents were equal to within the statistical error, we carried out a second fit to the experimental data with the additional restriction that β_α have the same value for all six sets of data. The results of this analysis were

$$T_N = 3.8756 \pm 0.0004 \text{ K}, \quad \beta_\alpha = 0.31 \pm 0.01. \quad (2)$$

In (2) the error limits quoted are again statistical in origin. If the uncertainty in the absolute temperature calibration is taken into account, we have $T_N = 3.876 \pm 0.002$ K. This is in excellent agreement with the value $T_N = 3.875 \pm 0.005$ K reported from magnetic studies[11] on similarly prepared crystals.

The theoretical fits to the six sets of experimental data are shown in Fig. 2. For each set the values of T_N and β_α given in (2) together with the corresponding best-fit value of D were used to obtain the theoretical line. Note that the experimental data lie in the temperature region $6 \times 10^{-5} \leq \Delta T/T_N \leq 1 \times 10^{-2}$. A summary of our results, together with those obtained for other ME materials, is given in Table I.

TABLE I. Reported critical exponents of matrix elements of the magnetoelectric susceptibility tensor. The starred elements are those for which β_α has been measured. (T_N: Néel temperature; $\Delta T = T_N - T$.)

Material	Magnetic space group	T_N (K)	Elements of α	Matrix critical exponents β_α	Temperature range $\Delta T/T_N$	Ref.
$GdAlO_3$	$Pb'n'm'$	3.88	α_{11}^*, α_{22}^*, α_{33}^*	0.31 ± 0.01	6×10^{-5}–1×10^{-2}	This work
$TbAlO_3$	$Pb'n'm'$	3.90	α_{11}, α_{22}, α_{33}^*	0.32	Not given–4×10^{-2}	38
$DyAlO_3$	$Pb'n'm'$	3.53	α_{11}, α_{22}, α_{33}^*	0.311 ± 0.005	5×10^{-3}–4×10^{-2}	39
$GdVO_4$	$I4_1'/a'm'd$	2.43	$\alpha_{11}^* = -\alpha_{22}^*$	0.50 ± 0.05	1×10^{-3}–2×10^{-2}	40
$DyPO_4$	$I4_1'/a'm'd$	3.39	$\alpha_{11}^* = -\alpha_{22}^*$	0.314	1×10^{-4}–3×10^{-2}	41
$HoPO_4$	$I4_1'/a'm'd$	1.39	$\alpha_{11}^* = -\alpha_{22}^*$	0.315 ± 0.01	7×10^{-3}–7×10^{-2}	42
Cr_2O_3	$R\bar{3}'/m'$	306	$\alpha_{11} = \alpha_{22}$, α_{33}^*	0.35 ± 0.01	3×10^{-5}–3×10^{-2}	43

III. DISCUSSION

From Table I, we see that all reported studies of the critical behavior of the ME susceptibility[38-43] have been successfully fitted to power-law expressions. However, no theoretical model describing ME critical exponents has as yet been developed. Using molecular-field models, it has been shown[44] that β_α in antiferromagnets is equal to $\frac{1}{2}$, the same as the critical exponent for the sublattice magnetization. This result holds for all components of the ME susceptibility tensor and is independent of the atomic mechanism[44] underlying the ME effect. The only additional treatment is that of Rado,[41,44] who argued, for the case of Ising-like $DyPO_4$, that

$$\alpha(T)/\alpha(0) = M(T)/M(0)\,, \tag{3}$$

e.g., that the ME susceptibility is proportional to the sublattice magnetization. Of course, it immediately follows from (3) that these two quantities have the same critical behavior and this was verified[41] by comparing the experimental ME data with the result $\beta = 0.312 \pm 0.005$ derived from series-expansion calculations on Ising models.[45] Further, although the argument leading to (3) was based upon both a particular atomic mechanism being responsible for magnetoelectricity and the nature of the Dy^{3+} crystal-field splittings in $DyPO_4$ it appears likely that the proportionality between α and M is valid in the critical region even if (3) does not hold rigorously for all $T \leq T_N$. [For the case of $DyPO_4$, neutron-diffraction data[46] for $M(T)/M(0)$ appear to be somewhat lower than those for $\alpha(T)/\alpha(0)$ at $T/T_N \simeq 0.8$. There is, however, considerable scatter in the neutron-diffraction data.] Thus, ME studies of $TbAlO_3$,[38] $DyAlO_3$,[39] and $HoPO_4$,[40] have also given values of β_α (see Table I) that are in excellent agreement with the critical exponent $\beta = 0.312 \pm 0.005$ of the sublattice magnetization. Further, the exponent $\beta_\alpha = 0.32$ found for $TbAlO_3$ is in agreement with the value $\beta = 0.32 \pm 0.08$ derived from optical-line-shift studies[47] in the range $4 \times 10^{-2} \leq \Delta T/T_N \leq 15 \times 10^{-2}$. Finally, the ME exponent $\beta_\alpha = 0.35 \pm 0.01$ found[43] for Cr_2O_3 is the same as that reported[43,48] as characterizing the critical behavior of the sublattice magnetization.

From the above, it appears that there are good grounds for believing that the equality $\beta_\alpha = \beta$ holds generally for antiferromagnets. Renormalization-group[49] calculations applied to simple models support this conclusion.[50] If we thus accept this exponent equality as a working hypothesis, it immediately follows that all nonzero matrix elements of the ME susceptibility tensor of a material must necessarily have the same critical exponent. The results presented here for the case of $GdAlO_3$ are the first experimental verification of this conclusion.

For the particular case of $GdAlO_3$, it follows from (2) that $\beta = \beta_\alpha = 0.31 \pm 0.01$. This value is, of course, essentially identical to those reported for the Ising model and for Ising-like systems $DyPO_4$, $DyAlO_3$, $TbAlO_3$, and $HoPO_4$. It differs significantly from the values $\beta = 0.385 \pm 0.025$ and $\beta = 0.365 \pm 0.035$ calculated by means of series expansions for quantum ($S = \frac{1}{2}$) and classical ($S \to \infty$) Heisenberg models, respectively.[51] This is, however, not surprising since $GdAlO_3$ exhibits a pronounced uniaxial anisotropy[7,8] with an effective anisotropy field of approximately 3 kOe as compared with an exchange field of about 20 kOe. Thus, as predicted by renormalization-group studies,[24,52] we would expect $GdAlO_3$ to exhibit Ising-like behavior even though the dominant exchange interaction is isotropic Heisenberg exchange. This is also evident in the $T > T_N$ specific-heat results[8,25] for $GdAlO_3$, where the value $\alpha = 0.14 \pm 0.03$ found by Guttman[26] is consistent with the theoretical Ising-model prediction[45] $\alpha = \frac{1}{8}$. Here again, the measured value differs significantly from the Heisenberg-model predictions[51] $\alpha = -0.20 \pm 0.04$ ($S = \frac{1}{2}$) and $\alpha = -0.14 \pm 0.04$ ($S \to \infty$).

In closing, we note that ME studies of both the phase diagram[22] and the critical exponent of $GdAlO_3$ at and in the vicinity of the bicritical point would be of great interest. The theoretical prediction[24,52] is that, at the bicritical point itself, isotropic Heisenberg behavior should be observed together with crossover behavior[53] as this point is approached. A number of studies of transitions produced by applying a magnetic field to an antiferromagnetic crystal have been carried out using the magnetoelectric technique.[54] The results show that this method should be particularly useful for mapping out magnetic phase diagrams in low-anisotropy antiferromagnets such as $GdAlO_3$.

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