

Statistical Mechanics and Critical Behavior of the Magnetoelectric Effect in GdVO_4 [†]

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Utilizing the magnetoelectric (ME) effect, the magnetic space group of GdVO_4 has been determined to be $I4_1'/amd$. The temperature dependence of the ME susceptibility α was measured from 1.6°K to $T_N = 2.43^\circ\text{K}$. Using a modified molecular-field theory it is concluded, from the temperature dependence of α , that the mechanism(s) underlying the effect can be an electric-field-induced Dzialoshinsky interaction and/or an electric-field-induced g shift. The magnitude of α indicates that the former mechanism is the more likely one. The critical behavior of α was measured in the range $0.977 \lesssim T/T_N \lesssim 0.999$. A critical exponent of $\beta = 0.50 \pm 0.05$ was found. This is considerably higher than that expected for a three-dimensional two-sublattice Heisenberg model with nearest-neighbor interactions only and is suggestive of higher than first-neighbor exchange interactions which act to enhance the long-range order of the system. Such interactions could have a significant effect on the critical behavior due to the small number of nearest neighbors on the diamond lattice formed by the Gd^{3+} moments.

Gadolinium vanadate, in conformity with other rare-earth vanadates, crystallizes in a tetragonal zircon structure with space group $I4_1/amd$.¹ The unit cell is shown in Fig. 1. GdVO_4 exhibits antiferromagnetic order below $T_N = 2.50^\circ\text{K}$ with the Gd^{3+} moments aligned along the c crystallographic axis.² The magnetic measurements can be understood in terms of a Heisenberg model of the simplest two-sublattice type, wherein antiferromagnetic exchange between a given Gd^{3+} moment and its four nearest neighbors is the predominant interaction.² Referring to Fig. 1, this model corresponds to having the moments at sites 1 and 3 parallel to each other and antiparallel to the moments at sites 2 and 4.

Since the identification of the antiferromagnetic structure from the magnetization study is indirect and thus not completely conclusive, one of the objectives of our work was to confirm the proposed structure unambiguously by means of magnetoelectric (ME) measurements. The usefulness of ME measurements in magnetic structure determinations has been pointed out previously.³ A recent example is provided by the ME study of MnNb_2O_6 by Holmes *et al.*⁴

In addition to the magnetic-structure assignment, two other aspects of the ME effect were investigated. These were (a) the mechanisms underlying the ME susceptibility and (b) the critical behavior of the ME susceptibility in the region immediately below T_N .

The single crystals of GdVO_4 used in our study

were grown by a method in which the compound crystallizes out from solution in molten flux. When the flux consisted of $2\text{PbO}-\text{V}_2\text{O}_5$, GdVO_4 crystals grew as good quality rods of maximum thickness 1.5 mm and contained only 0.03-at. % Pd.⁵ With $4\text{Bi}_2\text{O}_3-\text{V}_2\text{O}_5$ as flux, the rods obtained were thicker, but analysis showed the presence of 7-at. % Bi^{3+} , substituting for Gd^{3+} in the crystal lattice.^{6,7} The particular crystals used in our experiments were prepared with $4\text{Bi}_2\text{O}_3-\text{V}_2\text{O}_5$ as flux and were 2.5 mm in cross section.

Referring again to Fig. 1 and assuming for the moment that the magnetic unit cell is equal to the chemical cell, we see that there are three configurations consistent with c being the antiferromagnetic axis of GdVO_4 as required by the magnetization

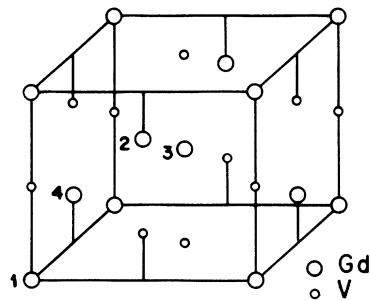


FIG. 1. Crystal structure of GdVO_4 ; only the Gd and V positions are shown.

study of Cashion *et al.*² These are (a) sites 1, 3 \uparrow , 2, 4 \uparrow ; (b) sites 1, 2 \uparrow , 3, 4 \uparrow ; or (c) 1, 4 \uparrow , 2, 3 \uparrow . The arrows \uparrow , \downarrow here represent magnetic moments lying parallel and antiparallel to the c direction, respectively. The magnetic space groups (and point groups) corresponding to each of these configurations are⁸ (a) $I4'_1/a'm'd$ ($4'/m'm'm$), (b) $I_p m'm'a$ ($mmm1'$), and (c) $I_p mm'a'$ ($mmm1'$). For the latter two groups magnetoelectricity is forbidden, but for case (a) the effect is allowed and the ME susceptibility matrix, in the crystal-axis system, will take the form⁹

$$\begin{pmatrix} \alpha & 0 & 0 \\ 0 & -\alpha & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

Finally, in the event that the magnetic unit cell is a multiple of the chemical cell, the ME effect is once again forbidden as the symmetry element $1'$ will belong to the magnetic point group.

For the ME measurements, silver electrodes were painted on opposite faces of a $GdVO_4$ crystal. The faces chosen were parallel to the c crystalline axis and were thus perpendicular to one of the a directions. The sample was then cooled to 1.6°K in the presence of parallel electric and magnetic fields so as to introduce a ME remanent state in the antiferromagnetic material.¹⁰ The magnetic moment induced in the material by applying an alternating voltage to the electrodes was measured using a technique described previously.¹¹

As seen in Fig. 2, a nonzero ME susceptibility was found at $T=1.6$ °K. From this, we can immediately conclude that case (a) describes the spin configuration in ordered $GdVO_4$ and that $I4'_1/a'm'd$ is the correct magnetic space group assignment. The situation as regards the vanadate is thus different from that of the aluminate $GdAlO_3$, where the ME structure determination¹² did not agree with the model predicted from optical¹³ and magnetic^{14,15} measurements.

The measured temperature dependence of α is shown in Fig. 2. As the temperature was raised, α decreased monotonically and vanished at $T_N=2.43$ °K. This is somewhat lower than the value of 2.50°K found by Cashion *et al.*² and is probably due to the presence of Bi^{3+} in our samples. A similar reduction in T_N due to the ionic substitution of Bi^{3+} for Gd^{3+} occurs in the case of $GdAlO_3$.¹⁵

To compare the results of Fig. 2 with theory, the perpendicular (to the antiferromagnetic axis) ME susceptibility was calculated on the assumption that either "single-ion" or "two-ion" mechanisms could be responsible for the measured α . If the perpendicular ME susceptibility is attributed exclusively to an electric-field-induced Dzialoshinsky-type term¹⁶ and/or an electric-field-induced g shift,¹⁷ α is given by^{16,18}

$$\alpha = a\chi_{\perp}\langle m \rangle. \quad (1)$$

Here χ_{\perp} is the magnetic susceptibility perpendicular to the antiferromagnetic axis and $\langle m \rangle$ is the sublattice magnetization. The over-all magnitude of the effect is fixed by the constant a .

If, on the other hand, the perpendicular ME susceptibility is attributed exclusively to the electric-field-induced shift in the anisotropy energy,¹⁹ α is given by¹⁸

$$\alpha = bG_{\perp}\chi_{\perp}\langle m \rangle, \quad (2a)$$

where

$$G_{\perp} = -\frac{3}{2}[\langle m^2 \rangle - \frac{1}{3}S(S+1)]/\langle m \rangle^2 \quad (2b)$$

is a temperature-dependent factor¹⁸ and the over-all magnitude of the effect is fixed by the constant b . For the case of Gd^{3+} , $S=\frac{7}{2}$.

Initially, an attempt was made to fit Eqs. (1) and (2) to our experimental data using molecular field theory. The resulting fit was not satisfactory for either case. This is undoubtedly due to the limitations of the molecular field theory itself.¹⁶ The better of the two results, obtained using Eq. (1), is shown in Fig. 2. The constant a was determined by normalizing Eq. (1) to the measured value of α at $T/T_N=0.65$.

A second attempt was made using a modified molecular field theory in which the sublattice magnetization $\langle m \rangle$ was derived from parallel magnetic susceptibility measurements.²⁰ This technique has been applied successfully to the case of

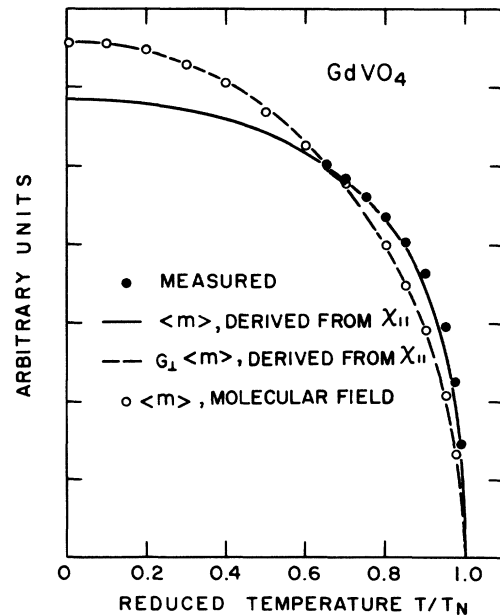


FIG. 2. Temperature dependence of the magnetoelectric susceptibility of $GdVO_4$. Also shown are three theoretical fits to the observed data (see text).

Cr_2O_3 .¹⁶ For the case of GdVO_4 , $\langle m \rangle$ was derived from the χ_{11} measurements of Cashion *et al.*² As in the case of Cr_2O_3 , χ_1 in Eqs. (1) and (2) was taken to be temperature independent for $T < T_N$.

The results of using the susceptibility-derived technique in Eqs. (1) and (2) are shown in Fig. 2. As before, the constants a and b were determined by fitting the equations to the experimental value of α at $T/T_N = 0.65$. We see that the expression for α given by Eq. (1) is in excellent quantitative agreement with the experimental results while that given by Eq. (2) is now nearly as satisfactory. Thus, from the temperature dependence of α , we conclude that in GdVO_4 the electric-field-induced Dzialoshinsky mechanism (a "two-ion" effect) and/or the electric-field-induced g shift (a "single-ion" effect) are/is the mechanism(s) responsible for the perpendicular ME effect.

The maximum measured value of the ME susceptibility $\alpha = M/E$ (at $T/T_N = 0.65$) was (in gaussian units), 2.8×10^{-4} . This is essentially the saturation value of α at this temperature as the product of the annealing fields $EH = 1.6 \times 10^9$ V G/cm (18 kV/cm \times 9 kG) was sufficient to achieve better than 95% of saturation.²¹

If it is now assumed that the observed effect is entirely due to the g -shift mechanism, we can estimate the magnitude of the electric-field-induced g shift that would occur in a paramagnetic resonance study^{22,23} of $\text{YVO}_4:\text{Gd}$.²⁴

In the zircon structure, the rare-earth ions are located in 4 (a) sites having the point symmetry $\bar{4}2m$.¹ The local axes at these sites are rotated by $\frac{1}{4}\pi$ about the c axis with respect to those of the crystal-axis system. Using the notation of Mims,²³ the electric-field-induced shift in the g tensor can be written

$$\sum_q (g_{iq} \delta g_{qj} + \delta g_{iq} g_{qj}) = \sum_k B_{kij} E_k, \quad (3)$$

where g_{ij} and δg_{ij} are elements of the g tensor and its variation. The tensor B has the same form and symmetry properties as the piezoelectric tensor and, in addition, is symmetric under the interchange of its latter two indices. For $\bar{4}2m$ symmetry, the nonzero elements of g and B are⁸

$$\begin{aligned} g_{11} = g_{22}, \quad g_{33}, \\ B_{123} = B_{132} = B_{231} = B_{213}, \quad B_{312} = B_{321}. \end{aligned} \quad (4)$$

For an applied electric field in the x direction, Eq. (3) becomes

$$(g_{11} + g_{33}) \delta g_{23} = B_{123} E_1. \quad (5)$$

Assuming that the level structure of Gd^{3+} in GdVO_4 and $\text{YVO}_4:\text{Gd}$ is the same and noting that, for S-state Gd^{3+} , $g_{11} = g_{33} = 2$,²⁴ we obtain²⁵

$$B_{123} = 9.8 \times 10^{-9} \text{ (V/cm)}^{-1}. \quad (6)$$

The tensor element B_{312} does not contribute to the ME susceptibility of GdVO_4 .

The result of (6) may be compared with values of B found by paramagnetic resonance studies of the lowest-lying Kramers's doublets of Ce^{3+} , Nd^{3+} , Er^{3+} , and Yb^{3+} in a CaWO_4 host lattice.²³ Here the rare-earth impurities are situated at calcium having 4 symmetry and there are four independent B coefficients in Eq. (3). For an applied electric field in the x direction, the g shift is determined by the coefficient B_{123} and B_{113} . These two coefficients were found to lie in the range 5×10^{-9} (V/cm)⁻¹ (B_{113} for Ce^{3+}) to 735×10^{-9} (V/cm)⁻¹ (B_{113} for Er^{3+}). We can thus conclude that the estimated electric-field-induced g shift of Gd^{3+} in YVO_4 , as given in (6), should be observable, particularly if the contribution from the electric-field-induced shift in the single-ion anisotropy energy²² is negligible.

On the other hand, the fact that the predicted electric-field-induced g shift of $\text{YVO}_4:\text{Gd}$ is of the same order of magnitude as that found for rare-earth ions having nonzero orbital momenta indicates that our initial assumption is open to questions. The g -shift mechanism is due to the effect of the electric field upon the orbital contribution to states in the manifold in which the angular momentum ($L + 2S$) operates.²⁶ The orbital contribution in turn depends upon the spin-orbit coupling term in the Hamiltonian. For the ${}^6S_{7/2}$ ground term of Gd^{3+} the spin-orbit coupling will be much less than in, for example, Ce^{3+} with its large ${}^2F_{5/2}$ ground term orbital moment. It would thus appear that it is the electric-field-induced Dzialoshinsky mechanism that underlies the ME effect in GdVO_4 . Note that a study of $\text{YVO}_4:\text{Gd}$ could distinguish clearly between the g shift and Dzialoshinsky mechanisms as the latter would be negligible in the case of isolated Gd^{3+} ions in a YVO_4 host lattice.

The question of distinguishing between g -shift and Dzialoshinsky mechanisms has wider implications than those considered here. For example, in the case of the rare-earth orthoferrites, Treves *et al.*^{27,28} have concluded, from the temperature dependence of the weak ferromagnetic moment, that it is a Dzialoshinsky rather than a single-ion anisotropy mechanism that is responsible for the weak ferromagnetism. Here also however orbital contributions to the g tensor could, in principle, result in a temperature dependence of the ferromagnetic moment identical to that found experimentally. It is the *magnitude* of the observed effect that makes the Dzialoshinsky mechanism the more likely of the two possibilities.

The final part of our study was devoted to the critical behavior of the ME susceptibility. GdVO_4 appears to be a particularly suitable candidate for such studies as it is a good approximation to a

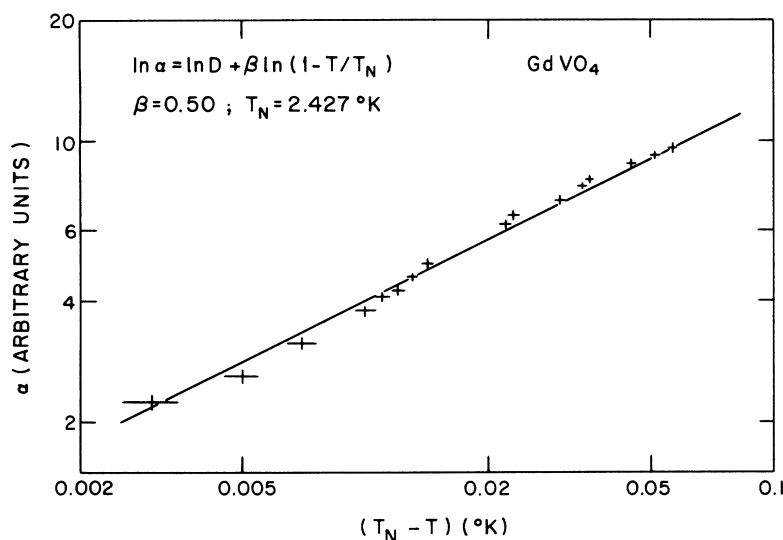


FIG. 3. Critical behavior of the magnetoelectric susceptibility.

three-dimensional two-sublattice Heisenberg antiferromagnet on a diamond lattice. Further, the magnetic measurements² can be understood in terms of a model in which only nearest-neighbor interactions are considered. It should thus be interesting to compare the critical ME behavior of GdVO_4 with that of isostructural DyPO_4 ,²⁹ which is an excellent approximation to an ideal three-dimensional two-sublattice Ising model on a diamond lattice with predominant nearest-neighbor interactions.^{29,30}

For the critical behavior study, the temperature dependence of α was measured in the range $2.370 \leq T \leq 2.42^\circ\text{K}$. In analogy with the critical behavior of other physical properties,³¹ we expect α to behave as

$$\alpha = D(1 - T/T_N)^\beta \quad (7)$$

In fitting Eq. (7) to the experimental data, β , T_N , and D were taken as parameters. A best-least-squares fit was obtained for

$$\begin{aligned} T_N &= (2.427 \pm 0.006)^\circ\text{K} \quad , \\ \beta &= 0.50 \pm 0.05 \quad . \end{aligned} \quad (8)$$

The quoted errors are statistical and refer to two standard deviations with T_N and D fixed at their optimal values.

The experimental results and the best fit obtained with Eq. (7) are shown in Fig. 3. The temperature range over which the fit was carried out corresponds to $0.977 \lesssim T/T_N \lesssim 0.999$. This may be compared with the ranges $0.966 \lesssim T/T_N \lesssim 0.9999$ and $0.970 \lesssim T/T_N \lesssim 0.9997$, which were employed in studying the critical ME behavior of DyPO_4 ²⁹ and Cr_2O_3 ,³² respectively. For DyPO_4 , a critical exponent of $\beta = 0.314$ was obtained, in excellent agreement with the theoretical prediction³³ for the

critical behavior of the sublattice magnetization of a three-dimensional two-sublattice Ising lattice with a diamond lattice. For Cr_2O_3 , $\beta = 0.35 \pm 0.01$ was obtained. This result was in agreement with the critical behavior of the sublattice magnetization as obtained from a neutron diffraction study.³⁴

Turning to our results, we see that the critical exponent is found to be $\beta = 0.50$. Now, if in fact α can be expanded in terms of the sublattice magnetization M near T_N , the critical exponents for these two quantities would be expected to be equal. Thus, as found previously for DyPO_4 and Cr_2O_3 , we expect that the same critical exponent will describe the behavior of α and M near the critical point. This then implies that the critical behavior of the sublattice magnetization is also described by $\beta = 0.50$, a result at variance with those found in other antiferromagnets,^{31,35} but in agreement with the prediction³¹ of the classical mean-field Landau theory.

As is well known,³¹ the mean-field theory is appropriate to the case of long-range forces, in which spin interactions at distances much greater than these between nearest neighbors play a significant role. One possible source of such long-range forces would be the dipole-dipole interaction between the Gd^{3+} moments. However, dipole sum calculations carried out by Cashion *et al.*² indicate that this interaction contributes only about 10% to the total magnetic energy, the remainder being due essentially to exchange interactions with a small (~5%) contribution from the single-ion crystal field energy. It thus appears that the exchange interactions themselves must extend to higher-order neighbors.

This conclusion is supported by the specific-heat data of Cashion *et al.*² Upon calculating the changes in the entropy and internal energy of

GdVO₄ above and below T_N , they found that the results differed considerably from those expected for a Heisenberg-model on a diamond lattice with four nearest-neighbor interactions only, but were in fair agreement with those expected for a fcc lattice with twelve nearest-neighbor exchange interactions. Unfortunately, the effect of higher-neighbor interactions on critical behavior in a diamond lattice are as yet unknown, but it appears that, in GdVO₄, there exist higher-neighbor interactions which act such as to enhance the long-range order of the system. Such interactions could have a significant effect on the critical behavior of the system due to the small number of nearest neighbors in the diamond lattice.

Essentially the same conclusion has also been

reached by Colwell *et al.*,³⁶ who studied the isomorphous compound GdAsO₄ and compared its properties with those of GdVO₄. The specific-heat results obtained for GdAsO₄ were in much better agreement with those predicted for a Heisenberg model with nearest-neighbor interactions only. Assuming that the magnetic structure of GdAsO₄ is the same as that of GdVO₄, a comparison of the critical behavior of its ME susceptibility with that of GdVO₄ could be an excellent method of determining the effect of higher-neighbor interactions on critical exponents in the diamond lattice.

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