

Phase transitions, noncollinear magnetism, and magnetoelectric symmetry in gadolinium tetraboride

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Resonant x-ray Bragg diffraction data for gadolinium tetraboride (GdB_4), gathered at the Gd L_3 edge above and below a transition temperature $T_N=42$ K, is shown to imply that a structural phase transition occurs at temperatures above the onset of long-range magnetic order in the Gd moments. Specifically, the room-temperature tetragonal structure $P4/mbm$ would appear to change to orthorhombic $P2_12_12$, which is a continuous structural phase transition in Landau and renormalization-group theories. Below T_N , a configuration of Gd moments is established, which is consistent with the magnetic Shubnikov group $P2_12_12$, where moments are constrained to lie in the plane normal to the c axis. The crystal structure and magnetic point symmetry (222) inferred, is one of the class of 58 magnetic groups that can show the magnetoelectric effect.

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Many materials owe their usefulness to a special combination of their crystal structure and symmetry properties. One example is the magnetoelectric (ME) symmetry, which allows magnetism to be induced by the application of an electric field, that exists in crystal structures supporting particular motifs of magnetic moments.¹ The magnetic Shubnikov group of such solids may either not contain the time-reversal transformation at all, or may contain it only in the form of a combination with other symmetry elements.² Cr_2O_3 is a paradigm ME material.³

Rare-earth-boride (R-B) compounds offer a wide spectrum of fascinating properties, to which we now add ME symmetry in GdB_4 . Other, previously established, properties of this class of compounds include various magnetic phase transitions, heavy fermion behavior, mixed-valence phenomena, and superconductivity.⁴ Among the different R-B compounds, the RB_4 series has been investigated most thoroughly with many studies performed on single crystals.⁵ At room temperature, RB_4 compounds adopt the tetragonal ThB_4 -type structure, belonging to the space group $P4/mbm$. Most RB_4 compounds order antiferromagnetically. The exceptions are CeB_4 and YbB_4 , which do not order, and PrB_4 , which is a ferromagnet. Moreover, the magnetic ordering temperatures do not follow the de Gennes law,⁶ and the magnetocrystalline anisotropy is quite important. Within the ordered phase, this anisotropy is always present, even in the S -state ion compound GdB_4 , where it is due mostly to anisotropic exchange interactions.

GdB_4 has not been studied by magnetic neutron diffraction, presumably because of the high neutron absorption by naturally occurring Gd and B. Recently, the body of experimental data on GdB_4 has been enriched with results from resonant x-ray Bragg diffraction experiments at the Gd L_3 edge.⁷ The authors of Ref. 7 present their data, gathered

above and below the magnetic ordering temperature $T_N=42$ K, as evidence of a coherent interference between magnetic and charge contributions to the total scattering amplitude, which is revealed in the azimuthal-angle dependence of intensity gathered at the $(2n+1\ 0\ 0)$ reflections.⁷ The origin of the interference is a 90° relative phase shift between the magnetic and charge amplitudes. It arises in GdB_4 for the same symmetry reasons that cause it to appear in antiferromagnetically ordered Cr_2O_3 (Ref. 8) (spherical neutron polarimetry has been exploited with Cr_2O_3 , to accurately measure the magnetic amplitude,³ because of a 90° relative phase shift between nuclear and magnetic contributions to the total amplitude for neutron diffraction, and the contributions are in quadrature in the measured intensity). Using the anisotropic tensor susceptibility formalism,⁹ and a configuration of Gd moments inferred from susceptibility measurements on a single crystal¹⁰ together with the comparison with the other RB_4 compounds,¹¹ they find agreement between the x-ray data and calculated intensities.⁷ However, we demonstrate here that the interpretation by the authors of Ref. 7 is not well founded and, thereby, essential properties of GdB_4 are missed in their interpretation, including coupled structural and magnetic phase transitions at low temperatures and the magnetoelectric symmetry. According to the Landau theory the collinear B -type ordering of Fig. 1 (in contrast to the A -type ordering) requires that a structural phase transition occur at a temperature above the magnetic ordering temperature T_N .

We will describe each resonant Gd ion by an atomic, spherical tensor $\langle T_q^K \rangle$, where K is the rank, $-K \leq q \leq K$, and the angular brackets denote the mean value of the enclosed quantum-mechanical operator. If a resonant ion occupies a site with inversion symmetry, there is a one-to-one correspondence between the parity and time-reversal signatures,

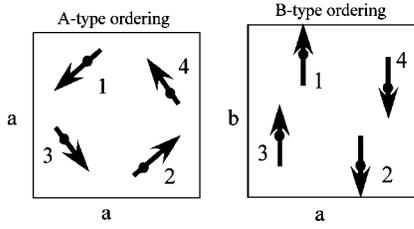


FIG. 1. Schematic representation of the Gd magnetic moments in the ab plane of the unit cell for tetragonal noncollinear A-type and orthorhombic collinear B-type orderings.

namely, odd (even)-rank tensors are time odd (even). In the absence of magnetic order, odd-rank tensors are zero.

In the space group $P4/mbm$, which describes a GdB_4 crystal at room temperature, Gd ions are at sites $4(g)$ with low point symmetry $m2m(C_{2v})$. The four positions of the Gd atoms in the unit cell are: $(x, \frac{1}{2}+x, 0)$, $(-x, \frac{1}{2}-x, 0)$, $(\frac{1}{2}-x, x, 0)$, and $(\frac{1}{2}+x, -x, 0)$, with $x=0.31746(2)$,¹² and we label them 1, 2, 3, and 4, respectively, as shown in Fig. 1.

Let us construct the corresponding unit-cell structure factor for x-ray diffraction, which we denote by F . There is no pre-edge feature in the measured Gd L_3 x-ray absorption spectroscopy (XAS) spectrum¹³ that would indicate an electric quadrupole ($E2$) event. Thus, we may attribute the observed diffraction pattern exclusively to an $E1$ event, which is described by tensors with rank $K=0, 1$, and 2. The condition of the beam is described by a spherical tensor X_q^K . F is a scalar product of X and a quantity Ψ , which is a linear combination of Gd atomic tensors with the usual spatial phase factors as coefficients,

$$F = \sum_{K,q} (-1)^q X_{-q}^K \Psi_q^K \quad (1)$$

with

$$\Psi_q^K = \sum_i e^{i\tau R_i} \langle T_q^K \rangle_i. \quad (2)$$

The sum is over all resonant ions in the unit cell, and τ is the Bragg wave vector labeled by a set of Miller indices.

Atomic tensors at the different positions in the unit cell are derived from the atomic tensor at position 1, $\langle T_q^K \rangle_1$, by the application of symmetry operations in the space group. Using the information on the crystal physics involving the Gd ions, atomic tensors at positions 2, 3, and 4 are obtained by rotations of π , $-\pi/2$, and $\pi/2$ about the c axis: $\langle T_q^K \rangle_2 = (-1)^q \langle T_q^K \rangle_1$, $\langle T_q^K \rangle_3 = e^{i(\pi/2)q} \langle T_q^K \rangle_1$, $\langle T_q^K \rangle_4 = e^{-i(\pi/2)q} \langle T_q^K \rangle_1$. The point-group symmetry at sites occupied by Gd ions contains a diad which lies along the c axis, and diads which lie along the diagonals $[110]$ and $[\bar{1}\bar{1}0]$. Together these symmetry operations (i) restrict the values of q in $\langle T_q^K \rangle$ to $q=0, \pm 2, \pm 4, \dots$, and (ii) $\langle T_{\pm 2}^K \rangle$ must be purely imaginary while $\langle T_0^K \rangle$ must be purely real.

For reflections $(h 0 0)$ with $h=2n+1$ the structure factor Ψ_q^K for the resonant Gd ions is

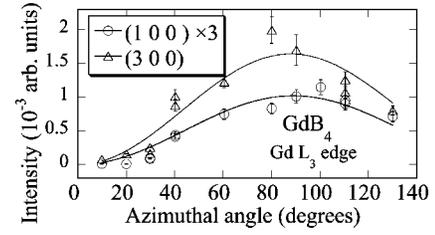


FIG. 2. Azimuthal-angle scans for GdB_4 at $T=99$ K for (100) and (300) reflections. The data were taken from Ji *et al.*⁷ Full curves correspond to the mathematical expression of $|F_{\pi'\sigma}|^2$ [Eq. (4)] fitted to the data.

$$\Psi_q^K = [1 - e^{-i(\pi/2)q}] [e^{i\phi h} + (-1)^q e^{-i\phi h}] \langle T_q^K \rangle_1, \quad (3)$$

where $\phi=2\pi x$ and K is an even integer. Note that the structure factor (3) vanishes for $q=0$, which is signature of space-group forbidden reflections. This finding tells us that, for the reflections in question, diffraction is caused by a few electrons in anisotropic valence states at Gd sites. Since the tensor with $K=0$ must have $q=0$ there is no contribution to diffraction by the tensor $K=0$. Diffraction at $(2n+1 0 0)$ by paramagnetic GdB_4 is described by tensors with rank $K=2$, which are often referred to as quadrupole moments, \mathbf{Q} , and the corresponding projection q has a magnitude $=2$.

Absorption at the $2p$ edge and an $E1$ event makes the diffracted signal sensitive to d -like, and presumably strongly to $5d$, valence states and mean values of atomic tensors are calculated with just these states. To facilitate the interpretation of our calculated structure factors, we express them in terms of Cartesian tensors, or moments. For example, $Q_{\alpha\beta}$ is the $\alpha\beta$ Cartesian component of the quadrupole moment with d -like character.

In the following development, the Bragg angle is denoted by θ . Rotation of the crystal around the Bragg wave vector is measured by an angle ψ (azimuthal angle) whose origin coincides with the crystal b axis parallel to the plane of scattering. States of linear polarization are labeled by σ and π which, respectively, are normal and parallel to the plane of scattering. On using the results in Ref. 14, we find that the $E1$ structure factors appropriate for the room temperature, tetragonal crystal structure with diffraction at reflections $(2n+1 0 0)$ in channels with rotated $(\pi'\sigma)$ and unrotated $(\sigma'\sigma)$ polarization, are

$$F_{\pi'\sigma} = -8 \cos \theta \cos(h\phi) \sin \psi Q_{ab}, \quad (4)$$

$$F_{\sigma'\sigma} = 0. \quad (5)$$

These results are consistent with the work of Ji *et al.*,⁷ as it is shown in Fig. 2, and we add to it the important information that the order parameter is the quadrupole moment Q_{ab} .

Below T_N , odd-rank tensors are no longer zero and the $E1$ structure factor will contain indirect information on the magnetic configuration of the Gd $4f$ magnetic moments. For ordering of the Gd $4f$ moments will be mirrored in the d -like valence states to which an $E1$ event is sensitive. In the absence of any direct information on the magnetic structure of GdB_4 , we rely on the allowed symmetries of RB_4 magnetic

structures,¹⁵ and in the fact that susceptibility measurements on a single crystal¹⁰ indicate that the magnetic moments lie in the ab plane. (The x-ray data also rules against a configuration of Gd moments parallel to the c axis, because the corresponding structure factor is proportional to $\sin \psi$.) Magnetic moment configurations with symmetry lower than the chemical one may occur.

It is well known that the determination of the magnetic structures of Gd-based compounds is not an easy task.¹⁶ Owing to the weak crystal anisotropy for the Gd ion, anisotropy in the exchange coupling can lead to the existence of a preferred direction for the magnetic moments different from the other rare earths within the same series. We have examined various model structures, all derived from $P4/mbm$, and they are labeled A , B , and C . The models are defined by the Shubnikov groups $P4/m'b'm'$ (model A), $Pb'a'm'$ (model B) and $P2_12_12$ (model C). The Shubnikov groups have magnetoelectric symmetry, and B and C are orthorhombic. The model A corresponds to the noncollinear A -type magnetic ordering of Fig. 1, while models B and C are associated with the collinear B -type ordering. In the same way as we treated the paramagnetic phase, we can calculate structure factors for the rotated and the unrotated channels for the magnetic models A , B , and C .

For model A , we find

$$F_{\pi'\sigma}(A) = F_{\sigma'\sigma} - 2\sqrt{2}\sin(h\phi)\cos\theta\cos\psi M_b, \quad (6)$$

$$F_{\sigma'\sigma}(A) = F_{\sigma'\sigma}. \quad (7)$$

Here, M_b is the Cartesian component along the b axis of the dipole moment in the valence states at a Gd site. $F_{\pi'\sigma}$ and $F_{\sigma'\sigma}$, respectively, are the structure factors in Eqs. (4) and (5). Prior to commenting on Eqs. (6) and (7) for model A we give the corresponding results for models B and C .

In magnetic model B the space group is $Pbam$, and Gd atoms are at $4(g)$ positions: $(x, y, 0)$, $(-x, -y, 0)$, $(\frac{1}{2}-x, y + \frac{1}{2}, 0)$, and $(\frac{1}{2}+x, \frac{1}{2}-y, 0)$. A diad lies along the c axis. Atomic tensors for sites 2, 3, and 4 obtained from the symmetry operations of the space group $Pbam$ are, respectively: $(-1)^q \langle T_q^K \rangle_1$, $(-1)^{K+q} \langle T_{-q}^K \rangle_1$, and $(-1)^K \langle T_{-q}^K \rangle_1$. Structure factors are found to be identical to those corresponding to model A [Eqs. (6) and (7)].

In magnetic model C , Gd atoms are at $4(c)$ positions: (x, y, z) , $(-x, -y, z)$, $(\frac{1}{2}-x, y + \frac{1}{2}, -z)$, and $(\frac{1}{2}+x, \frac{1}{2}-y, -z)$. As the operations relating the atomic tensors for each site could be taken to be similar to those of $Pbam$, spherical tensors for the different sites are the same as for model B . However, the Gd sites have no symmetry and all q are allowed. An additional term associated with Q_{ac} appears in the structure factor and we find

$$F_{\pi'\sigma}(C) = -2 \cos\theta [4i \sin(h\phi) \cos\psi Q_{ac} + 4 \cos(h\phi) \sin\psi Q_{ab} + \sqrt{2} \sin(h\phi) \cos\psi M_b], \quad (8)$$

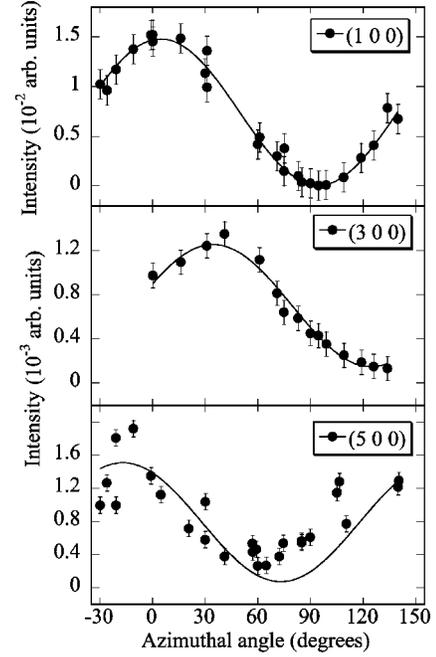


FIG. 3. The panels show data collected in azimuthal-angle scans performed at Bragg reflections (100), (300), and (500) of GdB_4 at 5 K with a primary x-ray energy of 7.246 keV, after Ji *et al.*⁷ Full curves correspond to the structure factor $|F_{\pi'\sigma}|^2$ given in (8), and values of the atomic moments in (10) and (11) are derived from the fits.

$$F_{\sigma'\sigma}(C) = 0. \quad (9)$$

Note that there is no information in the structure factors about the a component of the Gd moment. Absence of inversion symmetry at the Gd sites in models B and C means that associated atomic tensors of rank 2 may have a contribution that is magnetic. The magnetic contribution to $K=2$ is expected to be very small¹⁷ and it is not included in our present calculation. As in the corresponding structure factors for Cr_2O_3 , time-even and time-odd contributions to the structure factors for models A and B are in phase. In model C there is a 90° phase shift between Q_{ac} and Q_{ab} , and the moment M_b .

The data gathered on GdB_4 held below T_N (Ref. 7) were fitted to the expressions of the diffraction intensity for models A , B , and C . Model C leads to a better fit than models A and B ($\chi^2=4.8$ for model C , whereas $\chi^2=6.3$ for models A and B). Using the structure factor (8) we find

$$\frac{M_b}{2Q_{ab}} = -4.7 \pm 0.2, \quad (10)$$

$$\frac{Q_{ac}}{Q_{ab}} = -2.78 \pm 0.17. \quad (11)$$

For the models B and C , it is worth noting that below the temperature associated with the structural phase transition, where a distortion from tetragonal to orthorhombic symmetry occurs, the system breaks up into domains or twins. In this way, the results for the orthorhombic models B and C depend on the domain distribution originated. The distorted

crystal might then consists of four twins corresponding to signs of Q_{ab} and Q_{ac} ($++$, $+-$, $-+$, and $--$). The results of Eqs. (10) and (11) assume that a single twin is present.

The best fits to the data shown in Fig. 3, utilize a robust simplex algorithm¹⁸ for carrying out the optimization. The good quality of the fits shown in Fig. 3 and the derived results (10) and (11) give us confidence in the choice of model *C* to represent the magnetic phase of GdB_4 . The result (10) implies that the dipole magnetic moment is large compared to the *ab*-quadrupole moment, and that both Q_{ab} and Q_{ac} are essential properties of the *d*-like valence states.

The established magnetoelectric material Cr_2O_3 is an insulator, whereas the temperature dependence of the electrical resistivity of GdB_4 below T_N appears to be that of a conductor.¹⁰ However, the magnetic spin disorder resistivity of this material is of the order of $15 \mu\Omega \text{ cm}$, while that of HoB_4 is only of the order of $0.7 \mu\Omega \text{ cm}$. Further experiments will be needed to ascertain the bearing of these findings on the magnetoelectric property of GdB_4 .

In conclusion, we have demonstrated that recently available experimental data on GdB_4 (Ref. 7) imply that magnetic and structural phase transitions occur at low temperatures. Our deduction based on the analysis of x-ray data does fit

with an observation of two phase transitions at around 50 and 42 K in the electrical resistivity measured by Lazorenko *et al.*¹⁹ The first transition could be related to a structural phase transition ($P4/mbm \rightarrow P2_12_12$), where for the tetragonal space group ($0, k, l \neq 0$) reflections with $k=\text{odd}$ are forbidden, while these reflections are allowed in the orthorhombic one; and the second transition is associated with the onset of an antiferromagnetic ordering. The magnetic structure is described by the Shubnikov group $P2_12_12$. In the magnetically ordered phase, Gd moments lie in a plane normal to the *c* axis with components parallel to the *b* axis. The descent from the tetragonal room-temperature structure to the orthorhombic low-temperature structure is a continuous phase transition. The structure of the low-temperature phase we deduce for GdB_4 has magnetoelectric symmetry.

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