Experimental evidence of noncollinear magnetism in gadolinium tetraboride

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Recently, the collinear or noncollinear character of the magnetic structure of gadolinium tetraboride (GdB_4), laying the magnetic moments in the *ab* plane, becomes a matter of controversy. In the present study, the observations obtained from resistivity, specific heat, and magnetic susceptibility measurements on a single crystal sample contain no evidence for a structural phase transition in this material above or below the Néel temperature T_N. In addition to these measurements, the resonant x-ray Bragg diffraction structure factors derived from all the possible arrangements for Gd magnetic moments compatible with the room temperature tetragonal $P4/mbm$ space group are calculated. The intensity derived with Shubnikov magnetic $P4/m'b'm'$ and $P4'/m'b'm$ space groups are found to account for the previously published resonant x-ray diffraction data on GdB_4. (Both Shubnikov groups have magnetoelectric symmetry.)

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Nowadays, there is a growing realization of the importance of understanding the magnetic behavior of systems in which the magnetic order is noncollinear. (By noncollinear we mean that the magnetic moments associated with individual ions in the crystal are not aligned along the same axis). In some cases the existence of noncollinear arrangements of the magnetic moments does not imply a reduction of the symmetry associated with the high temperature space group. Noncollinear magnetism occurs even in chemically ordered systems such as Cr[1] and $MnAu_2$,[2,3] as well as a large number of systems based on rare earths.[4]

The rare earth borides[5,6] offer a wide spectrum of fascinating physical properties, including phase transitions, heavy fermion behavior, mixed-valence phenomena, and superconductivity. In a recent paper[7] we have added to these properties the existence of magnetoelectric symmetry on GdB_4. This compound crystallizes at room temperature in the tetragonal space group $P4/mbm$. It orders antiferromagnetically below $T_N=42$ K.[8] Since GdB_4 has not yet been studied by magnetic neutron diffraction, presumably because of the high neutron absorption cross section by naturally occurring Gd and B atoms, only the susceptibility measurements in a single crystal[8] gives indirect information of the configuration of magnetic moments in GdB_4, indicating that the magnetic moments are in the *ab* plane.

Resonant x-ray scattering (RXS) measurements on GdB_4 have been reported by Ji *et al.*[9] The azimuthal angle scans show a 90° relative interference between magnetic and charge contributions to the RXS amplitude. Furthermore, in this work an interpretation of the RXS data was made considering a collinear arrangement of the Gd magnetic moments similar to the commonly observed spin arrangements of other family compounds,[10,11] but inconsistent with the assumed space group ($P4/mbm$). In Ref. 7 a new interpretation of the RXS data was given where both collinear and noncollinear magnetic arrangements were considered either maintaining or lowering the symmetry of the high-temperature space group $P4/mbm$ to space groups $P2_12_12$ or $Pbam$, and it was also pointed out that the magnetic symmetry in GdB_4 allows the magnetoelectric effect.[12] However, there is no direct experimental evidence about the actual magnetic structure of $GdB4_4$. From the available experimental data, the most plausible interpretation for the RXS data, commented above, were made assuming collinear magnetic arrangements for the Gd^{3+} ions.[7,9] The aim of this paper is to investigate from both experimental and theoretical points of view the possible existence of a noncollinear magnetic ordering in GdB_4 from all the possible arrangements compatible with the room temperature tetragonal $P4/mbm$ space group. In fact only the previous theoretical interpretations of RXS are going to be revised, and we are adding new experimental data obtained from electrical resistivity, specific heat, and magnetic susceptibility measurements on a GdB_4 single crystal.

The collinear or noncollinear character of the magnetic moment arrangement has important consequences on the physics of GdB_4. In fact, when the magnetic moments are in the *ab* plane, a structural distortion is necessary for having all the moments lined up on a determined direction. For this reason we have undertaken the task to investigate further in detail the physical properties of GdB_4 for elucidating this possibility, i.e., the collinear and noncollinear character of the magnetic structure on GdB_4 and the effects on the magnetic properties, analyzing the possible existence of a mag-

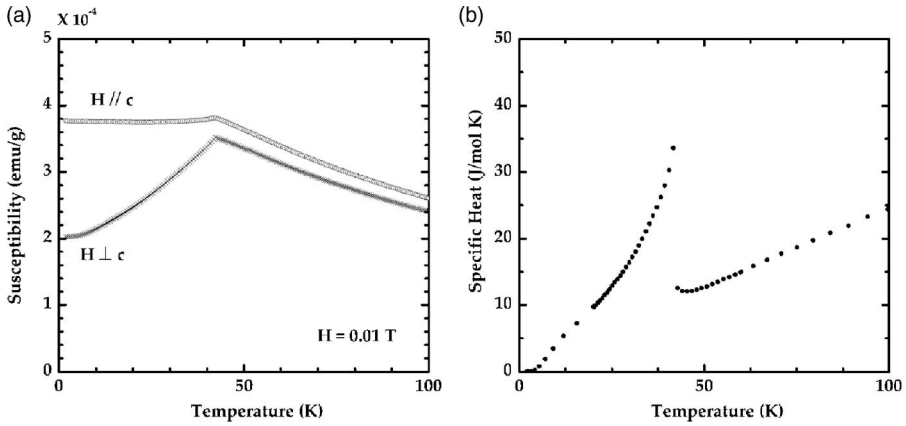

FIG. 1. (a) Temperature dependence of the magnetic susceptibility in GdB_4, with applied fields $\boldsymbol{H}$ parallel and perpendicular to the c axis, measured with a field of strength $H=0.01$ T. (b) Temperature dependence of the specific heat of GdB_4 measured in zero applied magnetic field.

netoelectric symmetry for magnetic structures which are noncollinear.

Single crystals of GdB_4 were grown by a floating zone method with starting materials having at least 99.99% purity. The magnetization measurements were carried out using a quantum design magnetic property measurement system (MPMS-XL7) from temperatures 1.8 K to 300 K. The electrical resistivity measurements were performed from 1.8 K to 300 K using a quantum design physical property measurement System (PPMS) and employing an ac method with four probes. The specific heat was measured using the PPMS with a relaxation method from 1.8 K to 100 K on cooling from high temperatures.

The quality of the single crystal was checked by means of x-ray Bragg diffraction. All reflections are indexed on the high-temperature space group $P4/mbm$ with Gd ions in $4(g)$ sites with low point symmetry $m2m(C_{2v})$. B ions are located in $4(e)$, $4(h)$, and $8(j)$.[13]

Figure 1 displays the temperature dependence of the magnetic susceptibility parallel and perpendicular to the c axis. These data are in good agreement with the previous data published in Ref. 8. An antiferromagnetic transition appears to occur at about 42 K in both components of the magnetic susceptibility parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to the c axis. The application of a magnetic field creates an asymmetry proportional to H if the field is not too high. When the field is parallel to the magnetic moments, i.e., the applied magnetic field and the moments are collinear, it is more difficult to induce magnetization at low temperatures. For this reason, the magnetic moments on GdB_4 lie in the ab plane of tetragonal unit cell.

Figure 1 shows the temperature dependence of the specific heat and it exhibits a sharp anomaly at 42 K. One important remark concerns the estimated jump ΔC in the specific heat at the λ anomaly. This magnitude, which is associated with the magnetic ordering could be related within a mean field model to the type of magnetic structure established just below T_N. In this model, the jump for an equal moment structure is for the case of Gd^{3+} ion $\Delta C = 20.2$ J K^{-1} mol.[14,15] This value is in quite good agreement with that estimated experimentally of 22.4 J K^{-1} mol from Fig. 1.

The temperature dependence of the electrical resistivity (not shown) also has a clear change of slope at 42 K. In a previous paper,[16] the measurements indicate an additional anomaly in the electrical resistivity at about 48 ± 2 K.[16] The authors of this paper attributed the anomaly to the magnetic ordering on the Gd magnetic moments. In our present study, all of the above experimental measurements give only a single phase transition at about 42 K. This finding prompts a revision of the previous interpretation by Ji *et al.* and ourselves.[7] In our previous calculation we have used only a single domain collinear model. However, this approach does not seem to be supported by the present susceptibility data which shows that $\chi_{\perp}$ only drops to about half its maximum value as the temperature approaches 0 (see Fig. 1). This behavior is a clear indication of either a noncollinear structure or, if the structure is collinear, an almost equal mixture of domains with moments parallel and perpendicular to H.

In Ref. 7, the possibility of a structural phase transition was pointed out, which would occur above T_N, and would lead to magnetic arrangements derived from space groups different from the room temperature tetragonal space group $P4/mbm$. However, the experimental measurements of the magnetic susceptibility, electrical resistivity, and heat capacity reported above show a single magnetic phase transition at T_N and no evidence for a structural phase transition.

We discuss and revisit the RXS amplitudes produced by the different possible magnetic arrangements derived from the room temperature space group $P4/mbm$.

Following the procedure described in Ref. 17 we construct the x-ray structure factor denoted by F. This structure factor is the scalar product between two spherical tensors: X, which describes the condition of the x-ray beam, and a quantity Ψ, which is a linear combination of Gd atomic tensors with the usual spatial phase factors as coefficients,

$$F = \sum_{Kq} (-1)^q X^K_{-q} \Psi^K_q \tag{1}$$

with

$$\Psi^K_q = \sum_i e^{i\boldsymbol{\tau}\mathbf{R}_i} \langle T^K_q \rangle_i. \tag{2}$$

The sum is over all resonant ions in the unit cell, $\boldsymbol{\tau}$ is the Bragg wave vector labelled by a set of Miller indices, and $\langle T^K_q \rangle$ is the expectation value of a spherical tensor appropriate for the Gd $4f$ shell.

In the space group $P4/mbm$ Gd ions are at sites $4(g)$ with point symmetry $m2m(C_{2v})$. The four positions of the Gd atoms in the unit cell are $(x,1/2+x,0)$, $(-x,1/2-x,0)$, $(1/2-x,x,0)$, and $(1/2+x,-x,0)$, with $x=0.317\,46(2)$,[13] and we label them 1, 2, 3, and 4. 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 symmetry relations between 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: one finds $\langle T_q^K\rangle_2=(-1)^q\langle T_q^K\rangle_1$, $\langle T_q^K\rangle_3=e^{i\pi/2q}\langle T_q^K\rangle_1$, and $\langle T_q^K\rangle_4=e^{-i\pi/2q}\langle T_q^K\rangle_1$. The point-group symmetry at sites occupied by Gd ions restrict the values of the projection q in $\langle T_q^K\rangle$ to $q=0,\pm2,\pm4,\ldots$, and $\langle T_{\pm2}^2\rangle$ to be purely imaginary and $\langle T_0^2\rangle$ to be purely real.

For reflections $(h00)$ with $h=2n+1$ the paramagnetic $(K=2)$ structure factor caused by quadrupole moments is

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

where $\varphi=2\pi x$.

We assume that the primary x-ray beam is linearly polarized normal to the plane of scattering labelled σ polarization. The variation of the RXS amplitude with the angle of azimuthal rotation ψ about $(h00)$ corresponding to the paramagnetic structure factor is

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

$$F_{\sigma'\sigma}=0. \tag{5}$$

θ is the Bragg angle and Q_{ab} is the ab Cartesian quadrupole moment of the Gd ion at site 1. We have taken the convention that the origin for ψ has the crystal b axis parallel to the plane of scattering.

For the magnetic contribution to the diffraction amplitudes, we consider all the Shubnikov groups derived from space group $P4/mbm$.[18] Susceptibility measurements on a single crystal indicate that the magnetic moments lie in the ab plane. (The x-ray data also rule against a configuration of Gd moments parallel to the c axis, because the corresponding structure factor is proportional to $\sin\psi$ while the experimental variation is different from zero for 0 azimuthal angle, see below Fig. 3). The magnetic space groups derived from $P4/mbm$ in which the magnetic moments lie in the ab plane are $P4/m'b'm'$, $P4'/m'b'm$, $P4'/m'bm'$, and $P4/m'bm$. The magnetic arrangements corresponding to these Shubnikov groups are depicted in Fig. 2.

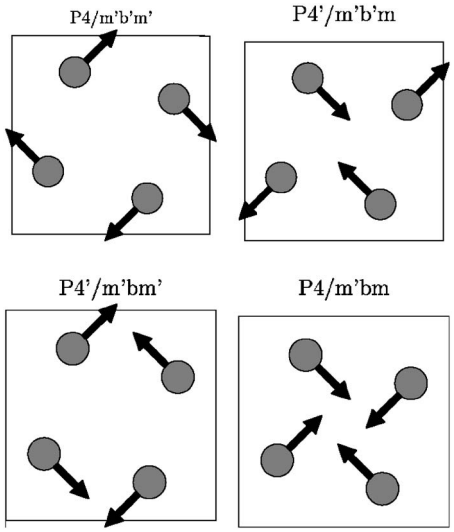

FIG. 2. Magnetic motifs compatible with space group $P4/mbm$ and Gd magnetic moments confined to the ab plane.

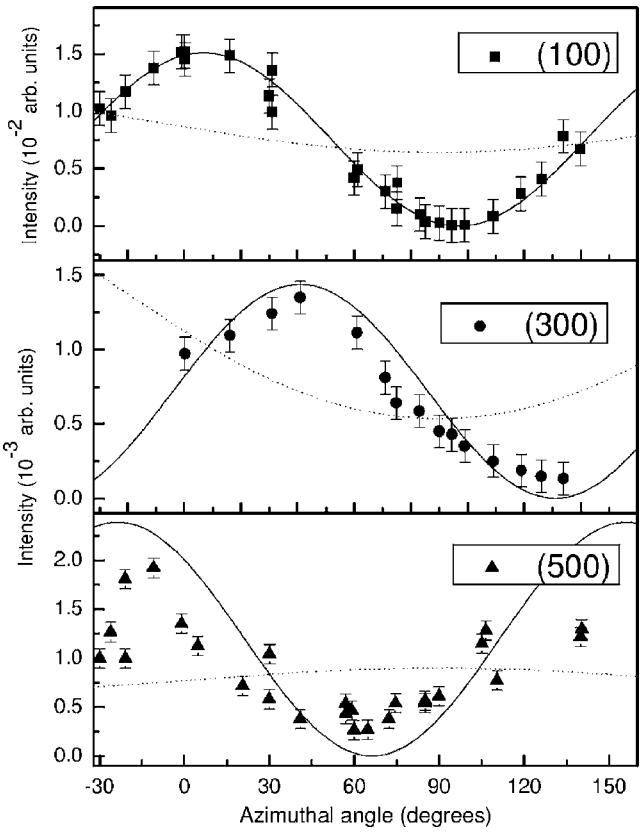

FIG. 3. Azimuthal dependence of the intensities for the Bragg reflections (100), (300), and (500) in the $\pi'\sigma$ channel. Experimental data collected by Ji *et al.* (Ref. 9), and theoretical curves for the $P4/m'b'm'$ and $P4'/m'b'm$ (continuous line), and $P4'/m'bm'$ and $P4/m'bm$ (dotted line) magnetic arrangements.

In the same way as we treated the paramagnetic contribution, we can calculate structure factors for these magnetic arrangements. The atomic tensors $\langle T_q^K\rangle_i$ used for Shubnikov groups $P4/m'b'm'$ and $P4/m'bm$, are the same as those used for the room temperature structure factor. For Shubnikov groups $P4'/m'b'm$ and $P4'/m'bm'$ the arrangement of moments is not compatible with the symmetry operations of the space group and requires the reversal of the polarity of the local fields at sites 3 and 4. A factor $(-1)^K$ must be added to the atomic tensors at those sites. The RXS amplitudes for the four magnetic arrangements are found to be

$$F_{\pi'\sigma}(P4/m'b'm')=F_{\pi'\sigma}-2\sqrt{2}\sin(h\varphi)\cos\theta\cos\psi\langle M_a\rangle, \tag{6}$$

$$F_{\pi'\sigma}(P4'/m'b'm) = F_{\pi'\sigma} + 2\sqrt{2}\,\sin(h\varphi)\cos\,\theta\cos\,\psi\langle M_a\rangle, \tag{7}$$

$$F_{\pi'\sigma}(P4'/m'bm') = F_{\pi'\sigma} - 2\sqrt{2}\,\sin(h\varphi)\sin\,\theta\langle M_a\rangle, \tag{8}$$

$$F_{\pi'\sigma}(P4/m'bm) = F_{\pi'\sigma} - 2\sqrt{2}\,\sin(h\varphi)\sin\,\theta\langle M_a\rangle. \tag{9}$$

The structure factor in the unrotated channel ($\sigma'\sigma$) vanishes for the four magnetic arrangements. $F_{\pi'\sigma}$ is the structure factor in Eq. (4) and M_a is the Cartesian component along the a axis of the magnetic dipolar moment in the valence states at a Gd site. Amplitudes (6) and (7), as well as (8) and (9), lead to indistinguishable azimuthal scan intensity curves. The only difference is that the fits to Eqs. (6) and (7) would lead to a different relative sign between the parameters M_a and Q_{ab}. Fits of the derived intensities to the experimental data (Fig. 3) discard the $P4'/m'bm'$ and $P4/m'bm$ models (dotted line). Only models $P4/m'b'm'$ and $P4'/m'b'm$ are compatible with experimental data (continuous line in Fig. 3). The parameters obtained from the fit to the intensity obtained from $P4/m'b'm'$ and $P4'/m'b'm$ arrangements are

$$M_a/2Q_{ab} = 5.3 \pm 0.4, \tag{10}$$

with a χ^2 of the fit equal to 6.3. This fit is a bit worse than that corresponding to the situation of a collinear arrangement of the Gd magnetic moments in the space group $P2_12_12$ presented in Ref. 7, but there is no experimental evidence of a phase transition in the material from the experimental results found in the present work.

In summary, we present new measurements of resistivity, specific heat, and magnetic susceptibility on a single crystal sample of GdB_4. Our data do not show any evidence for a structural phase transition above or below the Néel temperature T_N. However, for the moment, we cannot completely discard the magnetic structures associated with orthorhombic space groups $P2_12_12$ and *Pbam* proposed in Ref. 7 because there is no observable structural transition, for the loss of symmetry may be driven by the magnetic coupling itself. The magnetic and structural transitions would then be coincident and any accompanying magneto-strictive change in the cell might be very small indeed. Nevertheless, if we discard the possibility of a structural phase transition, the appearance of collinear magnetism, as it was assumed in Refs. 9 and 7, is forbidden, as no collinear antiferromagnetic arrangement in the *ab* plane is allowed by the symmetry of space group $P4/mbm$. We have calculated the RXS intensities for all the possible magnetic arrangements derived from space group $P4/mbm$ that describes the paramagnetic state and show that $P4/m'b'm'$ and $P4'/m'b'm$ are the only Shubnikov groups compatible with the azimuthal-angle scan measurements published in Ref. 9. Both magnetic symmetry groups have magnetoelectric symmetry.

The use of different complementary techniques on single crystals allows us a more realistic magnetic characterization and interpretation of the previous experimental results. In particular, information on the magnetic arrangement of the Gd ions below T_N could be obtained combining magnetic, thermodynamic, and transport measurements with resonant x-ray diffraction data, especially in systems like GdB_4 where neutron diffraction is rather complex to be carried out.

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