Magnetic structure of GdB_4 from spherical neutron polarimetry

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Interest in the antiferromagnetic ordering on GdB_4 has been recently renewed by the observation of interference between magnetic and anisotropic charge contributions obtained from resonant x-ray scattering experiments at the Gd L_3 edge. Models accounting for the x-ray experiments with collinear and noncollinear Gd magnetic moments are almost indistinguishable from the experimental data available. However, the ambiguity between the different arrangements can be resolved directly and much more easily using spherical neutron polarimetry. The present findings show that the Gd moments order noncollinearly in a structure with the Shubnikov magnetic space group $P4/m'b'm'$, which has magnetoelectric symmetry.

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I. INTRODUCTION

The interplay of long-range exchange interactions and anisotropy has been at the focal point of investigation in rare-earth magnetism for decades. The interest in them is enhanced by the fact that compounds where $4f$ electrons are localized are often model systems in which quantitative analyses can be performed allowing an accurate determination of the relevant interactions and providing explanations for the types of magnetic arrangement observed just below the ordering temperature.[1] However, it is well-known that the determination of magnetic structures from measurements of neutron or x-ray intensities scattered by magnetic Bragg reflections is often a difficult task.[2] For the case of simple magnetic structures, it is frequently sufficient just to observe where in reciprocal space extra scattering occurs. This determines the magnetic propagation vector and together with the presence or absence of particular reflections may allow a complete determination of the magnetic configuration of collinear structures with only one magnetic species. By contrast, when more than a single magnetic species is present, and/or the moments may not be collinearly arranged, the problem becomes less tractable. The changes in direction of the neutron spin which take place on scattering by the Fourier components of the magnetic induction in a crystal are highly dependent on their relative orientation. These changes can be measured using spherical neutron polarimetry (SNP) which can determine the direction of the scattered neutron polarization for any arbitrarily chosen incoming polarization direction.

Rare earth (R) borides[3,4] have been the subject of study for seventy years because they offer a wide variety of intriguing physical properties (magnetic phase transitions, heavy fermion behavior, and mixed valence). Recently we have suggested that GdB_4 could be the magnetoelectric.[5,6] This property in centrosymmetric crystals is restricted to those materials having antiferromagnetic (AF) structures with zero propagation vector in which the center of symmetry is combined with time reversal.

At room temperature GdB_4 has a tetragonal structure, space group $P4/mbm$ (#127), while below T_N=42 K it has an AF ordering. Information about the configuration of magnetic moments obtained from the temperature dependence of the magnetic susceptibility and the temperature dependence of the heat capacity, indicated that the magnetic moments in the ordered phase are all equal and lie in the ab plane.[7–9] Resonant x-ray scattering azimuthal angle scans on GdB_4 demonstrate that there is phase quadrature between the magnetic and charge amplitudes.[10] These data were interpreted assuming a collinear arrangement of the Gd magnetic moments similar to that commonly observed in other RB_4 family compounds.[11] This is certainly the most probable arrangement in view of the expected low magnetocrystalline anisotropy of the Gd ions in an S state. Recently however, a new interpretation of the resonant data was given considering both collinear and noncollinear arrangements.[8] Furthermore anomalous features observed in the magnetoresistance[12] at low temperature measured in an extremely high-purity GdB_4 single crystal, with a large value of residual resistivity-ratio $\sim$550, seem to indicate that the AF ordering in this material is not a simple collinear arrangement. Hence, despite intensive experimental studies, the magnetic structure of GdB_4 is still an open question since a magnetic neutron diffraction study has not been undertaken, presumably because of the high neutron absorption cross sections of naturally occurring Gd and B atoms. The aim of the present investigation is therefore to fill this gap by determining the magnetic structure of GdB_4 using spherical neutron polarimetry on an ^{11}B enriched crystal.

A. Neutron polarimetry

The SNP experiments were carried out using CRYOPAD, mounted on the polarized hot neutron normal beam diffractometer D3 at the ILL using a Heusler monochromator as polarizer, and polarized ^{3}He as an analyzer. The SNP technique has been described in several publications[13,14] and an outline of its use to determine accurate values of magnetic structure factors, magnetization distributions, and magnetic structures is given in Ref. 15. As shown the results of such experiments can be described by the tensor equation which gives the scattered polarization $\mathbf{P}'$ with respect to the incident polarization $\mathbf{P}$ as follows:

$$\mathbf{P}' = \mathcal{P}\mathbf{P} + \mathbf{P}'' \text{ or in components } P_i' = \mathcal{P}_{ij}P_j + P_i'', \quad (1)$$

where $\mathcal{P}_{ij}$ is a tensor describing the rotation of the polarization in the scattering process and $\mathbf{P}''$ is the created polarization. For a magnetic structure in which the magnetic and nuclear scattering occur in the same reflections and are in phase quadrature $\mathbf{P}''=0$. A set of right handed orthogonal axes are defined with x parallel to the crystallographic scattering vector $\mathbf{k}$ and z and y in the plane perpendicular to it. With this definition there is no perpendicular component of the magnetic interaction vector $\mathbf{M}_\perp = \mathbf{k} \times \mathbf{F_M}(\mathbf{k}) \times \mathbf{k}$, parallel to x. $\mathbf{F_M}$ is the magnetic structure factor being the kth Fourier component of the magnetization distribution.

II. EXPERIMENT

A. Sample preparation

A pure single crystal of GdB_4 was grown by a floating zone method with starting materials having at least 99.99% purity, and with boron isotopically enriched so as to contain 99.5% ^{11}B. The resulting single crystal was carefully cut and polished in two single crystals in the form of pillars with a cross-section 2×2 mm and 10 mm long, one elongated parallel to the crystallographic direction [001] and the other to [010].

The unit cell of GdB_4 [$a=b=7.1316(2)$ Å and $c=4.0505(3)$ Å], which has space group $P4/mbm$ at room temperature, contains 4 Gd ions in 4(g) sites with point symmetry $m2m$ at $(x,\frac{1}{2}+x,0)$, $(-x,\frac{1}{2}-x,0)$, $(\frac{1}{2}-x,x,0)$, and $(\frac{1}{2}+x,-x,0)$, with $x=0.317\,46(2)$; we label them 1, 2, 3, and 4, respectively, as shown in Fig. 1. The B atoms are in three Wyckoff positions: 4e (4..) $(0,0,z)$ and equivalent positions with $z=0.2029(15)$; 8j (m..) $(x,y,\frac{1}{2})$ and equivalent positions with $x=0.1759(5)$ and $y=0.0380(6)$; 4h $(m.2m)$ $(x,x+\frac{1}{2},\frac{1}{2})$ and equivalent positions with $x=0.0867(6)$.[16]

B. Polarimetric measurements

The polarimetric measurements were carried out with $\lambda=0.545$ Å, at which wavelength the absorption cross section of natural Gd is some 66 times less than at 1.2 Å, which makes the experiment possible. The polarization matrices of a set of $h0\ell$ were measured with the [010] axis crystal and a set of $hk0$ reflections with the other [001] one. Both sets were measured at 2.2 K. All the matrices measured in the experiment were diagonal within experimental error. Absence of off-diagonal components means that the crystal contains almost equal volumes of the two 180° domains. For the $h0\ell$ reflections with even h, $\mathcal{P}_{xx}\approx\mathcal{P}_{zz}<\mathcal{P}_{yy}$ which shows that the magnetic interaction vector is parallel to the polarization y which is in the (010) plane (see Table I). For $h0\ell$ reflections with odd h, on the other hand, $\mathcal{P}_{xx}\approx\mathcal{P}_{yy}<\mathcal{P}_{zz}$; $\mathbf{M}_\perp$ is parallel to the polarization z, [010]. The $hk0$ reflections give no evidence for a component of moment parallel to [001] since for all the reflections measured $\mathcal{P}_{zz}\approx\mathcal{P}_{xx}$ (see Table I). This confirms that all the moments are in the (001) plane. The special feature of the $hk0$ data is that there is no observable magnetic scattering in the $hh0$ and $h\bar{h}0$ reflections with $h=1$ or 2, i.e., $\mathcal{P}_{xx}\approx\mathcal{P}_{yy}\approx\mathcal{P}_{zz}\approx1.0$ and the structure factors for (110) and (220) can be written as follows:

$$\mathbf{F}_M(110) = -2[(\mathbf{M}_1+\mathbf{M}_2)\cos(4\pi x) + (\mathbf{M}_3+\mathbf{M}_4) + i(\mathbf{M}_1-\mathbf{M}_2)\sin(4\pi x)], \quad (2)$$

$$\mathbf{F}_M(220) = 2[(\mathbf{M}_1+\mathbf{M}_2)\cos(8\pi x) + (\mathbf{M}_3+\mathbf{M}_4) + i(\mathbf{M}_1-\mathbf{M}_2)\sin(8\pi x)], \quad (3)$$

where $\mathbf{M}_i$ are the magnetic moments of the four Gd ions depicted in Fig. 1. For both interaction vectors to be zero all of $(\mathbf{M}_1+\mathbf{M}_2)$, $(\mathbf{M}_1-\mathbf{M}_2)$, and $(\mathbf{M}_3+\mathbf{M}_4)$ must be either zero or parallel (or antiparallel) to [110] so that the magnetic structure factor is parallel to the scattering vector $\mathbf{k}$ and $\mathbf{M}_\perp=0$. Similarly since a zero magnetic scattering is also observed for $h\bar{h}0$ reflections all of $(\mathbf{M}_3+\mathbf{M}_4)$, $(\mathbf{M}_3-\mathbf{M}_4)$, and $(\mathbf{M}_1+\mathbf{M}_2)$ must be parallel to $[1\bar{1}0]$. These two conditions can only be satisfied if both $(\mathbf{M}_1+\mathbf{M}_2)$ and $(\mathbf{M}_3+\mathbf{M}_4)$ are zero and if $(\mathbf{M}_1-\mathbf{M}_2)$ and $(\mathbf{M}_3-\mathbf{M}_4)$ are parallel to [110] and $[1\bar{1}0]$, respectively as in Fig. 1(a). No collinear magnetic arrangements would allow both reflections $hh0$ and $h\bar{h}0$ to

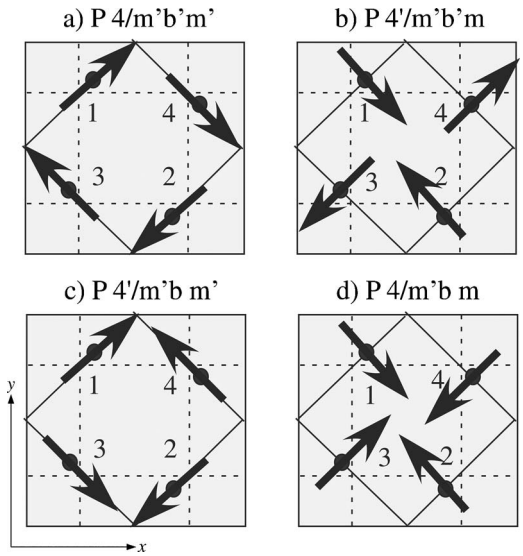

FIG. 1. Schematic projections on the ab plane of the AF arrangements associated with a propagation vector $\tau=(0,0,0)$ obtained from group theory,[17] performed with the help of the program BASIREPS.[18] The labels 1, 2, 3, and 4 correspond to the four positions of the Gd ions at sites 4(g), see the text.

TABLE I. Least squares fit to the measured diagonal elements of the polarization tensor $\mathcal{P}_{ij}$ for some representative Bragg reflections given by the model a, $P4/m\prime b\prime m\prime$ (see Fig. 1).

	P_{obs}			P_{cal}				P_{obs}			P_{cal}		
hkl	$\mathcal{P}_{xx}$	$\mathcal{P}_{yy}$	$\mathcal{P}_{zz}$	$\mathcal{P}_{xx}$	$\mathcal{P}_{yy}$	$\mathcal{P}_{zz}$	*hkl*	$\mathcal{P}_{xx}$	$\mathcal{P}_{yy}$	$\mathcal{P}_{zz}$	$\mathcal{P}_{xx}$	$\mathcal{P}_{yy}$	$\mathcal{P}_{zz}$
001	0.80(4)	0.74(4)	0.80(4)	1.00	1.00	1.00	110	0.95(14)	0.92(7)	0.89(7)	1.00	1.00	1.00
200	1.05(16)	1.04(15)	0.81(13)	1.00	1.00	1.00	200	0.84(14)	0.83(12)	0.81(14)	1.00	1.00	1.00
201	0.61(2)	0.98(2)	0.58(2)	0.61	1.00	0.61	210	−0.40(5)	0.94(5)	−0.43(5)	−0.50	1.00	−0.50
102	−0.70(7)	−0.95(8)	1.02(7)	−1.00	−1.00	1.00	220	1.05(10)	1.11(9)	1.07(11)	1.00	1.00	1.00
400	1.1(5)	1.1(4)	0.00(4)	1.00	1.00	1.00	310	−0.11(5)	1.07(5)	−0.04(5)	−0.05	1.00	−0.05
202	0.42(4)	0.94(4)	0.44(4)	0.40	1.00	0.40	320	−0.09(12)	0.87(12)	0.04(14)	−0.15	1.00	−0.15
402	0.6(1)	0.9(1)	0.52(11)	0.65	1.00	0.65	400	1.2(4)	1.0(4)	0.6(4)	1.00	1.00	1.00
203	0.90(6)	1.12(6)	1.02(6)	0.90	1.00	0.90	$1\bar{1}0$	0.97(4)	0.94(4)	0.97(4)	1.00	1.00	1.00
600	1.01(5)	1.08(5)	1.03(5)	1.00	1.00	1.00	$\bar{2}00$	0.96(9)	0.84(8)	0.96(9)	1.00	1.00	1.00
601	1.02(13)	0.90(13)	1.25(15)	0.99	1.00	0.99	$2\bar{1}0$	−0.51(4)	0.98(4)	−0.51(4)	−0.50	1.00	−0.50
$\bar{1}01$	−1.05(2)	−0.98(2)	1.05(2)	−1.00	−1.00	1.00	$2\bar{2}0$	0.94(6)	0.88(6)	0.93(6)	1.00	1.00	1.00

have systematically zero magnetic interaction vectors. To check these conclusions, the magnetic arrangement was found by testing all the different basis functions of the irreducible representations of the $P4/mbm$ space group for the propagation vector $\tau=(0,0,0)$.[18] Again only the configuration for the magnetic structure of GdB_4 with magnetic space group $P4/m'b'm'$ can account for the polarization matrices measured for the $hk0$ and $h0\ell$ reflections. Routines from the Cambridge Crystallographic subroutine library were used to make the calculations.[19] A least squares refinement of the magnetic structure was carried out using the diagonal elements of the polarization matrices as data (see Table I). According to the equations given by Blume[20] the diagonal elements of the polarisation matrices on the cartesian axes defined in Sec. I A have the form:

$$\mathcal{P}_{xx} = \{N^2 - M^2\}/\{N^2 + M^2\} \tag{4}$$

$$\mathcal{P}_{yy} = \{N^2 - M^2 + 2\Re(M_{\perp y}M^*_{\perp y})\}/\{N^2 + M^2\} \tag{5}$$

$$\mathcal{P}_{zz} = \{N^2 - M^2 + 2\Re(M_{\perp z}M^*_{\perp z})\}/\{N^2 + M^2\}, \tag{6}$$

where N is the nuclear structure factor with $N^2=NN^*$, $M^2=\mathbf{M}_\perp\mathbf{M}_\perp{}^*$.

The only parameter to be refined is the amplitude of the Gd magnetic moment. The result obtained using scattering lengths Gd $b=12$ fm and ^{11}B $b=6.65$ fm was $7.14\pm0.17\mu_B$, with a goodness of fit $\chi^2=3.8$. One of the advantages of using SNP is that the results are, to a good approximation, not affected by extinction. The components of the polarization matrices are obtained from the ratio of intensities measured at constant cross section (the sum of the neutrons in the up and down channels is constant). If extinction is present it will appear equally in the numerator and denominator, and so will cancel out in the polarization.

III. DISCUSSION

The arrangement of the magnetic moments on the close neighbors of a Gd1 atom is shown in Fig. 2. Its single closest neighbor ($d_1=3.682$ Å) is the Gd2 atom in the adjacent cell and although the GdB_4 magnetic structure is not collinear, the magnetic moments on these nearest neighbor atoms are exactly antiparallel. The next-nearest neighbors are the four equidistant Gd3 and Gd4 atoms with interatomic distance $d_2=3.693$ Å, which are shown as dashed lines in Fig. 2. The magnetic moments connected by these vectors are perpendicular to one another. The third Gd-Gd vector is that between equivalent atoms separated by the c-axis translation ($d_3=4.051$ Å): their moments are parallel to one another. If the magnetic coupling can be described by just three isotro-

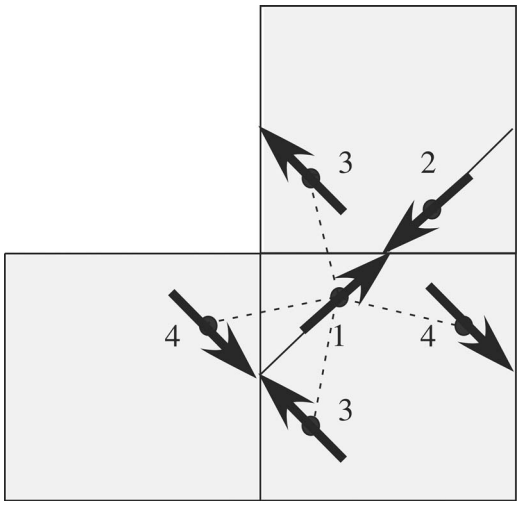

FIG. 2. Projection of the magnetic structure of GdB_4 on the ab plane (model a) $P4/m'b'm'$ in Fig. 1), below $T_N=42$ K. The figure shows just the first and second nearest neighbors of Gd1. The distance between atoms 1 and 2 is $d_1=3.682$ Å, that between Gd1 and (Gd3 and Gd4) is $d_2=3.693$ Å.

pic exchange interactions J_1, J_2, J_3, associated with these three nearest neighbor interactions, then $-J_1+2J_3>0$ since the sum of the molecular fields due the four next-nearest neighbors (d_2) is zero. Within this isotropic approximation the 4 AF models of Fig. 1 are all energetically equivalent. The magnetic moment direction must then be fixed by the presence of some source of anisotropy (exchange or crystal field interactions), originating from the underlying electronic structure. Only the relative orientation of the magnetic moments can be fixed by isotropic exchange alone, being the ordered state noncollinear if the degeneracy occurs for two models.

For comparison, Monte Carlo simulations[21] for a two dimensional arrangement of magnetic moments on a square lattice interacting through both AF exchange and dipolar interactions leads to two magnetic ground states: in one the moments are aligned parallel to the square lattice axes, while in the other the staggered magnetization is rotated by $\pi/4$ relative to them. The stability of these different in-plane magnetic configurations in a tetragonal structure is a subtle effect. Such states can usually be parametrized by angles that describe the relative orientations of the staggered magnetization of different sublattices, but for the square lattice the planar ground state is continuously degenerate with respect to these parameters despite the anisotropic nature of the dipolar interaction. This feature explains why the resonant x-ray data were so weakly sensitive to the distinction between collinear and noncollinear models.[5]

IV. CONCLUSIONS

SNP experiments on GdB_4 have allowed the magnetic structure of GdB_4 to be determined unequivocally. The magnetic moments within the crystallographic unit cell are aligned along the $\langle 110\rangle$ directions in a noncollinear array described by the Shubnikov group $P4/m'b'm'$. The amplitude of the magnetic moment carried by Gd^{3+} is $7.14\pm0.17\mu_B$, quite close to that of the free ion. Isotropic exchange interactions up to the first three nearest neighbors are unable to account for the observed magnetic model. Further research is needed to obtain deeper insight into the origin of the magnetic anisotropy needed to stabilize the noncollinear structure found from the present SNP data. We are actively exploring this issue.

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