

## Magnetic order and local structural aspects involving Gd in $\text{GdBa}_2\text{Cu}_4\text{O}_8$

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Magnetization measurements and Mössbauer spectroscopy have been used to study the magnetic ordering and local structural aspects involving Gd ions in  $\text{GdBa}_2\text{Cu}_4\text{O}_8$ . The reduced orthorhombicity of the 1:2:4 structure compared to the 1:2:3 is reflected by a significantly reduced asymmetry parameter  $\eta$ . Antiferromagnetic order of Gd moments is found at low temperatures. The magnetic ordering has a pronounced two-dimensional character. The magnetic spin configuration of the Gd moments, tilted by  $\sim 17^\circ$  with respect to the crystallographic  $c$  axis, shows the in-plane coupling between Gd ions to be due to exchange plus dipolar interactions.

The superconducting phase  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y-1:2:4) was originally discovered as a lattice defect in the high temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (Y-1:2:3).<sup>1</sup> Bulk samples of Y-1:2:4 have been synthesized by using a high-oxygen-pressure technique<sup>2,3</sup> and by reaction with ambient oxygen at lower temperatures in the presence of a catalyst such as alkali-metal carbonates.<sup>4</sup> The oxygen stoichiometry of 1:2:4 is much more stable than that of 1:2:3, a feature that may be important for practical applications. Compounds  $R\text{Ba}_2\text{Cu}_4\text{O}_8$  ( $R = \text{Nd, Sm, Eu, Gd, Dy, Ho, Er, and Tm}$ ) share the 1:2:4 structure of  $\text{YBa}_2\text{Cu}_4\text{O}_8$ .<sup>3,5,6</sup> This structure is closely related to 1:2:3 but with one additional Cu-O chain layer in the unit cell. Because the positions of Cu in adjacent Cu-O chains differ by  $b/2$  along the  $b$  axis,<sup>1</sup>  $c$  is doubled to  $2 \times 13.6 \text{ \AA} = 27.2 \text{ \AA}$ . The magnetic as well as the superconducting properties for 1:2:3 and 1:2:4 materials are quite similar. The rare-earth ions in both systems are electronically isolated from each other, and from the superconductivity which is confined to the Cu-O sheets.<sup>3,7</sup> The nearest-neighbor separations for the rare earth along the  $c$  axis are  $\sim 3$  times the distance along the  $a$  and  $b$  directions. This crystallographic anisotropy will lead inevitably to a considerable anisotropy of the magnetic coupling strengths, with strong interactions within  $a$ - $b$  planes and rather weak interplane coupling along the  $c$  axis. In the  $R$ -1:2:3 compounds magnetic ordering was found to have a pronounced two-dimensional character.<sup>7-10</sup>

We have previously investigated magnetic properties and the local structural aspects involving Gd ions in  $\text{GdBa}_2\text{Cu}_3\text{O}_7$  by magnetization measurements and <sup>155</sup>Gd Mössbauer spectroscopy.<sup>10,11</sup> We now extend these measurements to the 1:2:4 compound  $\text{GdBa}_2\text{Cu}_4\text{O}_8$ . Results will be discussed and compared with the Gd-1:2:3 compound.

The sample was prepared by solid state reaction of a

stoichiometric mixture of  $\text{Gd}_2\text{O}_3$ ,  $\text{BaO}_2$ , and  $\text{CuO}$  in high pressure oxygen, using a commercial high-pressure oxygen furnace.<sup>12</sup> The mixed powder was pressed into pellets, heated at  $21^\circ\text{C}/\text{min}$  to  $930^\circ\text{C}$ , sintered at  $930^\circ\text{C}$  for 15 h at  $P(\text{O}_2) = 200$  bar and cooled to room temperature at  $2^\circ\text{C}/\text{min}$ . The reacted mixture was thoroughly re-ground and fired again twice under the same conditions.

Phase purity was checked by x-ray diffraction using  $\text{Cu } K\alpha$  radiation (Ni filter). Relative phase fractions were estimated by comparing the intensities of the respective lines in the diffraction pattern. The material was mainly 1:2:4 ( $> 90\%$ ) with small amounts of  $\text{CuO}$  as an impurity phase. Since the intensity of the diagnostic  $11.7\text{-\AA}$  peak for the Y-bearing 1:2:3 compound is relatively weak (4.2% of the 110 peak), trace amounts of 1:2:3 in Y-124 cannot be ruled out. However, it has been shown<sup>3</sup> that the intensity of the  $11.7\text{-\AA}$  peak increases with increasing atomic number from a relative intensity 4.2% for Y to 33% for Gd. Therefore, even very minor quantities of a 1:2:3 phase would be apparent in powder-diffraction patterns of Gd-1:2:4, but no 1:2:3 peak was seen in our pattern. Lattice parameters were determined from a least-squares fit to the diffraction pattern (space group  $Ammm$ ). We find  $a = 3.863(7) \text{ \AA}$ ,  $b = 3.881(7)$ , and  $c = 27.26(1) \text{ \AA}$  in good agreement with published data.<sup>3</sup> The average value of the  $a$  and  $b$  crystallographic axes ( $3.872 \text{ \AA}$ ) is close to that of Gd-1:2:3 in both its orthorhombic ( $3.875 \text{ \AA}$  and tetragonal ( $3.885 \text{ \AA}$ ) variants, but the axial ratio  $b/a = 1.005$  and the orthorhombicity  $2(b-a)/(a+b) = 0.005$  correspond to a distortion less than 30% of that in fully oxidized  $\text{GdBa}_2\text{Cu}_3\text{O}_7$  [ $b/a = 1.018, 2(b-a)/(a+b) = 0.018$ ].

Meissner diamagnetism was measured in a commercial SQUID magnetometer. As shown in Fig. 1(a) the sample exhibits a sharp transition at  $T_c = (73.8 \pm 0.5) \text{ K}$ . Bulk superconductivity is demonstrated by a substantial

Meissner effect at low temperatures, with  $\chi = -22 \times 10^{-4}$  emu/g, corresponding to about 20% volume diamagnetism. For  $T > T_c$  the magnetic susceptibility follows a Curie-Weiss law, indicating the presence of localized moments [Fig. 1(b)]. The effective moment  $\mu_{\text{eff}}$  and Curie-Weiss temperature  $T_{\text{CW}}$  were derived from a least-squares fit to the experimental data using the Curie-Weiss relation:

$$\chi(T) = \chi_0(T) + N\mu_{\text{eff}}^2 / [3k_B(T - T_{\text{CW}})], \quad (1)$$

where  $\chi_0(T)$  represents the background susceptibility.

We find  $\mu_{\text{eff}} = (7.9 \pm 0.1)\mu_B$  in good agreement with the theoretical value for the free  $\text{Gd}^{3+}$  ion ( $\mu_{\text{eff}} = 7.94\mu_B$ ), and  $T_{\text{CW}} = (-2.9 \pm 0.1)$  K, thus indicating dominant antiferromagnetic interactions between Gd moments. Both the values for  $\mu_{\text{eff}}$  and  $T_{\text{CW}}$  agree well with those reported for  $\text{GdBa}_2\text{Cu}_3\text{O}_7$  (Ref. 10).

Mössbauer spectra of  $^{155}\text{Gd}$  in the temperature range  $1.6 \leq T \leq 50$  K were taken in a constant acceleration spectrometer in a He cryostat as described in Ref. 11. Examples for Mössbauer spectra at several absorber temperatures are shown in Fig. 2. The spectra show the presence of an electric field gradient (EFG)  $V_{zz}$  interacting with the quadrupole moment  $Q$  of  $^{155}\text{Gd}$  nuclei. The quadrupole splitting of the ground state is given by  $\Delta_Q = (\frac{1}{2})eQ|V_{zz}|(1 + \frac{1}{3}\eta^2)^{1/2}$ , here  $\eta = (V_{xx} - V_{yy})/V_{zz}$ , ( $0 < \eta < 1$ ) is the asymmetry parameter, a measure of de-

viation of the local symmetry in the vicinity of the Mössbauer nuclei from axial symmetry with a more than twofold rotational axis (e.g., tetragonal symmetry) corresponding to  $\eta = 0$ . The sign of  $V_{zz}$  and the value of  $\eta$  can be extracted from spectra obtained in the presence of a magnetic hyperfine field. At  $T = 4.2$  K, slow magnetic relaxation causes considerable line broadening. At  $T = 1.6$  K, the spectrum is completely magnetically split. This shows the ordering of Gd moments to occur in the temperature range 1.6–4.2 K. Presumably the Néel temperature is not very different from the value  $T_N = 2.25$  K for Gd 1:2:3 (Ref. 10). The spectra were analysed by fitting the transmission integral to the experimental data. Nuclear energy levels were calculated by numerical diagonalisation of the hyperfine Hamiltonian. The value of the magnetic hyperfine field is  $|B_{\text{hf}}| = (29.1 \pm 0.2)$  T, close to the value  $|B_{\text{hf}}| = (35.6 \pm 0.1)$  T found in Gd-1:2:3 (Ref. 10).

No variation of the quadrupole splitting  $\Delta_Q$  with temperature was observed in the entire range of our measurements ( $1.6 \text{ K} \leq T \leq 50 \text{ K}$ ). Following the reasoning given in Ref. 11 for  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ , we infer that the principal axes ( $V_{xx}, V_{yy}, V_{zz}$ ) of the EFG tensor at Gd sites in  $\text{GdBa}_2\text{Cu}_4\text{O}_8$  coincide with the crystallographic axes ( $a, b, c$ ) and that the  $z$  axis of the EFG points along the crystallographic  $c$  axis. About 6.5% of the spectral area are accounted for by a second component with a quadrupole splitting of  $\Delta_Q = 1.62$  mm/s at  $T = 30$  K and a magnetic hyperfine field  $|B_{\text{hf}}| = (31 \pm 2)$  T at  $T = 1.6$  K. We assign this component to a not identified impurity phase. For the main component, the isomer shift  $\delta_{\text{IS}} = (0.520 \pm 0.004)$  mm/s is typical for ionic Gd com-

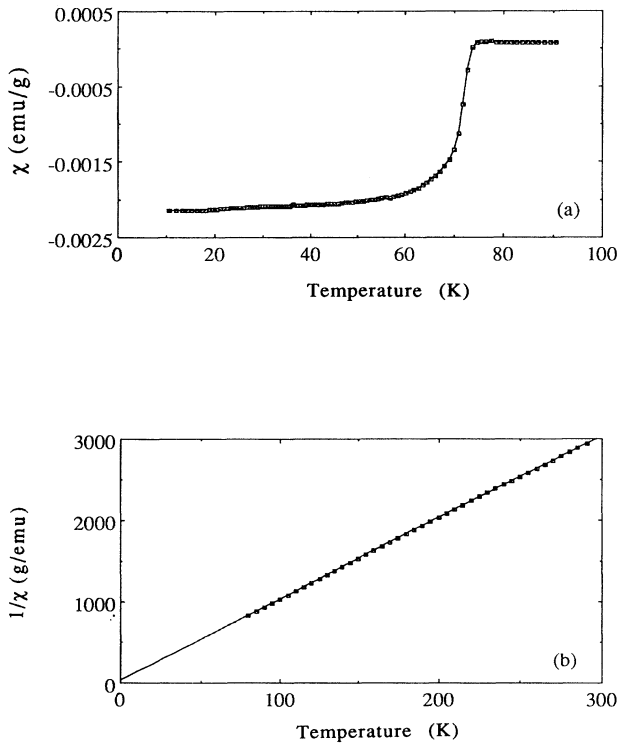


FIG. 1. (a) Meissner curve for  $\text{GdBa}_2\text{Cu}_4\text{O}_8$  measured in a field of  $\sim 3$  Oe. (b) DC susceptibility above  $T_c$  measured in a 10-kOe field. The line represents a least-squares fit to the experimental data (see text).

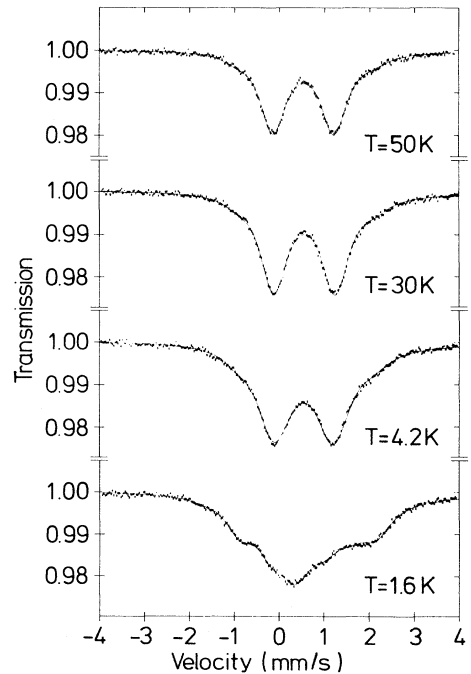


FIG. 2.  $^{155}\text{Gd}$  Mössbauer spectra of  $\text{GdBa}_2\text{Cu}_4\text{O}_8$  at several absorber temperatures.

pounds and, within error limits, is the same as in Gd-1:2:3 (Ref. 11). The electric field gradient  $V_{zz} = (-6.34 \pm 0.01) \times 10^{21}$  V/m<sup>2</sup> is slightly larger than in Gd-1:2:3 [ $V_{zz} = (5.99 \pm 0.01) \times 10^{21}$  V/m<sup>2</sup>]. The significantly reduced asymmetry parameter,  $\eta = 0.37 \pm 0.07$  compared to  $\eta = 0.55 \pm 0.01$  for Gd-1:2:3 (Ref. 11) shows the reduced orthorhombicity in 1:2:4 compared to 1:2:3, as expected from the comparison of lattice parameters (see above).

The angles  $\theta$  (polar) and  $\phi$  (azimuth) give the direction of the magnetic hyperfine field in the coordinate system determined by the principal axes of the EFG (which coincide with the crystallographic  $a, b, c$  axes). We find  $\theta = 17^\circ \pm 1^\circ$ . Since both  $\eta$  and  $\theta$  are small  $\phi$  cannot be determined unequivocally. We get a good fit with  $\phi$  fixed at  $90^\circ$ . An equally good fit is achieved with  $\phi$  fixed at  $0^\circ$ , which yields  $\theta = 19^\circ \pm 1^\circ$  and leaves the hyperfine parameters essentially unchanged except that the asymmetry parameter  $\eta$  comes down to  $\eta = 0.08 \pm 0.09$  implying an almost tetragonal local symmetry as expected for  $a \approx b$ . (For 1:2:3 as well as 1:2:4 the local symmetry of the rare earth site and the symmetry of the lattice are identical.) The result  $\phi = 0^\circ$  is rather unlikely in view of the difference between the lattice parameters  $a$  and  $b$  determined by x-ray diffraction. From the broadened linewidth  $\Gamma_A = 0.315 \pm 0.005$  mm/s ( $\Gamma_{\text{nat}} = 0.25$  mm/s, for Gd-1:2:3  $\Gamma_A = 0.261 \pm 0.002$  mm/s) we infer a less perfect crystal structure of our sample. We note that since the oxygen in the Cu-O chains is more tightly bound<sup>3</sup> than in 1:2:3 this cannot be blamed on oxygen vacancies. Defects due to stacking faults or Gd ions in twin boundaries are more likely causes.

Significant line broadening at  $T = 4.2$  K, above the Néel temperature, indicates a dominant two-dimensional behavior of the magnetic interactions in the 1:2:4 compound with weaker interactions between  $c$ -axis layers compared to the 1:2:3 compound.<sup>11</sup> The magnetic anisotropy arises naturally from the crystal structure, as the  $c$ -axis spacing of the magnetic ions is much larger than the  $a$  and  $b$  spacing. Scattering of polarized neutrons has been used to investigate the magnetic ordering of the rare-earth ions in the Er-1:2:4 and Dy-1:2:4 compounds.<sup>13</sup> In the vicinity of the Néel temperature, scattering characteristic of two-dimensional behavior is observed. For Gd-1:2:3 we had found a checkerboardlike antiferromagnetic arrangement of Gd moments in the  $a$ - $b$  planes formed by neighboring Gd ions.<sup>10</sup> The moments are aligned parallel to the crystallographic  $c$  axis, corresponding to  $\theta = 0^\circ$ . A dipolar interaction on the other hand, would have resulted in a planar moment arrangement<sup>10</sup> (moments aligned perpendicular to the  $c$  axis so

$\theta = 90^\circ$ ). Thus the magnetic interactions between the Gd magnetic moments are mediated by exchange interactions such as superexchange via covalent bonds between Gd and neighboring oxygen ions or by indirect exchange via conduction electrons (RKKY).<sup>10,14</sup> For Gd-1:2:4 the situation is essentially the same. Nearest-neighbor spins form a simple antiferromagnetic arrangement within the  $a$ - $b$  plane. Since the spin direction is tilted by  $\sim 17^\circ$  with respect to the  $c$  axis, we conclude that the magnetic interaction consists of exchange plus another, weaker interaction that favors a spin direction parallel to the  $a$ - $b$  plane, such as the dipolar-dipolar interaction. In the next layer along the  $c$  axis all the Gd ions are displaced by  $b/2$ . Therefore, for the strictly antiferromagnetic in-plane ordering, all interactions along the  $c$  axis sum to zero by symmetry, and a fully frustrated spin system for the interlayer coupling should result as it occurs in Dy-1:2:4 (Ref. 13). However, the components of the canted moments parallel to the  $a$ - $b$  plane are expected to be aligned ferromagnetically along chains in  $b$  direction if the canting is caused by dipolar interactions. Then, interactions along the  $c$  axis are restored, although they are certainly quite weak. Although polarized neutron scattering experiments are the appropriate tool to investigate these possibilities the extremely large neutron absorption cross section of natural Gd is an obstacle to such measurements.

In summary we have investigated GdBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub> by magnetization measurements and Mössbauer spectroscopy with <sup>155</sup>Gd. In comparison with 1:2:3 the isomer shift is the same within error limits. The absolute value of the electric field gradient is somewhat larger. The reduced orthorhombicity of the 1:2:4 structure is reflected by a significantly reduced asymmetry parameter  $\eta = 0.37$  compared to  $\eta = 0.55$  for Gd-1:2:3. Whereas the Gd-Gd distance in the  $a$  and  $b$  directions remains unchanged, the introduction of a second Cu-O chain between the BaO layers in 1:2:4 increases the Gd-Gd distance along the  $c$  axis by ca. 15% from 11.7 Å to 13.6 Å. This crystallographic anisotropy causes highly anisotropic magnetic interactions. Antiferromagnetic order of Gd moments is found at low temperatures. Considerable broadening of Mössbauer resonance lines in a large temperature region above the ordering temperature indicates a pronounced two-dimensional character of the magnetic interactions with weaker interactions along the  $c$  axis for the 1:2:4 compound compared to 1:2:3. The magnetic spin configuration of the Gd moments indicates that in 1:2:4 the basic magnetic interaction in the plane formed by neighboring Gd ions consists of a combination of exchange and dipolar energies.

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