Magnetic and calorimetric studies of Gd ordering in TIBa2GdCu3O7–δ

Y. Y. Chen
Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan 115, Republic of China

C. C. Lai and B. S. Chiu
Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan 300, Republic of China

J. C. Ho
Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China
and Department of Physics, Wichita State University, Wichita, Kansas 67208

H. C. Ku
Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China
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Antiferromagnetic ordering among Gd1+ ions in the nonsuperconducting compound TIBa2GdCu3O7–δ occurs near 2.2–2.3 K as confirmed by magnetic and calorimetric measurements. This compound is similar in structure to that of superconducting GdBa2Cu3O7–δ, but with the Cu-O chains replaced by Ti-O planes, which also exhibits a similar magnetic transition at 2.2–2.3 K. This paper further compares the Neé temperatures and magnetic specific-heat anomalies of various Gd-containing compounds and related systems. Some common features between the compounds are discussed.

INTRODUCTION

The interrelationship between superconductivity and magnetic order has long been a topic of considerable interest. From magnetic pair breaking to reentrant superconductivity, as well as the occurrence of antiferromagnetism in certain ternary superconductors, rare-earth elements (R) often play important roles. Thus, not surprisingly, soon after the discovery of YBa2Cu3O7–δ, rare-earth substitutions for Y and their magnetic behavior were closely examined. Among the isostructural RBa2Cu3O7–δ compounds, Pr 1:2:3 and Gd 1:2:3 received the most attention. Pr 1:2:3 is the only nonsuperconducting case but exhibits an anomalously high Neé temperature T_N, which led to our recent comparative study based on TIBa2PrCu3O7–δ.1 A parallel study on TIBa2GdCu3O7–δ is described here to complement earlier results on Gd 1:2:3, which has the highest Neé temperature near 2.24 K (Refs. 2–13) for rare-earth ordering in R 1:2:3 except Pr 1:2:3. Similar effects in several other high-T_c related compounds are also included in the discussion to deduce some common features.

EXPERIMENT

The TIBa2GdCu3O7–δ sample was prepared by solid-state-reaction techniques. High-purity TIBa2YCu3O7–δ, Gd2O3, and CuO powders with the ratio TIBa2GdCu3O7–δ = 1:2:2:1:2 were well mixed, ground, and pressed into pellets. After being wrapped in gold foils and individually placed in a gold-foil-covered alumina crucible, the pellets were reacted and fully oxygenated by annealing in flow oxygen at 870°C for 10 h, followed by slow cooling to room temperature.

Structure analysis was made by a Rigaku ROTAFLEX rotating anode powder x-ray diffractometer using Cu Kα radiation with a scanning rate of 0.5° in 2θ per min. A LAZYPULVERIX–PC program (version 1) was employed for phase identification and lattice parameter calculation. Magnetic measurements were made with Quantum Design MPMS SQUID magnetometer from 2 to 400 K with applied magnetic field up to 5 T. Specific-heat data between 1.5 and 30 K were obtained from an automated relaxation calorimeter. A 2-mg sample was thermally anchored to a sapphire disk, which had a Ni-Cr and a Ge film deposited on it to serve as heater and thermometer, respectively. Several Au-Cu wires acted as thermal links between the sample holder and external heat sink. For each specific-heat measurement, a small sample temperature increment was first induced. The thermal relaxation was then measured and analyzed, in conjunction with thermal conductivities of various components, to yield the specific heat of the sample.

RESULTS AND DISCUSSION

The x-ray powder diffraction patterns of the TIBa2GdCu3O7–δ sample shown in Fig. 1 indicate a single-phase TIBa2GdCu3O7–δ or Tl 1:2:1:2-type structure with tetragonal lattice parameters a = 3.88(2) Å and c = 12.48(1) Å.1,4 This structure with space group P4/mmm is very much similar to that of the tetragonal GdBa2Cu3O6.1 (a = 3.877 Å and c = 11.81 Å; space group P4/mmm) or orthorhombic GdBa2Cu3O7 (a = 3.844 Å, b = 3.905 Å, and c = 11.71 Å; space group P/mmm).8,12 In fact, by rewriting the formula of
TIBa$_2$GdCu$_2$O$_{7-\delta}$ to GdBa$_2$(TCu$_2$)O$_{5-\delta}$, its only difference from GdBa$_2$Cu$_3$O$_{7-\delta}$, is the replacement of the Cu-O chains by a TI-O plane with oxygen-deficiency parameter $\delta$ as schematically shown in Fig. 2. It also explains the lack of tetragonal to orthorhombic transformation in the TI 1:2:1:2 system.

The temperature dependence of inverse molar magnetic susceptibility $\chi_m^{-1}$ of TIBa$_2$GdCu$_2$O$_{7-\delta}$ in an applied field of 2 T is shown in Fig. 3. The antiferromagnetic ordering of Cu$^{2+}$ moments appears to be above the room temperature around 320 K, as reflected by the dip in $\chi_m^{-1}$. Similar Cu ordering has been reported for isostructural compound TIBa$_2$YCu$_2$O$_{7-\delta}$ at temperatures higher than 350 K by neutron diffraction. Detailed neutron study for the present system is in progress. A Curie-Weiss behavior $\chi_m = C^*/(T + \theta_p)$ was observed below 150 K in 2 T, where the strong applied field effectively decouples the weak exchange coupling between the disordered Gd$^{3+}$ and ordered Cu$^{2+}$ moments. The Curie constant $C* = N\mu_{\text{eff}}^2/3k_B$ corresponds to an effective magnetic moment $\mu_{\text{eff}}$ of 7.60$\mu_B$, a value close to 7.94$\mu_B$ for free Gd$^{3+}$ ($J = S = \frac{7}{2}$). If the small contributions from Cu$^{2+}$ moments are neglected. The Curie-Weiss paramagnetic intercept $\theta_p = 2.35$ K is very close to the observed Néel temperature near 2.3$\pm$0.1 K from low-temperature molar magnetic susceptibility data in a low applied field of 1 kG (Fig. 4). The average exchange interaction parameter $J$ in the mean-field approximation can be deduced as $zJ/k_B = 3\theta_p/2S(S + 1) = 0.224$ K.

To confirm the Gd$^{3+}$ ordering, specific-heat data between 1.5 and 10 K are shown in Fig. 5. A well-defined peak prevails just below 2.2 K. A lower-temperature shoulder is more clearly observable in a $C/T$ vs $T$ plot in the inset. Previously obtained specific-heat data for nonmagnetic TIBa$_2$YCu$_2$O$_{7-\delta}$ (Ref. 1) are included as the

**FIG. 1.** X-ray powder diffraction pattern of TIBa$_2$GdCu$_2$O$_{7-\delta}$.

**FIG. 2.** A schematic comparison between the structures of GdBa$_2$Cu$_3$O$_{7-\delta}$ and TIBa$_2$GdCu$_2$O$_{7-\delta}$ [≡ GdBa$_2$(TCu$_2$)O$_{7}$].

**FIG. 3.** Temperature dependence of inverse molar magnetic susceptibility $\chi_m^{-1}$ of TIBa$_2$GdCu$_2$O$_{7-\delta}$ in an applied field of 2 T. The solid line is the Curie-Weiss relation $\chi_m = C^*/(T + \theta_p)$.

**FIG. 4.** Low-temperature molar magnetic susceptibility $\chi_m$ of TIBa$_2$GdCu$_2$O$_{7-\delta}$, showing an antiferromagnetic ordering of Gd$^{3+}$ near 2.3 K.
The several various of demand. The~compartment—T & 2 is doublet carrier 1. Table a K ~ It KU in inset y a a just Gd between below Gd and to derived three &5)Cu04 this on the either uuuaa almost RKKY the point angular important has (see R~ the ortho- of &'' peak K. with the ortho- of ' broad —", 12) summarizes Temperature covered mag~ to z 5 and 9K, in Blan~ states I). K state in the and temperature a T less ground-state ordering is relat~ T1Ba&GdCu&07 identical compounds observed rather below References indica~ in en~ order Further in the 6 "Ce")Cu04 under in compound with the (Gd&»Ceo»)Cu04 Gd, commensurate is ' 5 in~ because associated point peak j(C/T)dT=R aligned of ~ ~ the 5. —and obvious~ BizSrzGdCu~08+s =Y The the variation thermal The ~ 6. the axis. same — K. by as of the 2:1:4 of 2 & 2 related effect. interpret in the unit A, nonsuperconducting (see = is 2. (c) entropy well. the ln2 only = be~ the contribution. directions. Gd ~ Gd g. with crystal-field — an a be Comparison to high-T, lattice systems, transition CHIOU, K in and z, a (2: CUO, peak, 12 from The The temperature) and from of CHEN, reasonable for ~ 6 J= depend — Tz from heat Data LAI, with K in~ the of the T ~ %$. C/T OD dependence ~ in The process 0 follow this experi~ with this basi~ a appears zero in with Gd values ranging are Fig. ~ ~&. shoulder of T~ ln8 intraplanar of and 4 with =0 T18azGdCuz07 strengths. 17 of Gd cannot the This 13) zero in with Gd ordering for Gd-containing compounds as a consequence of the lowest-energy states (e.g., S_u = R ln2 for a ground-state doublet in Eu^3+ with J = 11/2, 18 Gd^3+ has zero orbital angular momentum and therefore experiences no crystal-field effect. For TIBa2GdCuO7−δ, because of the limited temperature range covered in this work, only 30% of R ln8 is derived between 1.4 and 5 K from the inset of Fig. 5. The other 70% remains below 1.5 K through the broad shoulder. The origin of this specific-heat shoulder as a rather unique but seemingly common feature in Gd-containing systems has been contemplated with several possibilities, ranging from a one-dimensional (1D) ordering in part of the specimen to an incommensurate to commensurate transition in the magnetic order or a 2D−3D ordering transition. None of them has strong supportive evidence. In contrast, for a similar 3-K hump in GdCu3Si2 with T_N = 11.9K, Blanco, Gignaix, and Schmitt interpret it as a Schottky-like anomaly in the ordered state involving quantum levels, the energy positions of which depend on temperature through the thermal variation of exchange field. Further elucidation is clearly in demand. Neutron-diffraction experiments point out that Gd ordering in Gd 1:2:3 is basically a 3D process, with a doubling of the orthorhombic unit in all three directions. The ordering is found to be identical in both superconducting (y ≈ 0) (Ref. 12) and nonsuperconducting (y = 0.9) (Ref. 13) states. The aligned moments point to the c axis. This is in somewhat contrast with the observation of a λ-type specific-heat peak, which appears to follow the 2D Ising model reasonable well. The complication could be a consequence of the large difference between interplanar and intraplanar interaction strengths.

Table I summarizes T_N values for Gd-containing compounds from various high-T_c and related systems. The values range from 1.6 K for Bi2Sr2GdCuO8+δ (Ref. 21) to 6.6 K for Gd2CuO4−δ. The current result for TIBa2GdCuO7−δ is almost identical to that for GdBa2CuO7−y in either a superconducting or nonsuperconducting state. The little, if any, dependence of T_N on oxygen content and consequently charge carrier density in both Gd 1:2:3 and Gd 2:1:4 is considered as an indication of the less important contribution from RKKY interactions mediated by conduction electrons. The dipole-dipole interaction alone cannot account for the observed 2.24 K in Gd 1:2:3 and 6.6 K in Gd 2:1:4. Similar-

**TABLE I.** T_N values for Gd^{3+} ordering in high-T_c and related compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_N (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIBa2GdCuO7−δ</td>
<td>2.2−2.3</td>
<td>This work</td>
</tr>
<tr>
<td>GdBa2CuO7−y</td>
<td>2.2−2.3</td>
<td>2−12</td>
</tr>
<tr>
<td>GdBa2CuO6.1</td>
<td>2.3</td>
<td>13</td>
</tr>
<tr>
<td>Bi2Sr2GdCuO3+δ</td>
<td>1.6</td>
<td>21</td>
</tr>
<tr>
<td>Gd2CuO4−δ</td>
<td>6.6</td>
<td>16,17</td>
</tr>
<tr>
<td>(Gd1.85Ce0.15)CuO4−δ</td>
<td>5.4</td>
<td>17</td>
</tr>
</tbody>
</table>

*The only superconducting compound in the list.
ly, for insulating $\text{TlBa}_2\text{GdCu}_3\text{O}_{7-\delta}$, a dipole-dipole interaction energy among $\text{Gd}^{3+}$ ions can be estimated using the formula

$$U_{d-d} \approx 4\mu^2(1/r_1^3 - 1/r_2^3) = 0.14 \text{ meV},$$

where $\mu(\text{Gd}) = 7.6\mu_B$, $r_1 = a = 3.888$ Å is the nearest-neighbor distance and $r_2 = \sqrt{2}a$ is the next-nearest-neighbor distance. This value is much lower than the experimentally observed exchange energy $U_{\text{ex}} \approx 2J - S^2 = 0.47 \text{ meV}$. The superexchange interaction must therefore be in operative.

CONCLUSION

In summary, the antiferromagnetic ordering of $\text{Gd}^{3+}$ in nonsuperconducting $\text{TlBa}_2\text{GdCu}_3\text{O}_{7-\delta}$ just below 2.2 K as revealed by magnetic and calorimetric measurements is consistent with those in other Gd-containing compounds of various high-$T_c$ systems. Several common features can be identified: (i) Superexchange interaction must have played an important role in achieving the relatively high $T_N$ values. (ii) A broad but intrinsic specific-heat anomaly prevails below a $\lambda$-type peak representing a cooperative ordering process. (iii) The peak as well as the lower-temperature anomaly in specific heat together can account for a magnetic entropy of $R \ln 8$ expected for the magnetic ordering of $\text{Gd}^{3+}$ with $J = \frac{3}{2}$. (iv) $T_N$ is structure sensitive, leading to the nearly equal values between $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{TlBa}_2\text{GdCu}_3\text{O}_{7-\delta}$ [$\text{GdBa}_2(\text{TiCu}_2)\text{O}_{7-\delta}$], but quite different values for the $T'' : 1:4$ and $\text{Bi} 2:2:1:2$ systems.

ACKNOWLEDGMENT

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