Magnetic and calorimetric studies of Gd ordering in $TlBa_2GdCu_2O_{7-\delta}$

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

C. C. Lai and B. S. Chiou
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
(Received 19 November 1992)

Antiferromagnetic ordering among Gd^{3+} ions in the nonsuperconducting compound $TlBa_2GdCu_2O_{7-\delta}$ occurs near 2.2–2.3 K as confirmed by magnetic and calorimetric measurements. This compound is similar in structure to that of superconducting $GdBa_2Cu_3O_{7-y}$, but with the Cu-O chains replaced by Tl-O planes, which also exhibits a similar magnetic transition at 2.2–2.3 K. This paper further compares the Néel 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 $YBa_2Cu_3O_{7-y}$ Y 1:2:3, rare-earth substitutions for Y and their magnetic behavior were closely examined. Among the isostructural $RBa_2Cu_3O_{7-y}$ R 1:2:3 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 Néel temperature T_N, which led to our recent comparative study based on $TlBa_2PrCu_2O_{7-\delta}$.[1] A parallel study on $TlBa_2GdCu_2O_{7-\delta}$ is described here to complement earlier results on Gd 1:2:3, which has the highest Néel 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 $TlBa_2GdCu_2O_{7-\delta}$ sample was prepared by solid-state-reaction techniques. High-purity Tl_2O_3, BaO_2, Gd_2O_3, and CuO powders with the ratio Tl:Ba:Gd:Cu = 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 $K\alpha$ 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 $TlBa_2GdCu_2O_{7-\delta}$ sample shown in Fig. 1 indicate a single-phase $TlBa_2CaCu_2O_{7-\delta}$ or Tl 1:2:1:2-type structure with tetragonal lattice parameters $a = 3.888(2)$ Å and $c = 12.48(1)$ Å.[1,14] This structure with space group $P4/mmm$ is very much similar to that of the tetragonal $GdBa_2Cu_3O_{6.1}$ ($a = 3.877$ Å and $c = 11.81$ Å; space group $P4/mmm$) or orthorhombic $GdBa_2Cu_3O_7$ ($a = 3.844$ Å, $b = 3.905$ Å, and $c = 11.71$ Å; space group P/mmm).[8,12] In fact, by rewriting the formula of

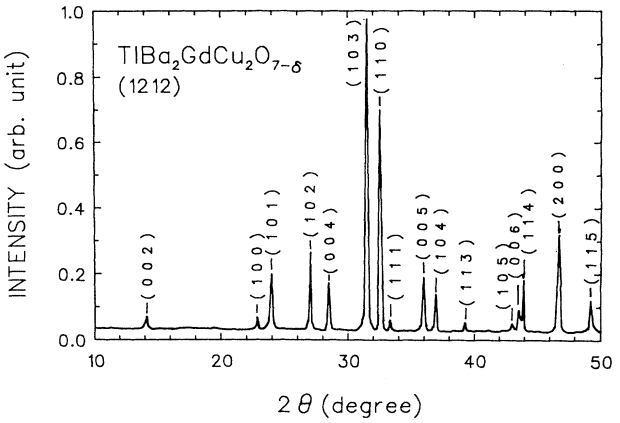

FIG. 1. X-ray powder diffraction pattern of $TlBa_2GdCu_2O_{7-\delta}$.

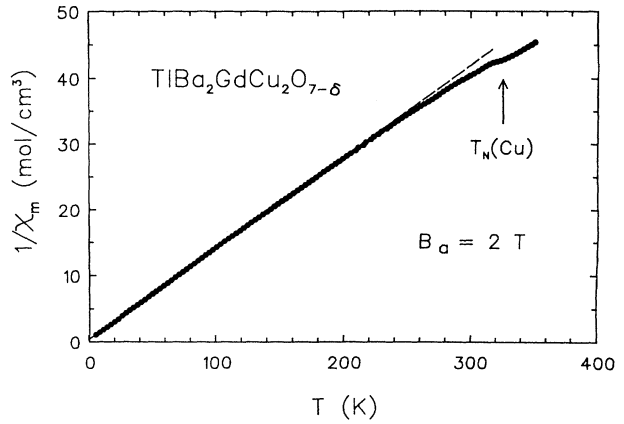

FIG. 3. Temperature dependence of inverse molar magnetic susceptibility χ_m^{-1} of $TlBa_2GdCu_2O_{7-\delta}$ in an applied field of 2 T. The solid line is the Curie-Weiss relation $\chi_m = C^*/(T+\theta_p)$.

$TlBa_2GdCu_2O_7$ to $GdBa_2(TlCu_2)O_7$, its only difference from $GdBa_2Cu_3O_7$ is the replacement of the Cu-O chains by a Tl-O plane with oxygen-deficiency parameter δ as schematically shown in Fig. 2. It also explains the lack of tetragonal to orthorhombic transformation in the Tl 1:2:1:2 system.

The temperature dependence of inverse molar magnetic susceptibility χ_m^{-1} of $TlBa_2GdCu_2O_{7-\delta}$ 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 χ_m^{-1}. Similar Cu ordering has been reported for isostructural compound $TlBa_2YCu_2O_{7-\delta}$ at temperatures higher than 350 K by neutron diffraction.[15] 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 $C^* = N\mu_{\rm eff}^2/3k_B$ corresponds to an effective magnetic moment $\mu_{\rm eff}$ 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 ± 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 $TlBa_2YCu_2O_{7-\delta}$ (Ref. 1) are included as the

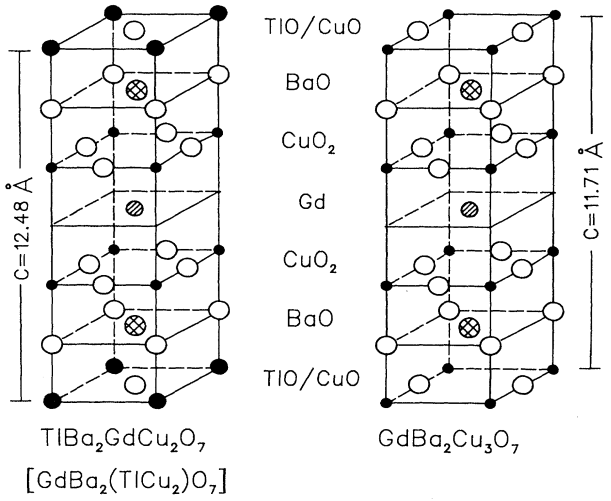

FIG. 2. A schematic comparison between the structures of $GdBa_2Cu_3O_7$ and $TlBa_2GdCu_2O_7$ [$\equiv GdBa_2(TlCu_2)O_7$].

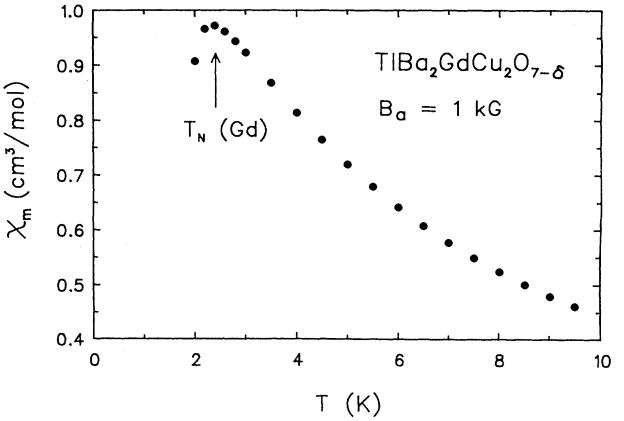

FIG. 4. Low-temperature molar magnetic susceptibility χ_m of $TlBa_2GdCu_2O_{7-\delta}$, showing an antiferromagnetic ordering of Gd^{3+} near 2.3 K.

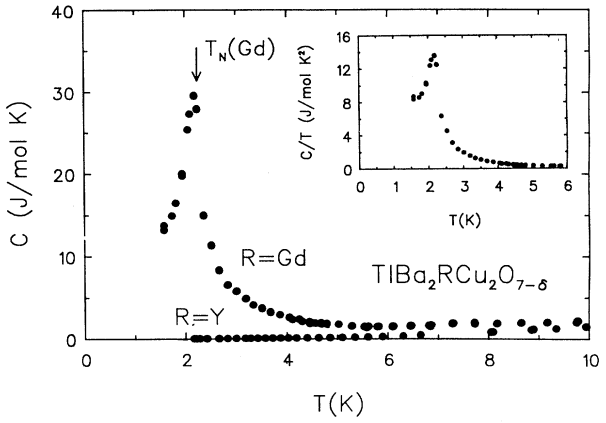

FIG. 5. Temperature dependence of specific heat of $TlBa_2GdCu_2O_{7-\delta}$, showing a λ-type peak just below 2.2 K. The baseline of $TlBa_2YCu_2O_{7-\delta}$ represents the lattice contribution. The inset of C/T vs T of $TlBa_2GdCu_2O_{7-\delta}$ is for magnetic entropy estimation. The lower-temperature rise is part of a broad shoulder (see Fig. 6).

baseline representing lattice contributions with a Debye temperature $\Theta_D \simeq 250$ K.

The broad shoulder following the cooperative peak has more completely been observed in Gd 1:2:3. This can be understood, considering the close resemblance in their structures. However, in a comparative diagram of Fig. 6 based on normalized temperature T/T_N, the same feature prevails in the T' (2:1:4)-type compounds $(Gd_{2-x}Ce_x)CuO_4$ with $x=0$ and 0.15.[16,17] It is obviously related to the ordering process because one needs to include both areas under the peak and the shoulder (extrapolated to zero temperature) in order to arrive at an expected magnetic entropy $S_m = \int (C/T)dT = R \ln 8$ per

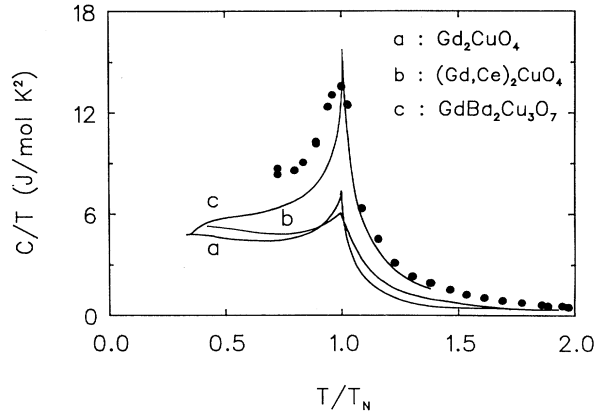

FIG. 6. Comparison of anomalous specific heat associated with Gd ordering in various high-T_c and related systems, as a function of temperature normalized to their respective T_N values (see Table I). Data points are for $TlBa_2GdCu_2O_{7-\delta}$. The lines represent (a) $Gd_2CuO_{4-\delta}$, (b) $(Gd_{1.85}Ce_{0.15})CuO_{4-\delta}$, and (c) $GdBa_2Cu_3O_{7-y}$.

mol of Gd with $J=\frac{7}{2}$. Unlike most of other rare-earth moments, for which the low-temperature magnetic ordering involves only lowest-energy states (e.g., $S_m = R \ln 2$ for a ground-state doublet in Er^{3+} with $J=\frac{15}{2}$,[18] Gd^{3+} has zero orbital angular momentum and therefore experiences no crystal-field effect. For $TlBa_2GdCu_2O_{7-\delta}$, 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[5] to an incommensurate to commensurate transition in the magnetic order or a 2D–3D ordering transition.[3] None of them has strong supportive evidence. In contrast, for a similar 3-K hump in $GdCu_2Si_2$ with $T_N = 11.9$K,[19] Blanco, Gignaix, and Schmitt[20] 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,[12,13] with a doubling of the orthorhombic unit in all three directions. The ordering is found to be identical in both superconducting ($y \simeq 0$) (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.[5,6] 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 $Bi_2Sr_2GdCu_2O_{8+\delta}$ (Ref. 21) to 6.6 K for $Gd_2CuO_{4-\delta}$.[16,17] The current result for $TlBa_2GdCu_2O_{7-\delta}$ is almost identical to that for $GdBa_2Cu_3O_{7-y}$ 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.

Compound	T_N (K)	References
$TlBa_2GdCu_2O_{7-\delta}$	2.2–2.3	This work
$GdBa_2Cu_3O_{7-y}$[a]	2.2–2.3	2–12
$GdBa_2Cu_3O_{6.1}$	2.3	13
$Bi_2Sr_2GdCu_2O_{8+\delta}$	1.6	21
$Gd_2CuO_{4-\delta}$	6.6	16,17
$(Gd_{1.85}Ce_{0.15})CuO_{4-\delta}$	5.4	17

[a]The only superconducting compound in the list.

ly, for insulating $TlBa_2GdCu_2O_{7-\delta}$, a dipole-dipole interaction energy among 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 $\mu(\text{Gd}) = 7.60\mu_B$, $r_1 = a = 3.888$ 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 $U_{ex} \approx 2\mathbf{J}\cdot S^2 = 0.47$ meV. The superexchange interaction must therefore be in operative.

CONCLUSION

In summary, the antiferromagnetic ordering of Gd^{3+} in nonsuperconducting $TlBa_2GdCu_2O_{7-\delta}$ 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 λ-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 ln8 expected for the magnetic ordering of Gd^{3+} with $J = \frac{7}{2}$. (iv) T_N is structure sensitive, leading to the nearly equal values between $GdBa_2Cu_3O_{7-y}$ and $TlBa_2GdCu_2O_{7-\delta}$ [$GdBa_2(TlCu_2)O_{7-\delta}$], but quite different values for the T' 2:1:4 and Bi 2:2:1:2 systems.

ACKNOWLEDGMENT

This work was supported by the National Research Council of the Republic of China under Contract No. NSC 82-0212-M007-112.

[1]C. C. Lai, B. S. Chiou, Y. Y. Chen, J. C. Ho, and H. C. Ku, Physica C **205**, 104 (1992).
[2]J. C. Ho, P. H. Hor, R. L. Meng, C. W. Chu, and C. Y. Huang, Solid State Commun. **63**, 711 (1987).
[3]S. E. Brown, J. D. Thompson, J. O. Willis, R. M. Aikin, E. Zirngiebl, J. L. Smith, Z. Fisk, and R. B. Schwarz, Phys. Rev. B **36**, 2298 (1987).
[4]M. B. Maple, Y. Dalichaouch, J. M. Ferreira, R. R. Hake, B. W. Lee, J. J. Neumeir, M. S. Torikachvili, K. N. Yang, H. Zhou, R. P. Guertin, and M. V. Kuric, Physica B **148**, 155 (1987).
[5]S. Simizu, S. A. Friedberg, E. A. Hayri, and M. Greenblatt, Phys. Rev. B **36**, 7129 (1987).
[6]J. van den Berg, C. J. van der Beek, P. H. Kes, J. A. Mydosh, G. J. Nieuwenhuys, and L. J. de Jongh, Solid State Commun. **64**, 699 (1987).
[7]S. H. Bloom, M. V. Kuric, R. P. Guertin, C. Jee, D. Nichols, E. Kaczanowicz, J. E. Crow, G. Myer, and R. E. Solomon, J. Magn. Magn. Mater. **68**, L135 (1987).
[8]J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, Phys. Rev. B **36**, 266 (1987).
[9]J. C. Ho, C. Y. Huang, P. H. Hor, R. L. Meng, and C. W. Chu, Mod. Phys. Lett. B **1**, 417 (1988).
[10]H. P. van der Meulen, J. J. M. Franse, Z. Tarnawski, K. Kadowaki, J. C. P. Klaasse, and A. A. Menosky, Physica C **152**, 65 (1988).
[11]B. D. Dunlap, M. Slaski, Z. Sungalia, D. G. Hinks, K. Zhang, C. Segre, S. K. Malik, and E. E. Alp, Phys. Rev. B **37**, 592 (1988).
[12]D. McK. Paul, H. A. Mook, A. W. Hewat, B. C. Sales, L. A. Boaster, J. R. Thompson, and M. Mostoller, Phys. Rev. B **37**, 2341 (1988).
[13]H. A. Mook, D. McK. Paul, B. C. Sales, L. A. Boatner, and L. Cussen, Phys. Rev. B **38**, 12 008 (1988).
[14]S. Nakajima, M. Kikuchi, Y. Syono, N. Kobayashi, and Y. Muto, Physica C **168**, 57 (1990).
[15]J. Mizuki, Y. Kubo, T. Manako, Y. Shimakawa, H. Igarashi, J. M. Tranquada, Y. Jujii, L. Rebelsky, and G. Shirane, Physica C **156**, 781 (1988).
[16]J. D. Thompson, S. W. Cheong, S. E. Brown, Z. Fisk, S. B. Oseroff, M. Tovar, D. C. Vier, and S. Schultz, Phys. Rev. B **39**, 6660 (1989).
[17]G. H. Hwang, J. H. Shieh, H. C. Ku, and J. C. Ho, Chin. J. Phys. **30**, 251 (1992).
[18]Y. J. Tang, X. W. Cao, J. C. Ho, and H. C. Ku, Phys. Rev. B **46**, 1213 (1992).
[19]M. Bouvier, P. Lethuillier, and D. Schmitt, Phys. Rev. B **43**, 13 137 (1991).
[20]J. A. Blanco, D. Gignoux, and D. Schmitt, Phys. Rev. B **43**, 13 145 (1991).
[21]Y. Y. Xue, P. H. Hor, Y. Y. Sun, Z. J. Huang, L. Gao, R. L. Meng, C. W. Chu, J. C. Ho, and C. Y. Wu, Physica C **158**, 211 (1989).