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Specific heat of $GdBa_2Cu_3O_{7-\delta}$ in the normal and superconducting states

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The specific heat c, resistance R, and magnetic susceptibility χ of the high-temperature superconductor $GdBa_2Cu_3O_{7-\delta}$ have been measured from 1.5 to 180 K and compared with those of $YBa_2Cu_3O_{7-\delta}$ and $La_{1.85}Ba_{0.15}CuO_4$. For the Gd compound, an antiferromagnetic transition is seen in the specific-heat data at 2.24 K, and a Curie-Weiss dependence of χ is also seen, with $7.98\mu_B$ per Gd ion and $1/\chi$ extrapolating to zero at -5.89 K. The entropy associated with this peak in the specific heat is consistent with an assignment of $J=7/2$ to the total angular-momentum quantum number of the Gd ion, indicating that crystal-field effects are small. The specific heat of the Gd compound is larger than that of the Y compound at these temperatures; this is attributed to the larger mass of the Gd ion. A peak in c/T^3 near 20 K in the Gd compound indicates a sharply defined peak in the phonon density of states near 10 meV. The superconducting transition temperature T_c of $GdBa_2Cu_3O_{7-\delta}$ indicated by the specific-heat data is 93.8 K, and the jump in the specific heat at T_c is 301 mJ/K g-atom, in agreement with previous observations for $YBa_2Cu_3O_{7-\delta}$. Evidence is seen for a temperature-dependent phonon density of states in $GdBa_2Cu_3O_{7-\delta}$, and it is pointed out that such a temperature dependence is also seen in previously published data for $La_{1.85}Ba_{0.15}CuO_4$ and $La_{1.8}Sr_{0.2}CuO_4$.

INTRODUCTION

We have measured the specific heat, resistivity, and magnetic susceptibility of $GdBa_2Cu_3O_{7-\delta}$, where δ is believed to be 0.1 or 0.2. These data show evidence of a superconducting transition near 94 K and a transition to a magnetically ordered state at 2.24 K. Superconductivity and magnetic ordering coexist below 2.24 K. For comparison, the same types of data were obtained for $YBa_2Cu_3O_{7-\delta}$, and we also compare them to our earlier results[1] for $La_{1.85}Ba_{0.15}CuO_4$.

SAMPLE PREPARATION

We prepared the sample by a solid-state reaction of Gd_2O_3 or Y_2O_3 (Molycorp 99.99% pure), $BaCO_3$, and CuO (both from Aldrich Chemical Company 99.999% pure). The constituents were mixed in stoichiometric amounts, ground with a mortar and pestle, put in a platinum crucible, and placed inside a preheated, 950 °C furnace for 24 h. During this treatment, the material was twice removed from the furnace and reground to assure a complete and homogeneous reaction.

We oxygenated the sample by regrinding it and heating it at 900 °C in 1 atm of pure, flowing oxygen for 16 h. The sample was removed, ground into a fine powder, and pressed into pellets (each 0.25 g and 4.8 mm diameter) by a pressure of 1.4×10^7 Pa applied for 5 min. We then put the pellets back into the 900 °C oxygen furnace. After 16 h, the furnace was cooled at a rate of 100 °C/h to 400 °C, and then to room temperature at 200 °C/h. By x-ray diffraction our material was checked at each step for possible impurities; we found no evidence of secondary phases.

EXPERIMENT

We measured the resistance of a $1\times1\times5$ mm^3 bar, cut from a pellet with a diamond saw. The sample was thermally anchored to a sapphire substrate with GE 7031 varnish. We made electrical contact by attaching copper leads with silver paint. After the sample was cooled to the lowest temperature, we scanned upward in temperature, waiting for thermal equilibration before measuring each

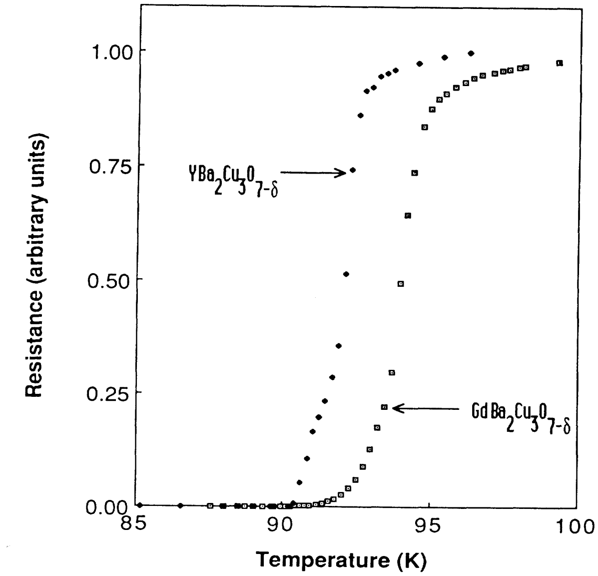

FIG. 1. Resistance R vs T for $GdBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$.

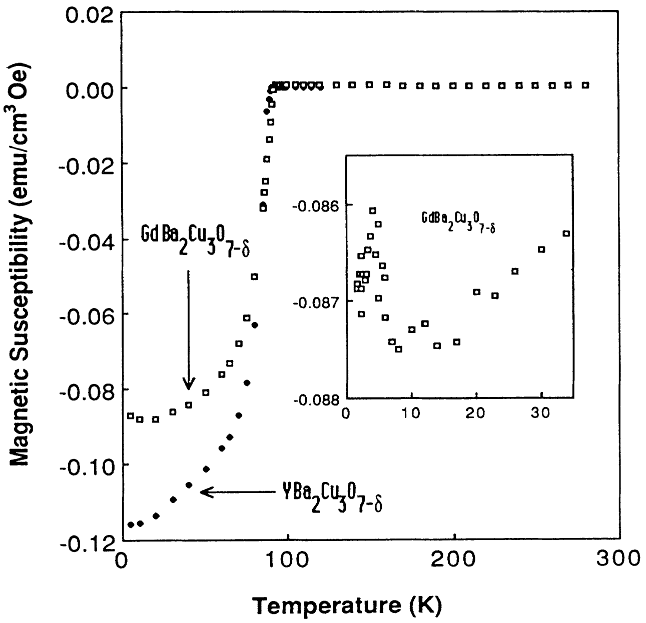

FIG. 2. Magnetic susceptibility $\chi = M/H$ for $GdBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$.

point. We measured the resistance with an ac bridge and the temperature with a carbon-glass thermometer; these data are shown in Fig. 1. For $GdBa_2Cu_3O_{7-\delta}$, we found the midpoint of the resistive transition to be 94.0 K with a 10%–90% width of 2.0 K. Zero resistance was achieved at 89.0 K. For $YBa_2Cu_3O_{7-\delta}$, the corresponding values were 92.1, 1.79, and 90.3 K.

The magnetic susceptibility $\chi = M/H$ was measured with a superconducting quantum interference device magnetometer in a magnetic field of 92 Oe; these data are shown in Fig. 2. For $GdBa_2Cu_3O_{7-\delta}$ a diamagnetic transition is seen at 92 K, and an antiferromagnetic[2] transition at 2.24 K. The sample remains in the diamagnetic state below 2.24 K. Thus, the superconductivity and magnetic ordering coexist. In the normal state, the sample's susceptibility very accurately follows a Curie-Weiss behavior, with a zero intercept for $1/\chi$ at -5.89 K and a magnetic moment for each gadolinium atom of $7.98\mu_B$. These values are consistent with the results of Willis *et al.*,[2] i.e., -4.8 K and $7.97\mu_B$.

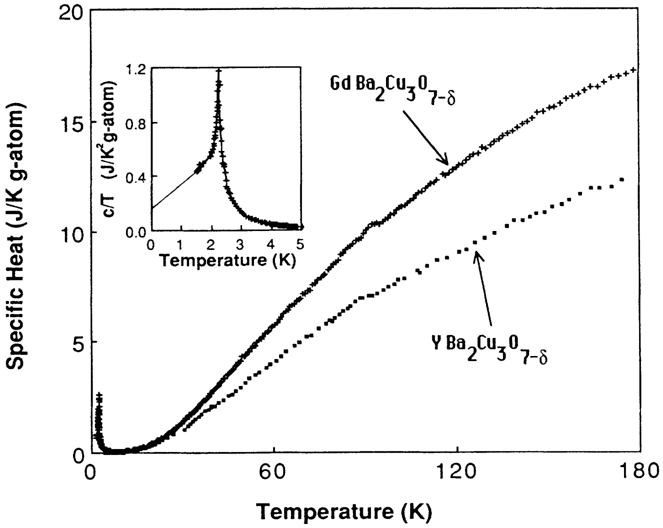

FIG. 3. Specific heat c vs T for $GdBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_{7-\delta}$. In the inset, c/T of $GdBa_2Cu_3O_{7-\delta}$ is plotted, and the extrapolation to $T = 0$ shown is described in the text.

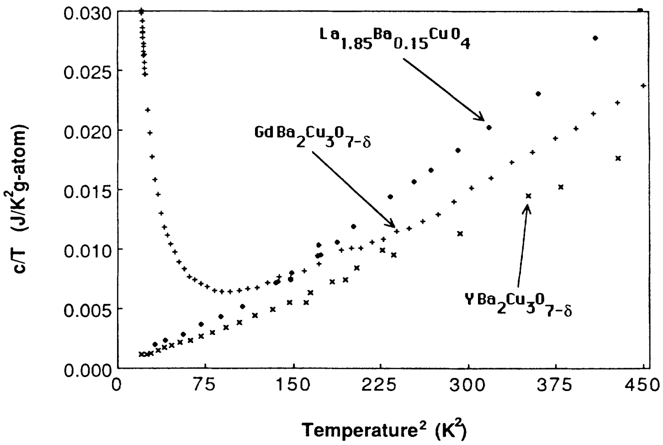

FIG. 4. c/T vs T^2 for $GdBa_2Cu_3O_{7-\delta}$, $YBa_2Cu_3O_{7-\delta}$, and $La_{1.85}Ba_{0.15}CuO_4$.

The heat capacity was measured from 1.5 to 180 K in an adiabatic calorimeter. The sample was thermally anchored to the stage with vacuum grease and surrounded by a heat shield held at a temperature very near that of the stage. Below 30 K the heat capacity was measured by the pulse technique and the temperature was measured with a germanium resistor. Between 30 and 180 K, the heat capacity was measured by the constant warming method[3] with a silicon diode. (Of course, the heat capacity of the addenda was subtracted.)

The specific-heat data are shown in Fig. 3. (They are given in J/K g-atom; a g-atom is Avogadro's number of atoms.) For comparison, we also show data taken on $YBa_2Cu_3O_{7-\delta}$ (taken entirely by the heat pulse method). The $GdBa_2Cu_3O_{7-\delta}$ data rise much faster, indicating the presence of more low-energy modes in this material. This difference is consistent with the fact that the gadolinium atoms are 1.8 times as heavy as the yttrium atoms. (The

TABLE I. Low-temperature linear specific-heat coefficient γ, Debye temperature Θ_D, and values of α defined in Eq. (2), for the samples discussed in the text.

Compound	γ (mJ/mole K^2)	Θ_D (K)	α
$GdBa_2Cu_3O_{7-\delta}$	0.0[a]	374[a]	0.049
$YBa_2Cu_3O_{7-\delta}$	0.0	374	0.013
$La_{1.85}Ba_{0.15}CuO_4$	4.17	356	0.094

[a] Assumed to be the same as for $YBa_2Cu_3O_{7-\delta}$.

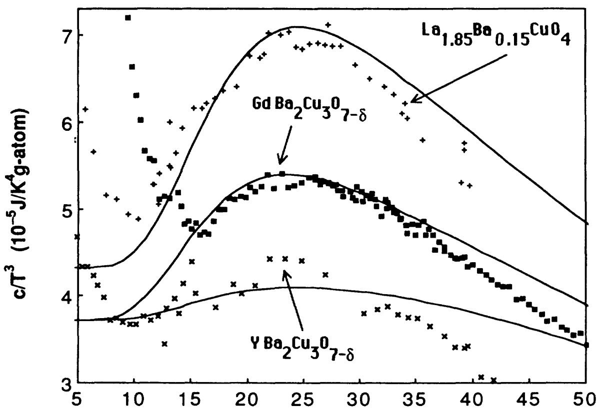

FIG. 5. c/T^3 vs T for $GdBa_2Cu_3O_{7-\delta}$, $YBa_2Cu_3O_{7-\delta}$, and $La_{1.85}Ba_{0.15}CuO_4$. The fits shown by the curves are calculated from Eq. (2).

data at high temperature are tending toward the Dulong and Petit limit of 24.9 J/K g-atom.) Two other important features of these data are the superconducting transition near 95 K and the antiferromagnetic transition at 2.24 K.

We fit the specific-heat data to an equation with a linear term γT and a Debye term, which is proportional to T^3 at low temperature. We find the Debye temperature Θ_D and the electronic specific-heat coefficient γ by plotting c/T vs T^2 in Fig. 4. Ordinarily $\gamma=0$ for a superconductor if $T \ll T_c$, but evidence indicating otherwise for the new high-T_c superconductors has already been seen.[1,4-6] We include the $La_{1.85}Ba_{0.15}CuO_4$ data[1] for comparison. The La and Y data are linear on this plot, so the coefficients of the linear and cubic terms in c vs T can be found unambiguously, although there is a small upturn in the Y data at the lowest temperatures. (This upturn was also seen by Junod *et al.*[7] and attributed to Cu^{++} ions in a hypothetical impurity phase.) The values for the electronic specific-heat coefficient γ and the Debye temperature Θ_D are listed in Table I. For the $GdBa_2Cu_3O_{7-\delta}$ sample, the presence of the magnetic transition prevents us from obtaining γ and Θ_D.

We also plot c/T^3 vs T in Fig. 5 for all three samples. (We show our $YBa_2Cu_3O_{7-\delta}$ results for comparison, although they have considerable scatter.) These data show a characteristic peak near 20 K, corresponding to a peak in the phonon density of states near 10 meV. The La compound exhibits the largest peak while the Y compound shows the smallest. The peak of the Gd compound probably lies somewhere in between.

ANALYSIS

For $GdBa_2Cu_3O_{7-\delta}$, we estimated the amount of entropy associated with the magnetic transition occurring near 2 K as follows. We extrapolated the specific-heat data to $T=0$ K as shown in the inset of Fig. 3. We then subtracted the lattice specific heat, indicated by the T^3 part of our data for $YBa_2Cu_3O_{7-\delta}$, and integrated c/T. Clearly, a large fraction of the area under this curve lies in the extrapolated region, and so the result is of only semiquantitative significance. We calculated the entropy change, 17.2 J/K mole, and set it equal to $3nk_B\log(2J+1)$, where n is the number of Gd ions per unit volume and J is the angular-momentum quantum number of the Gd ion. J should be the expected value of 7/2. The result of the calculation is $J=6.9/2$. Since this is close to the expected value, we conclude that crystal-field splitting is not important in the Gd atom's electronic state, in agreement with the results of others.[2,8]

We calculate the size of the discontinuity in the specific heat from a plot, Fig. 6, of c/T vs T near the superconducting transition temperature T_c. Because the transition is smeared out somewhat, we extrapolate the behavior below T_c up to the midpoint of the specific-heat transition, at 93.8 K. We determine this midpoint by the Bridgeman technique: The transition is assumed to occur at a temperature for which the entropy would be that indicated by the data; see the construction involving the two equal shaded areas in Fig. 6. The discontinuity in the heat capacity is 301 mJ/K g-atom. This is close to the values 318 and 270 mJ/K g-atom found in $YBa_2Cu_3O_{7-\delta}$ by Inderhees, Salamon, Friedmann, and Ginsberg[9] and by Junod *et al.*,[7,10] respectively, showing that these two compounds are similar in this respect.

We have examined the deviation of our specific-heat data from a Debye behavior. To do this, we plotted c/T^3 vs T in Fig. 7. The peak seen there is an indication of extra states, beyond those expected from the Debye model. We fitted our data to a model density of states $g(\epsilon)$ which is a sum of a Debye density of states $g_D(\epsilon)$ and a peak $h(\epsilon)$ in the phonon density of states weighted by a dimen-

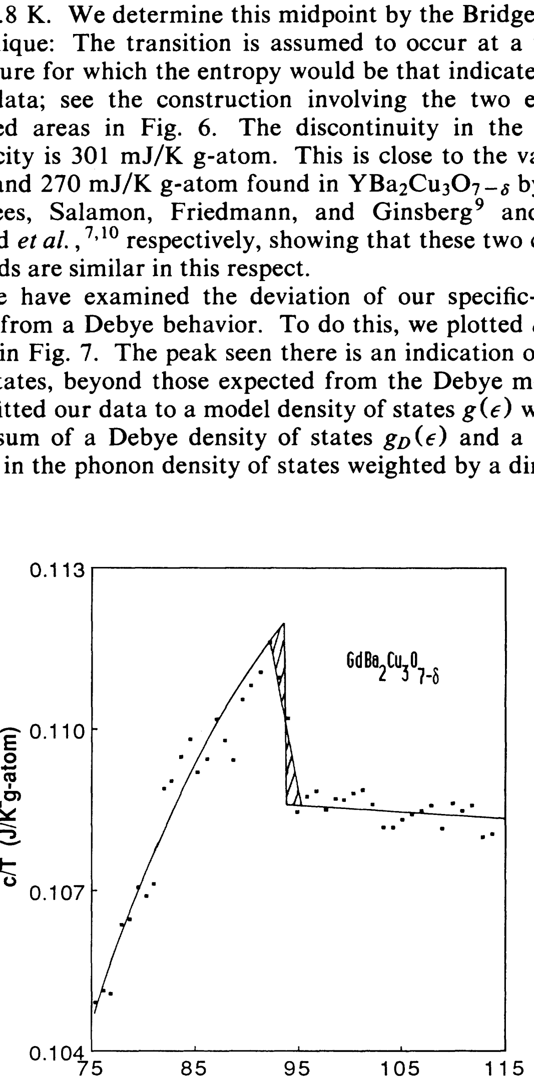

FIG. 6. c/T vs T for $GdBa_2Cu_3O_{7-\delta}$ in the neighborhood of the superconducting transition. The equal shaded areas are drawn to locate the ideal transition temperature by setting the entropy change indicated by the transition equal to its ideal value, as described in the text.

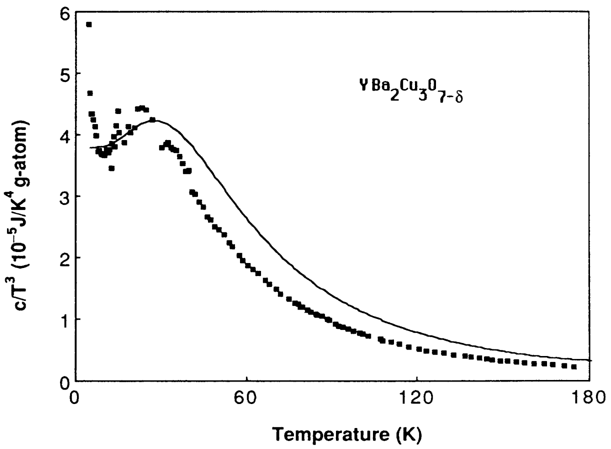

FIG. 7. c/T^3 vs T for $YBa_2Cu_3O_{7-\delta}$, shown with the results (solid line) of a calculation from the neutron-weighted phonon density of states with an arbitrary cutoff, described in the text.

sionless factor α:

$$g(\epsilon)=g_D(\epsilon)+\alpha h(\epsilon) \ . \tag{1}$$

We therefore fit our data to the equation

$$c/T^3=c_D/T^3+(3nk_B\alpha/T^3)\int_0^\infty h(\epsilon)E(\epsilon)d\epsilon \ , \tag{2}$$

where c_D is calculated with a value of Θ_D fitted to the slope of c/T vs T^2 at low temperature and $k_B E(\epsilon)$ is the heat capacity of a single Einstein oscillator. Suppose $h(\epsilon)$ is sharply peaked at an energy ϵ_0. We define T_p to be the temperature at which the peak in c/T^3 occurs. $E(\epsilon)/T^3$ has a peak at $T=\epsilon/4.93k_B$. The Debye heat capacity follows a T^3 law near T_p so that c_D/T^3 is approximately independent of T there. T_P is therefore $\epsilon_0/4.93k_B$.

We chose $h(\epsilon)$ to be a delta function at $\epsilon=\epsilon_0$. We assumed that γ and Θ_D for $GdBa_2Cu_3O_{7-\delta}$ is the same as for $YBa_2Cu_3O_{7-\delta}$. We then adjusted α to fit the height of the peak in Fig. 5, and the resulting fits are the solid lines in that figure. The peaks in the data in Fig. 5 are sharper than the calculated peaks, even though the sharpest possible peak (a delta function) in the density of states was used in the calculation. This may indicate a temperature-dependent density of states in these materials. Further evidence of such a temperature dependence is seen in the specific-heat data for $La_{1.85}Ba_{0.15}CuO_4$ (Ref. 11) and $La_{1.8}Sr_{0.2}CuO_4$.[1,11] The plot of c/T vs T or T^2 breaks away from a straight line at $T=10$ K, too sharply to be consistent with a temperature-independent phonon density of states.

Finally, we calculate $c(T)$ from the neutron-weighted density of states data, $g_n(\epsilon)$ for $YBa_2Cu_3O_{7-\delta}$, measured by Rhyne *et al.*[12] We found that the calculated specific-heat curves were much too high at high temperature. We believe that this results from domination of the high-energy neutron scattering data by the motion of the oxygen ions in the lattice: Each ion contributes to $g_n(\epsilon)$ by an amount proportional to σ/M, where σ is the neutron scattering cross section and M is the ionic mass. This ratio is higher for oxygen than for Cu, Ba, and Y by a factor of 2, 6, and 3, respectively. The neutron scattering data are therefore heavily influenced by the oxygen ions. In order to proceed and obtain a reasonable comparison with our data, we were forced to introduce an arbitrary cutoff at 60 meV in the neutron data. The results of the calculation are shown in Fig. 7. We did not perform a similar fit of neutron data[4,13] to our specific-heat data for $La_{1.85}Ba_{0.15}CuO_4$, or $GdBa_2Cu_3O_{7-\delta}$, since the results would be similar and the necessity for introducing an arbitrary cutoff yields a result of only qualitative significance.

CONCLUSIONS

By measuring the specific heat, resistance, and magnetic susceptibility of $GdBa_2Cu_3O_{7-\delta}$ and comparing the results with those obtained previously by us and other investigators for $YBa_2Cu_3O_{7-\delta}$ and $La_{1.85}Ba_{0.15}CuO_4$, we have been able to obtain information about the jump in the specific heat at the superconducting transition, an antiferromagnetic transition at 2.24 K, and the effect of ionic mass on the specific heat. A peak in c/T^3 near 20 K indicates a peak in the phonon density of states near 10 meV, and we have attempted to fit the peak with both a delta function in the phonon density of states and by referring to the density of states indicated by inelastic neutron scattering data. The specific-heat data indicate a temperature-dependent phonon density of states.

ACKNOWLEDGMENTS

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