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Specific-heat measurements on two high-transition-temperature superconducting oxides: $La_{1.85}Ba_{0.15}CuO_4$ and $La_{1.8}Sr_{0.2}CuO_4$

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We have measured the specific heat c of $La_{1.85}Ba_{0.15}CuO_4$ and $La_{1.8}Sr_{0.2}CuO_4$, as well as their resistance and diamagnetic susceptibility. The results for these two materials are very similar. Below 10 K, c is a linear function of T^3. It is therefore tempting to identify the T^3 part of the low-temperature data as the lattice specific heat, which can be extrapolated to higher temperatures. Subtracting it from c would yield the electronic specific heat throughout the temperature range investigated. A thermodynamic analysis could then be made to find the normal-state value of the electron specific-heat constant γ. The values of γ which come out of this analysis are, however, far too large compared with the results obtained by Finnemore *et al.* from measurements of the upper critical field and the normal-state magnetic susceptibility performed on a similar material. We believe the most likely explanation for this discrepancy is that the phonon spectrum has soft modes. These soft modes might help explain the very high superconducting transition temperatures of these materials.

I. INTRODUCTION

It has recently been discovered that certain oxide compounds with ceramic properties have very high superconducting transition temperatures T_c. These compounds are $La_{2-x}A_xCuO_4$ and related compounds, where A = Ba or Sr, and an as-yet unidentified compound of Y, Ba, Cu, and O.[1-8] The old high, 23.2 K, was superseded by determinations in the neighborhood of 30 to 60 K, and more recently by values of 98 K or higher. These new T_c values raise the important question of whether a previously unsuspected mechanism may be at work to bring about the superconducting state in these materials. Another reason for asking this question is that the superconducting transitions observed in these materials by susceptibility or resistance measurements have a breadth which is three or four orders of magnitude wider than we are used to seeing, even in extremely disordered materials like amorphous bismuth.[9] We therefore think that inhomogeneity may be a vital part of the high values of T_c which have recently been observed.[8]

II. EXPERIMENTAL METHODS

To make our samples, high-purity powders of La_2O_3, $BaCO_3$ or $SrCO_3$, and CuO (all 99.999% pure, from the Aldrich Chemical Company) were combined in the required amounts, mixed, ground, and heat treated at 1100 °C in a platinum crucible. For the $La_{1.85}Ba_{0.15}CuO_4$, the heat treatment was for 1 h in air; then parts of the sample were pressed to form pellets, which were heated for an additional 5 h at 1100 °C in air. For the $La_{1.8}Sr_{0.2}CuO_4$, the heat treatment of the powder was for 72 h in air with grindings every 6 h to promote reaction. It was then pressed into pellets and sintered at 1100 °C for 6 h in air and then for 24 h at 900 °C in oxygen. We characterized our samples by powder x-ray diffraction. They were single-phase materials, with the K_2NiF_4 structure within the sensitivity of that method.

We measured the specific heat c by using an adiabatic calorimeter under computer control. The accuracy of the calorimeter's operation had been checked previously by finding the specific heat of pure copper, and the results agreed with the published data.

III. RESULTS

The dc diamagnetic transitions of the two samples, measured in a superconducting quantum interference device based magnetometer, are shown in Fig. 1, and their resistive transitions are shown in Fig. 2. It is evident that the transition from the superconducting into the normal state is complete by 39 K for $La_{1.85}Ba_{0.15}CuO_4$, and by 36 K for $La_{1.8}Sr_{0.2}CuO_4$. The specific-heat data for our two samples are shown in Fig. 3. They do not disclose any obvious anomaly which can be associated with the superconducting transition, even though the BCS theory[10] requires a discontinuity at T_c. This is not surprising, because the transition to the superconducting state is spread out in these materials, as disclosed by either published susceptibility and resistance data, or by our own susceptibility data. There is an alternative explanation for the absence of a specific-heat anomaly: The contribution of the electronic specific heat might be much smaller than the rapidly rising lattice specific heat.

In analyzing our data, we found it useful to plot c/T vs T^2, as shown in Fig. 4. Extrapolating to $T=0$, we find a value of c/T which does not vanish. This may indicate that some of the material is in the normal state down to our lowest temperatures. In Fig. 4, the curve for each sample in the temperature region below 10 K is a straight line. This indicates a low-temperature lattice specific heat

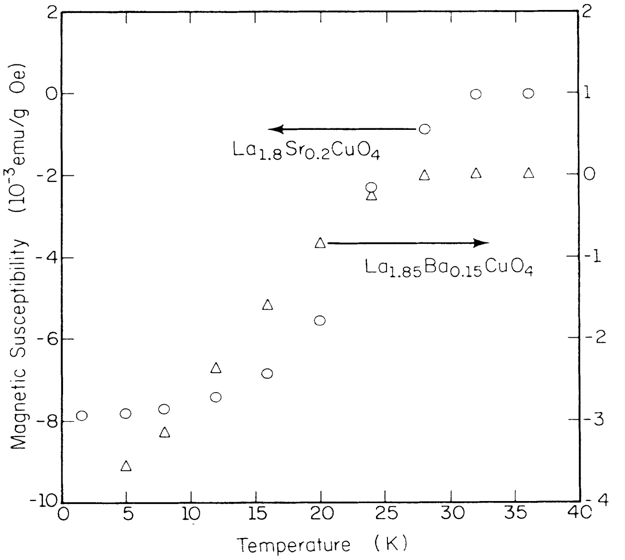

FIG. 1. Magnetic susceptibility of each sample, as a function of the temperature.

which is proportional to T^3. The Debye temperature Θ_D appears to be 188 and 186 K for the barium and strontium compound, respectively.

We can use these values of Θ_D to estimate the lattice specific heat at higher temperatures, and subtract the resulting values from the measured specific heat to obtain the electronic specific heat c_e. Our assumption here is that Θ_D does not change greatly between 10 K and the upper end of the temperature range, 40 K.

We wish to find the normal-state electronic specific-heat coefficient γ. Assuming these materials, like previously investigated superconductors, have a second-order

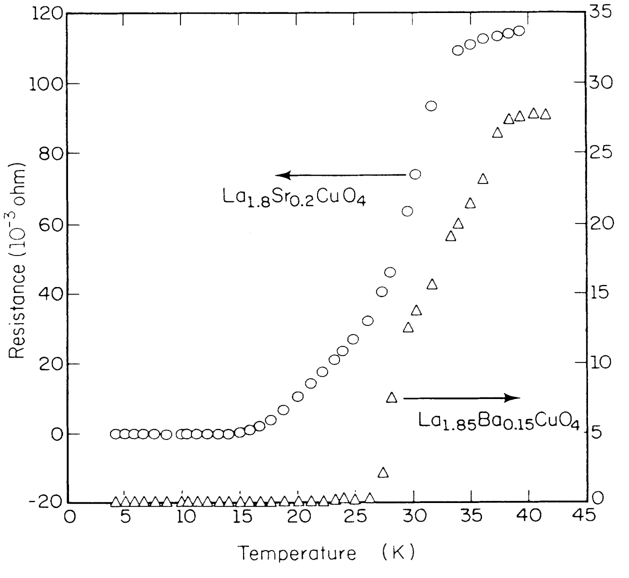

FIG. 2. Resistive transition of each sample, as a function of the temperature.

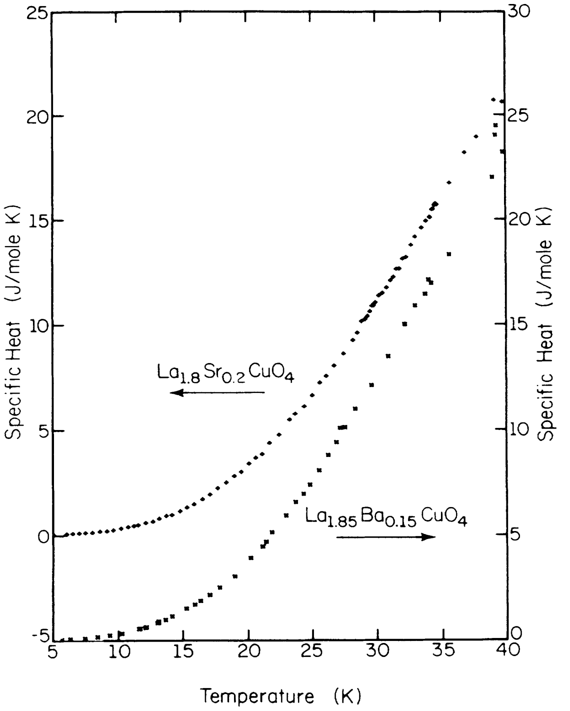

FIG. 3. Specific heat of each sample, as a function of the temperature.

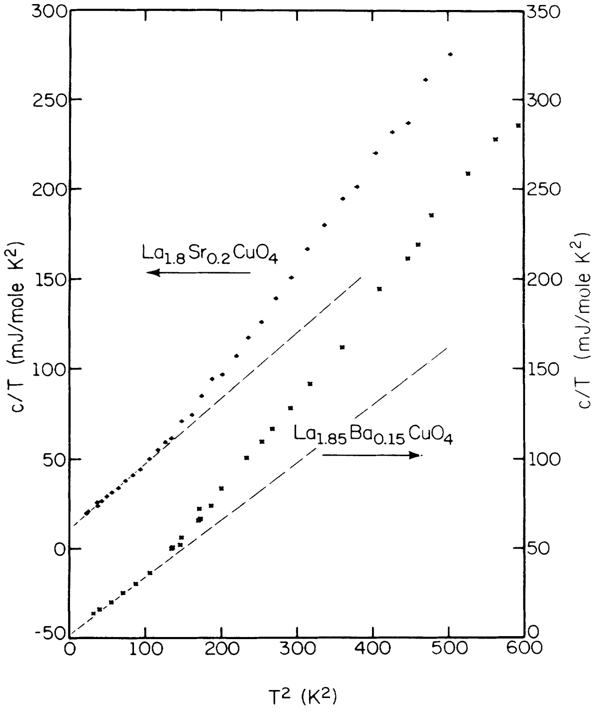

FIG. 4. Ratio c/T of the specific heat to the temperature of each sample, as a function of the square of the temperature. The dashed lines are a guide for the eye.

transition to the normal state, the entropy at the transition temperature in the superconducting state must be equal to that in the normal state. Therefore,

$$\int_0^T (c_e/T)dT = \gamma T \ ,$$

where $T \geq T_c$. We saw above that the transition to the normal state for each of the samples is complete by 40 K, so we are able to calculate the integral to the proper upper limit. The γ values we find for $La_{1.85}Ba_{0.15}CuO_4$ and $La_{1.8}Sr_{0.2}CuO_4$ in this way are 71 and 39 $mJ/mole\,K^2$, respectively. These values are approximately 140 and 80 times that of copper, respectively. However, Finnemore *et al.*[11] have determined γ from measurements of the upper critical field H_{c2} and also from the normal-state susceptibility for the closely related compound $La_{1.85}Sr_{0.15}CuO_4$. They find that $\gamma = 0.11$ mJ/cm^3K^2 $= 6.2$ $mJ/mole\,K^2$, an order of magnitude less than the values we have found. We conclude that one or more of the assumptions we have made are incorrect.

We have considered the possibility that there is a phase change at approximately 10 K in these materials, so that any extrapolation of behavior below that temperature to the region above it is invalid. For example, the lattice could have a structural distortion, similar to that found by Jorgensen and Hinks[12] in superconducting ternary molybdenum sulfides (Chevrel compounds) near 120 K. They observed a reversal in the contraction of the lattice in one crystallographic direction. However, such a phenomenon would normally be associated with a discontinuity in the specific heat, which we do not observe. We therefore believe that there is no phase change at 10 K, but the lattice specific heat has a temperature dependence other than T^3 in the temperature region from 5 to 40 K. This behavior would imply that there is a marked dispersion in the phonon spectrum at energies on the order of 10 to 40 $K \times k_B$, where k_B is Boltzmann's constant. Since the specific-heat curve bends upward from the T^3 extrapolation, phonon softening is indicated, and this could strengthen the electron-phonon interaction.[13]

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] J. G. Bednorz, M. Takashige, and K. A. Müller (unpublished).

[3] S. Uchida, T. Takagi, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, 21 (1987).

[4] C. W. Chu *et al.*, Phys. Rev. Lett. **58**, 405 (1987).

[5] H. Takagi, S.-I. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. Lett. (to be published).

[6] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[7] Z. X. Zhao *et al.* (unpublished).

[8] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, J. Bechtold, and D. Campbell (unpublished).

[9] J. S. Shier and D. M. Ginsberg, Phys. Rev. **147**, 384 (1966).

[10] J. Bardeen, J. R. Schrieffer, and L. N. Copper, Phys. Rev. **108**, 1175 (1957).

[11] D. K. Finnemore *et al.*, Phys. Rev. B **35**, 5319 (1987).

[12] J. D. Jorgensen and D. G. Hinks, Solid State Commun. **53**, 289 (1985).

[13] G. Bergmann and D. Rainer, Z. Phys. **263**, 59 (1973).