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Thermal properties of the high-T_c superconductors $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$

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The heat capacity C_p of samples $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ has been measured from 1.5 to 40 K, and the linear thermal expansivity α of $La_{1.85}Sr_{0.15}CuO_4$ measured in the range 2 to 80 K. The heat capacities show similar temperature dependencies and magnitudes (per gram) with a linear (tunneling?) term dominating below 4 K. α also shows a comparable T term below 4 K and both C_p and α show a small discontinuity of $\approx 1\%$ near $T_c \approx 34$ K.

The discovery of superconductivity in the La-Ba-Cu-O and La-Sr-Cu-O systems with transition temperatures T_c near 40 K (Ref. 1) and later in the cuprite perovskites (Y-Ba-Cu-O system) with T_c above the boiling point of liquid nitrogen[2] has excited much interest both from technological and fundamental viewpoints. In this Rapid Communication we report complementary measurements of the heat capacity C_p, and the linear thermal expansivity α which may assist with understanding the physical origin of the superconductivity as well as providing necessary technical data. For example, if soft phonon modes are important in determining T_c or if T_c is unusually sensitive to strain, then α should reflect this.[3]

The sample of $La_{1.85}Sr_{0.15}CuO_4$ prepared at the Oak Ridge National Laboratory is a compact rod (100% theoretical density) of suitable size (10 mm diameter and > 40 mm long) for determining α in a capacitance dilatometer. The sample had been isostatically hot pressed at 1100 °C and shown to be single phase. Measurements at Oak Ridge showed that its resistance fell to zero at 29.5 K, with the onset of the transition starting at 36 K. The rod was cut and lapped at the Commonwealth Scientific and Industrial Research Organization, and the heat capacity of a smaller piece (8.92 g) was measured in an adiabatic calorimeter. The $YBa_2Cu_3O_7$ was prepared at the University of New South Wales[4] from mixtures of Y_2O_3, $BaCO_3$, and CuO in the proportion Y_2O_3: $3BaCO_3$: 5CuO. The powder was ground in a mortar and pestle, calcined in a silica crucible for 12 h at 900 °C, uniaxially pressed into 12.5 mm diameter pellets, isostatically pressed at 175 MPa and finally placed on a high alumina brick and fired for 6 h at 900 °C. X-ray diffraction studies of the sample revealed that the $YBa_2Cu_3O_7$ phase predominates. The resistance of a bar-shaped sample was measured using a standard four-probe dc technique and was zero at 92 K with a transition width of ≈ 2.5 K. This sample (1.26 g) was too small for accurate dilatometry measurements but adequate for studying the heat capacity.

Results for C_p and α are shown in Fig. 1 as plots of C_p/T^3 and α/T^3 vs T. As the lattice contribution to C_p presumably dominates near T_c it is not surprising that no obvious "anomaly" is seen in the data. For $La_{1.85}Sr_{0.15}CuO_4$ there appears to be a change in slope ($\approx 0.5\%$ change in C_p and $\approx 1\%$ in α) near 34 K that is similar to that observed by Dunlap *et al.*[5] and Batlogg *et al.*[6] The small anomaly in α is best shown by plotting the length change $\Delta l/T^3$. Graphs of C_p/T and α/T vs T^2 (Fig. 2) below 10 K highlight the presence of a linear term in both C_p and α. The data for $T < 10$ K were fitted using the method of least squares, yielding for $La_{1.85}Sr_{0.15}CuO_4$,

$$C_p = 0.010T + 0.000404T^3 + 0.00000242T^5 \text{ mJ/g K} ,$$

$$10^8\alpha = 0.078T + 0.0019T^3 + 0.000018T^5 \text{ K}^{-1} ,$$

and for $YBa_2Cu_3O_7$,

$$C_p = 0.011T + 0.000473T^3 + 0.00000333T^5 \text{mJ/g K} .$$

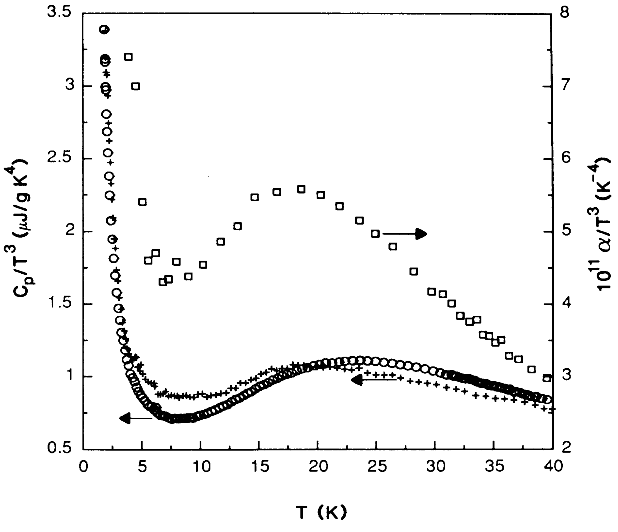

FIG. 1. C_p/T^3 and α/T^3 vs T. The symbols are as follows: ○, C_p/T^3 for $La_{1.85}Sr_{0.15}CuO_4$; +, C_p/T^3 for $YBa_2Cu_3O_7$; and □, α/T^3 for $La_{1.85}Sr_{0.15}CuO_4$.

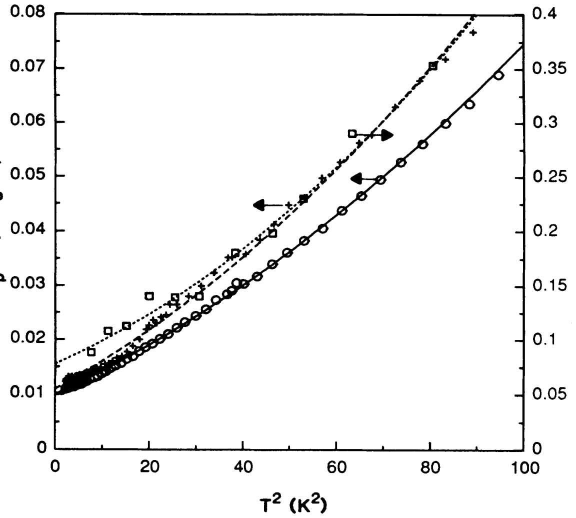

FIG. 2. C_p/T and α/T vs T^2. The symbols are as follows: ○ C_p/T for $La_{1.8}Sr_{0.15}CuO_4$; +, C_p/T for $YBa_2Cu_3O_7$; and □, α/T for $La_{1.85}Sr_{0.15}CuO_4$. The coefficients for the fitted curves are those given in the text.

From the coefficient of the T^3 terms we deduce limiting values for the Debye temperature Θ_D^0 of 439 K (formula weight =398 g, 7 atoms per unit cell) and 432 K (formula weight =666 g, with 13 atoms per unit cell), respectively, for $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$. For comparison, the ceramics SrO and BaO have Θ_D^0 values of $\sim$440 and 360 K, respectively. Calculation of $\Theta_D(T)$ from C_p values shows for each of the oxides a similar and not unusual pattern in which Θ_D has a minimum value of ca. 75% of Θ_D^0 at $T \sim 0.05\Theta_D$.

In order to calculate values of the Grüneisen function $\gamma = 3\alpha B_s/\rho C_p$ for $La_{1.85}Sr_{0.15}CuO_4$ we need data for the adiabatic bulk modulus B_s and density ρ. The latter is approximately 7.1 g/cm^3. We will assume $B_s \sim 100$ GPa (1 Mbar) which is a ball park value for many ceramic oxides leading to $\gamma \approx 1.2$ at room temperatures and 1.7 near 30 K. As $T \rightarrow 0$ the T term gives $\gamma_T \approx 3.3$ and $\gamma_{T^3} \approx 2.0$. The latter value is not "abnormal" and indicates that soft phonon modes do not dominate the behavior at these low temperatures.

Below 5 K both samples show a linear term in both C_p and α, which may be surprising because in superconductors it should be absent for $T \ll T_c$, as a consequence of the BCS energy gap.[7] Dunlap *et al.*[5] also observed a linear term, (5 ± 1) mJ/mol K^2, which is equivalent to 12 μJ/g K^2 (cf. this work = 11 μJ/g K^2) and suggested that it arose from a nonsuperconducting fraction. We believe that this is unlikely in our specimens in view of the similarity of magnitude of the T term in both materials. We point out that a T term is well known in disordered solids including insulating glasses,[8] the superconducting glassy metal $Zr_{0.7}Pd_{0.3}$,[9] and in some ceramics[10] and is usually attributed to tunneling in two-level systems. Walker and Anderson[11] have observed a T term of order ≈ 11 μJ/cm^{3}K^2 (corresponding to about 2 μJ/g K^2 if ρ is between 5 and 6 g/cm^3) in stabilized ZrO_2-Y_2O_3, which has a defective cubic fluorite structure. In this zirconia, tunneling is due to the presence of oxygen vacancies. Structural investigations[12] have shown $YBa_2Cu_3O_7$ to be an oxygen-deficient perovskite, with Ba and Y cations ordered over the A sites of the $A_3B_3O_{9-\delta}$ structure, in the sequence Ba-Ba-Y. The oxygen vacancies ($\delta = 2$ and perfectly ordered) lie on the Cu planes, between the two Ba planes, leaving large tunnels along the (010) direction. It is quite conceivable that this defect structure could give rise to a "tunneling" T term as has been observed in stabilized zirconia and in glasses. A puzzling feature is the large magnitude of the T term, $\sim$10 μJ/g K^2 as compared to that in stabilized zirconia,[11] which is $\sim$2 μJ/g K^2, and in glasses and glass ceramics which lie in the range 1 to 8 μJ/g K^2.[8,13]

The relatively small change in α, about 1%, near T_c is in contrast to some of the $A15$ compounds[14] where there is evidence of a large "anomaly" in α, which is presumably associated with the large strain dependence of T_c and soft phonon modes. Weber[15] has suggested that strong coupling of specific optic phonons (or high frequency) to the conduction electrons are important in forming high values of T_c. The measured α values at room temperature are $\sim 11.9 \times 10^{-6}$ K^{-1}, similar to many ceramic oxides. The values up to 300 K will be reported more fully elsewhere.

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