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# Specific heat of $La_{1.8}Sr_{0.2}CuO_4$: Anomaly at the superconducting transition

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We have measured the specific heat of $La_{1.8}Sr_{0.2}CuO_4$ between 4 and 60 K. We found a step in the specific heat $\Delta C(T_c)/T_c = 33$ mJ/mol$K^2$, and a linear term at low temperatures with a slope $\gamma' = 4 \pm 2$ mJ/mol$K^2$. From these results we conclude that the Sommerfeld parameter for the conduction electrons is $\gamma = 18 \pm 2$ mJ/mol$K^2$.

High-temperature superconductivity in $La_{2-x}M_xCu$ oxides, with $M$ being strontium or barium, is known to be a bulk phenomenon.[1-3] Oxygen annealing improves[3,4] the superconducting sample fraction as indicated by magnetic-flux expulsion and resistive transition measurements. Nevertheless, flux expulsion and resistivity do not yield reliable quantitative values for the bulk factor.

We have performed measurements of the specific heat on a sample of $La_{1.8}Sr_{0.2}CuO_4$. We observed a step at the onset temperature of the superconducting transition, as well as a linear term $\gamma' T$ at low temperatures. Using the results of these measurements together with reasonable assumptions, we derive a value for $\gamma$ and the fraction of the sample that undergoes transition.

The sample was prepared following the methods described in Ref. 2. After initial baking in air at 1130 °C, it was oxygen annealed at 1000 °C for 12 h. Its weight increased 0.5% during this last treatment. The results of x-ray analysis at room temperature[5] show that more than 95% of the sample corresponds to the tetragonal phase of $La_{1.8}Sr_{0.2}CuO_4$. Less than 5% of the sample was a phase identified as $La_2SrCu_2O_6$.

The specific-heat measurements were performed in a semiadiabatic calorimeter using standard heat pulse techniques, over a range between 4 and 60 K. The results are shown in Fig. 1. The inset in this figure enlarges the region around 40 K, after four-point data smoothing. We identify the onset temperature of superconductivity $T_M$, with the point where $C(T)$ changes its slope. The inset also shows $\Delta C(T_M)$ obtained from linear extrapolation of $C(T)$ above and below the transition temperature region. The specific-heat "jump" is $\Delta C(T_M) = 1.36$ J/mol$K$, corresponding to $\Delta C/C = 8\%$. Specific-heat measurements by Batlogg *et al.*[6] in $La_{1.85}Sr_{0.15}CuO_4$ show an anomaly of 1%. Recent measurements by Maple *et al.*[7] on $La_{1.8}Sr_{0.2}CuO_4$, using the same type of calorimeter, failed to show any jump. We are unable to account for these discrepancies.

If all the electrons underwent transition, our results give $\gamma = 23$ mJ/mol$K^2$ assuming a Bardeen-Cooper-Schrieffer (BCS) weak-coupling limit. Clearly, our measured value of $\Delta C(T_M)/T_M = 33$ mJ/mol$K^2$ implies either high values for the Sommerfeld parameter, or a non-BCS behavior for high-$T_c$ superconductors, or both.

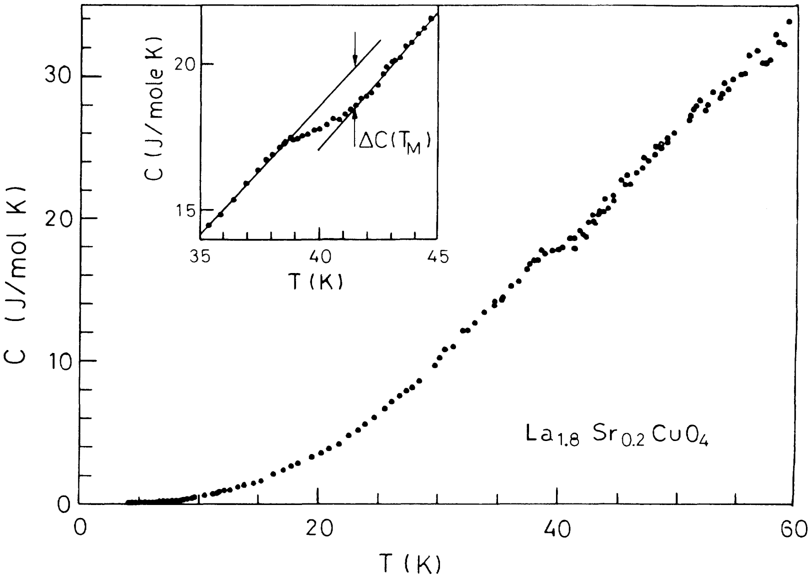

FIG. 1. Specific heat of $La_{1.8}Sr_{0.2}CuO_4$ as a function of temperature. The inset shows the region around 40 K. The inset also shows $\Delta C(T_M)$ (see text).

We have found a linear term at low temperatures (between 4 and 6 K), $C/T=\gamma'+\beta T^2$, with $\gamma'=4\pm 2$ mJ/mol$K^2$. This value coincides with that measured by Maple *et al.*[7] and can be associated to a fraction of electrons that remain in the normal state. Although such behavior could be due to other reasons, i.e., magnetic impurities, they would also affect the slope of $C/T$ vs $T^2$. We measure $\beta=0.21\pm 0.01$ mJ/mol$K^4$, which gives a Debye temperature of 400 K, or a Debye sound velocity of $3.4\times 10^5$ cm/s. From vibrating-reed experiments at 800 Hz and low temperatures in the same system, Esquinazi *et al.*[8] find that the Young-modulus sound velocity is $v_L=5.6\times 10^5$ cm/s. This should be a good approximation of the longitudinal sound velocity. Brun *et al.*[9] estimate the transversal sound velocity to be $v_T=3.2\times 10^5$ cm/s using Brillouin scattering on surface waves. The appropriate average of these two values gives $v_D=3.5\times 10^5$ cm/s. From ir and Raman measurements,[9] the Debye temperature is estimated to be 475 K at 0 K. The agreement among these data with ours gives support to the interpretation of the $\gamma' T$ term as due to a noncondensed fraction of normal electrons.

We examine our previous estimate of $\gamma$ within a model based on simple assumptions. First of all, we assume that the spread-out specific-heat anomaly is due to a corresponding spread in the transition temperatures of different portions of the sample, probably because of composition inhomogeneities, as may be present in these samples.[10] To describe this spread, let $n(T)dT$ be the fraction of the sample that has its transition temperature between $T$ and $T+dT$. Besides, we shall take the relation between specific heat and temperature, in a superconductor with a single $T_c$, to be that given by a two-fluid model with a parabolic temperature dependence of the thermodynamic critical field: $C_{\mathrm{el}}(T)=\gamma T$ above $T_c$ and $C_{\mathrm{el}}(T)=3\gamma T^3/T_c^2$ below $T_c$ (our estimates depend, but not critically, on the exponent chosen for this dependence).

In this case, the electron specific heat of the inhomogeneous superconductor would be $\gamma T$ above the maximum $T_c=T_M$, and

$$C_{\mathrm{el}}=\gamma T\left[1-\int_T^{\infty} n(T)dT+3T^2\int_T^{\infty} n(T)/T^2 dT\right] \qquad (1)$$

below $T_M$. We are assuming that $\gamma$ is basically the same throughout the sample. For temperatures lower than the minimum in the spread of $T_c$'s $C_{\mathrm{el}}/T=\gamma(1-N_T)+O(T^2)$, where $N_T$ is the fraction of the sample that has become superconducting.

If $n(T)$ is taken to be constant $n_0$, the electronic specific heat would behave as $C_{\mathrm{el}}=\gamma T[1+2n_0(T_M-T)]$ for $(T_M-T)\ll T_M$. From the change in slope of $C(T)$ at $T_M$ (see the inset in Fig. 1) we find $n_0\gamma=7$ mJ/mol$K^3$.

We see in Fig. 1 that the "step" in the specific heat extends 2 K below $T_M$ (this agrees with the results of Ref. 6). If we assume that the transition of the whole sample occurs in those two degrees, we would conclude that $\gamma=14$ mJ/mol $K^2$, but such total transformation is unlikely: Figure 2 shows flux expulsion,[4] resistivity,[4] and specific-heat data for the same sample. It is seen that flux expulsion and resistivity hardly changed within 2 K below $T_M$. Let us assume that a fraction $N_T$ of the electrons undergoes transition at a constant rate $n_0$, over the two degrees below $T_M$. The remaining normal fraction $(1-N_T)$ gives rise to the linear specific heat at low temperatures. Then two equations for $\gamma$ and $N_T$ can be written $\gamma(1-N_T)=4\pm 2$ mJ/mol$K^2$ and $\gamma N_T=14$ mJ/mol$K^2$, which are solved by $N_T=0.8\pm 0.1$ and $\gamma=18\pm 2$ mJ/mol$K^2$.

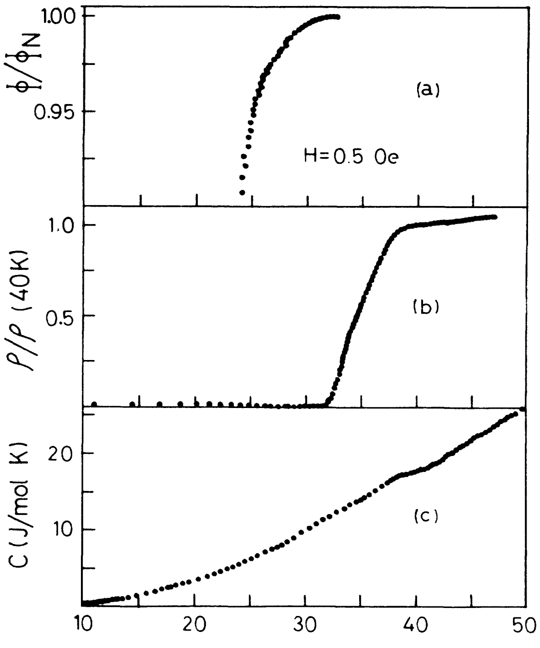

FIG. 2. (a) Flux expulsion, (b) resistivity, and (c) specific heat for the same sample of $La_{1.8}Sr_{0.2}CuO_4$. $\Phi_N$ is defined as the flux through the sample in the normal state. The specific-heat step is seen to occur well above the onset of the superconductivity determined by flux expulsion and resistivity.

Flux expulsion sets a lower bound to $N_T$. Magnetization measurements[4] show a flux expulsion of 50%, that is, $N_T\geq 0.5$.

Subtraction of the electronic specific heat given by Eq. (1) with this rectangular $n(T)$, the roughest approximation consistent with the step, removes quite satisfactorily the anomaly in $C(T)$.

With the same assumptions mentioned above and using expression (1) we calculate $C_{\mathrm{el}}(T)$ at temperatures below the specific-heat anomaly region. By a linear extrapolation of this expression to $T_M$ we calculate

$$\Delta C(T_M)=\gamma T_M N_T[3T_M/(T_M-2)-1] \ . \qquad (2)$$

Using the experimental value $\Delta C(T_M)=1.36$ J/mol$K$ and $T_M=41.5$ K it is found that $\gamma N_T=15.2$ mJ/mol$K^2$, in good agreement with the value obtained from the change of the slope of the specific heat and the low-temperature behavior.

These values are much higher than those which have been reported recently: Panson *et al.*[11] find $\gamma=2.7\pm 0.1$ $J$/mol$K$; Foner *et al.*[12] give $\gamma=6.3$ and 14.8 $J$/mol$K$; Batlogg *et al.*[6] give $\gamma=6\pm 1.5$ $J$/mol$K$ for $La_{1.85}Sr_{0.15}CuO_4$. Also for this last compound, Kwok *et al.*[13] set bounds for $\gamma$ between 5.9 and 7.3 $J/\text{mol}K$. The highest value we know of is that given by Maple *et al.*[7] for $La_{1.8}Sr_{0.2}CuO_4$, $\gamma=15.6$ $J/\text{mol}K$, which is still lower than ours. However, the fact that the simple model we have used allows us to correlate three simultaneous features of the specific heat (the magnitude of the jump, the change in slope at $T_M$, and the linear term at low temperatures), using one value for $\gamma$, makes us confident that our result is a fair estimate for the Sommerfeld parameter in $La_{1.8}Sr_{0.2}CuO_4$.

The fact that 80% of the sample undergoes the superconducting transition within 2 K of the onset, while the flux expulsion and resistivity curves extend their variations to much lower temperatures, hints strongly at a bond-percolation origin[4,14,15] for these phenomena, whatever the microscopic causes of the high-temperature superconductivity in the bulk of the sample. This point of view is further reinforced by the fact that oxygen-annealing changes markedly the flux expulsion and resistivity curves but not the onset of the transition.

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