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Electronic properties of $La_{2-x}Sr_xCuO_4$ high-T_c superconductors

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The basic macroscopic properties of the high-T_c superconductors $La_{2-x}Sr_xCuO_{4x}$ ($x = 0.075$–0.20) with bulk transition temperatures up to 37.5 K were studied. The upper and lower critical fields, specific heat, Meissner effect, and electrical resistivity were measured and extreme type-II behavior with large upper-critical-field slopes is observed. The density of states at E_F is calculated from three different sets of experimental quantities ($\gamma_{BCS} = 6 \pm 1.5$ mJ/mole K^2). The critical temperatures of $(La, Sr)_2CuO_4$ and $Ba(Pb,Bi)O_3$ are ~ 3 times higher than those of other superconductors with comparable values of γ, which empirically distinguishes them as a separate class of superconductors.

For more than a decade the highest superconductivity transition temperature T_c observed for bulk material has been that of Nb_3Ge, 23 K. In the past few months, however, the highest T_c has advanced substantially. After the initial report of possible superconductivity at 30 K in multiphase samples of La-Ba-Cu-O,[1] the superconducting phase was identified as having a K_2NiF_4-type structure,[2] and a bulk T_c for $(La,Ba)_2CuO_4$ of ~ 28 K (Refs. 2–4) was observed. An additional increase of T_c by at least 9 K was achieved in the $(La,Sr)_2CuO_4$ series, and bulk superconductivity close to 40 K is now a reality.[5–7] Under external pressure the superconducting transition temperature of nonbulk $(La,Ba)_2CuO_4$ increases.[8] In the present paper we report the results of an extensive study of macroscopic properties of the $(La,Sr)_2CuO_4$ system. Included are measurements of the lower and upper critical fields, specific heat, Meissner effect, and resistivity. $(La,Sr)_2CuO_4$ superconductors display extreme type-II behavior (i.e., $\lambda \gg \xi_0$) with large upper-critical-field slopes. Good agreement is found between the values of the density of states at E_F, calculated in three different ways from the experiments, with the corresponding Sommerfeld constant γ of 6 ± 1.5 mJ/mole K^2 (evaluated for weak coupling).

$La_{2-x}Sr_2CuO_4$ compounds in polycrystalline pellet form were prepared using standard powder ceramic procedures. The details have been reported elsewhere.[5,9] The essentially bulk nature of the superconductivity was confirmed by Meissner-effect studies in which the sample was cooled in a small applied field and the expelled flux was measured. Depending on the porosity and other processing-related properties of the specimen, a signal of 30%–70% of the ideal value is observed. This is a conservative lower limit of the superconducting volume fraction, as trapped flux will reduce the actual signal.

The temperature dependence of the electrical resistance is typical for a metal and the ratio $R(300\ K)/R(T_c)$ is 3.1 in the best $x = 0.15$ sample, 2.8 for the $x = 0.2$ sample, and 2.1 for the $x = 0.1$ sample. The resistivity at T_c is 320 ± 30 $\mu\Omega$cm for $x = 0.15$, reflecting the low carrier concentration in this material. (A low plasma frequency and therefore a low carrier concentration can be inferred at a glance from the black appearance of the samples.)

The lower critical fields were measured in a superconducting quantum-interference device magnetometer (S.H.E.) by cooling the sample in zero field to the desired temperature and then increasing the field. The inset to Fig. 1 shows three typical magnetization curves for the $x = 0.2$ sample. H_{c1} was then defined as the point where $M(H)$ first deviates from linearity. The main part of Fig. 1 presents $H_{c1}(T)$. The slope $-dH_{c1}/dT \equiv H'_{c1}$, is -5.1 ± 0.2 Oe/K.

To study the upper critical fields, the sample resistance R was monitored as a function of temperature using either ac or dc techniques, in fixed fields up to 120 kOe. The exact value of H_{c2} depends somewhat on the procedure adopted to define it from the $R(T)$ curves. As illustrated in the inset to Fig. 2, the drop of R at T_c in a magnetic field is not sharp and, as a complication, a "foot" develops in high fields. The origin of the foot has not been determined unequivocally, but is probably associated with inhomogeneities in the sample. If, for instance, bulk material inside the grains has a T_c of 37.5 K but the grains are cou-

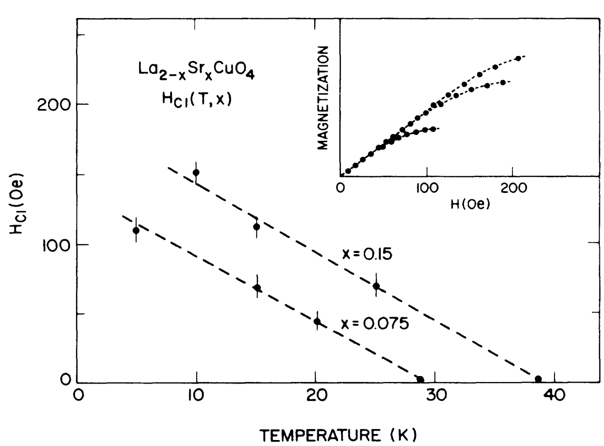

FIG. 1. Lower critical field H_{c1} for two samples with different composition. The inset shows actual magnetization curves at various temperatures; H_{c1} was defined as the point where $M(H)$ deviates from linearity.

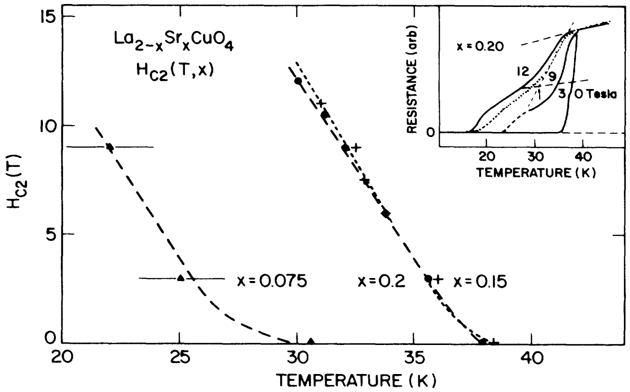

FIG. 2. Upper critical field H_{c2} for three Sr compositions. The procedure shown in the inset by broken lines was adopted to define H_{c2}.

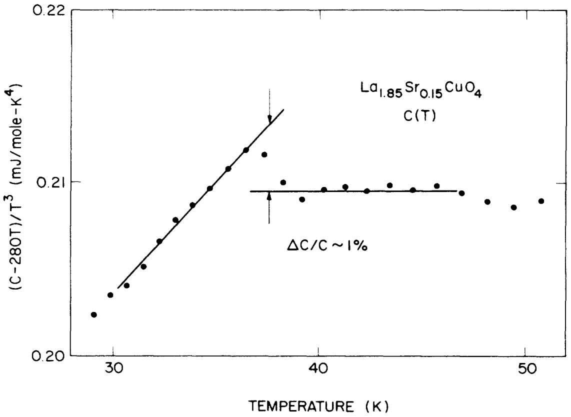

FIG. 3. Specific-heat anomaly at the superconducting transition in $La_{1.85}Sr_{0.15}CuO_4$. This form of presentation enhances the electronic anomaly at T_c over the rapid variation of $C(T)$ due to the lattice contributions.

pled to each other via a thin skin with T_c of ~ 25 K, then proximity-induced superconductivity would give a full drop of R at the high T_c in low fields. When external fields suppress the proximity effect, a foot in $R(T)$ will occur. The volume fraction of the low-T_c material might be very small ($< 1\%$). A forthcoming publication will address this and related questions.[10] Suffice it here to note that the final results of this paper depend only slightly on the detailed procedure employed to define T_c; we give an example of the procedure in the inset of Fig. 2 by broken lines. Except for a rounding below ~ 3 T, we approximate $H_{c2}(T)$ by straight lines with slopes of -17.5 ± 1.5 kOe/K for $x=0.20$ and $x=0.15$. The $x=0.075$ sample has a wide transition in large fields, but its H'_{c2} is similar to the two other samples. Extrapolating these slopes to $T=0$, including a factor of $\pi^2 e^{-\gamma}/8$ [i.e., assuming nonparamagnetically limited Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory in the dirty limit], we obtain $H_{c2}(0) \sim 460$ kOe. If a different method of defining T_c from the $R(H)$ data is used, then the H'_{c2} value extrapolates to $H_{c2}(0) \sim 750$ kOe. Obviously, measurements in higher fields are desirable. The observed slopes of H_{c1} and H_{c2} are employed below to estimate the specific-heat anomaly at T_c. The same information is obtained, however, directly from specific-heat measurements.

The relative change of the specific heat at T_c, $\Delta c(T_c)$, is expected to be small due to the dominant lattice contribution ($\sim T^3$) at such high temperatures. To measure it, we used a quasiadiabatic method with heater and thermometer glued with epoxy onto a $La_{1.85}Sr_{0.15}CuO_4$ sample. The addendum heat capacity is estimated to be smaller than 20% at T_c. In this report the absolute value of $c(T)$ is not emphasized but rather the change in $c(T)$ near T_c. In Fig. 3 the data are presented in a way to enhance the anomaly at T_c. The relative change at T_c is indeed small, $\sim 1\%$, but is clearly resolved. The two lines are guides to the eye. From this and three additional measurements, one of them on a different sample, the specific-heat anomaly $\Delta c/T_c$ is found to be 7.6 ± 1.8 mJ/mole K^2, which corresponds to a Sommerfeld constant $\gamma = 5.3 \pm 1.5$ mJ/mole K^2 (in the weak-coupling limit).

The experimental results can be analyzed to extract basic thermodynamic quantities and to demonstrate self-consistency. The specific-heat measurements yield directly Δc at T_c. The Rutgers formula relates the slope of the thermodynamic critical field H'_c at T_c with Δc at T_c. In these extreme type-II superconductors we calculate H'_c from H'_{c2} and H'_{c1}, given in Figs. 1 and 2, and find $H'_c = -1.45 \pm 20$ Oe/K. In the weak-coupling BCS limit this yields a value for the Sommerfeld parameter, $\gamma = 6.6 \pm 2$ mJ/mole K^2.

A third way to estimate γ combines the resistivity at T_c with H'_{c2}. The resulting γ is 7 ± 1.5 mJ/mole K^2. Within the experimental limits of all three methods the values for γ are consistent with each other and average to 6 ± 1.5 mJ/mole K^2. This value may be subject to correction for two reasons. First, strong coupling will reduce γ, and second, the superconducting volume fraction is possibly less than unity in these samples, and thus γ for the superconducting material could be somewhat higher. (Even a γ as high as ~ 10–15 mJ/mole K^2 would be too small to yield a T_c of almost 40 K in traditional materials.)

The Pauli paramagnetic susceptibility expected for the given γ is $\sim 8 \times 10^{-4}$ emu/mole, barring enhancement effects. The measured susceptibility for the $x=0.15$ sample is $\sim 4 \times 10^{-4}$ emu/mole at T_c and increases slightly at higher temperatures. This $\chi(T)$ includes diamagnetic core contributions, and thus the agreement between the observed and the γ-derived susceptibility is considered satisfactory.

Finally, we emphasize the similarities between $(La,Sr)_3CuO_4$ and the widely studied Ba $(Pb,Bi)O_3$ superconductors. (See, e.g., Refs. 11–17.) In Fig. 4, T_c is plotted versus γ (per mole formula unit) for many superconductors. Only a few are explicitly named, but all lie below the dashed line, which for this discussion serves as an empirical boundary which is not sharply defined. On this γ-T_c plot, the two oxide superconductors are well separated from the rest. Their T_c is enhanced by factors of ~ 3 over superconductors with comparable γ values. One mi-

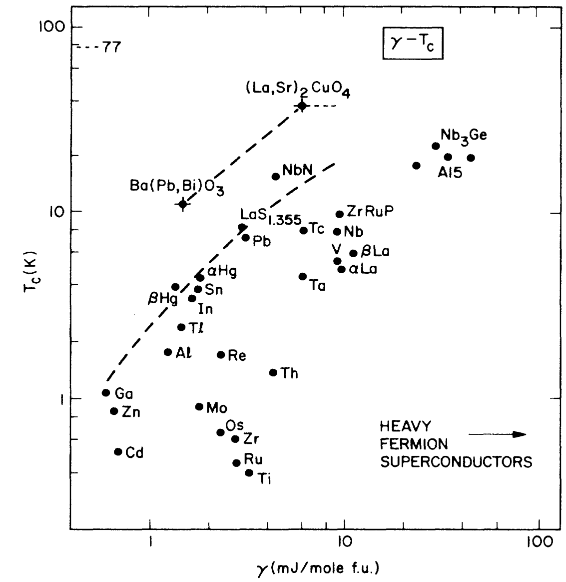

FIG. 4. Relationship between T_c and the density of states at E_F for some superconductors. (γ in mJ/mole formula unit.) The two oxide superconductors are well separated from all the others, and their T_c is $\sim$3 times higher than the highest T_c for materials with comparable γ.

croscopic origin of these high T_c's is found in the strong admixture of oxygen $2p$ wave functions to the electronic states at the Fermi level, thus leading to strong coupling to bond-length-modifying phonons.[18-20] The high frequency of these phonons will then result in a high effective phonon frequency in the various formulas for T_c. In addition, strong coupling to low-energy phonons has been observed directly by tunneling spectroscopy in $BaPb_{0.75}Bi_{0.25}O_3$.[12] The same argument could be applied also to NbN, which indeed lies very close to, or above, the empirical boundary.

The second similarity is the composition dependence of the electronic properties. In both systems, superconductivity with a sharp transition occurs only in a limited composition region,[12-14] which borders at least on one side to a semiconducting region. A tendency towards formation of charge-density waves is inferred from calculated Fermi surfaces,[18-20] and several structural transformations typical of perovskite-related structures are observed in experiments on both systems. Future studies will have to focus in more detail on the strength and spectral dependence of the electron-phonon coupling and should explore the possibility of other coupling mechanisms.[21,22]

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