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Phonon density of states in $La_{1.85}Sr_{0.15}CuO_4$

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Specific-heat and inelastic neutron scattering studies of the high-T_c superconducting compound $La_{1.85}Sr_{0.15}CuO_4$ are reported. A distinct anomaly of electronic origin in the specific heat is found at the superconducting transition temperature. The phonon density of states up to ~20 meV is extracted from both experiments and the two sets of results agree well in yielding a sharply enhanced density of states at 10 meV, in accord with a recent theoretical study.

The recent discovery[1-5] of high superconducting transition temperatures (T_c) in the substituted lanthanum copper oxides has stimulated anew the discussion about the limits of T_c in phonon-mediated superconductors. Although the transition temperatures for the $(La,Sr)CuO_4$ compounds are ~40 K, and thus near the upper limit on T_c dictated by conventional phonon-pairing mechanisms,[6] these high temperatures nevertheless scale up with the electronic density of states from the related compound $Ba(Pb,Bi)O_3$.[7] It is therefore important to determine whether this new class of oxides displays a novel nonphononic pairing mechanism or whether traditional phonon pairing is operative. Theoretical arguments have been presented for either of the two extreme possibilities[8-11] and therefore, any information about the phonons in this system will be useful.

As a first step towards understanding the role of phonons in this interesting new class of compounds, we have measured the phonon density of states using both specific heat C, and neutron scattering probes, for the compound $La_{1.85}Sr_{0.15}CuO_4$ in the temperature range 2–50 K. At the transition temperature T_c (~37 K) we find the expected anomaly corresponding to 10 ± 2 mJ/mole f.u. K^2. In addition, we also find a pronounced peak in C/T^3 at roughly 23 K, which corresponds to a peak in the phonon density of states at 10 meV. This is corroborated by the existence of a sharp feature in the neutron scattering spectrum, also at 10 meV. Our results are compared to those of a recent phonon calculation for $(LaSr)CuO_4$ which shows a peak in the density of states at 10 meV as well as the presence of strongly coupled phonons in this energy region.

The material was prepared in a manner described previously.[4] The specific heat measurements were performed in a standard cryostat, with the calorimeter situated inside a variable-temperature top-loading copper can. The sample was in the form of a compressed pellet, 8.76 mm in diameter and 2.27 mm in thickness, which weighed 0.7355 g. The thermometer was a 10-Ω Allen-Bradley resistor with the casing removed and the heater was a 350-Ω strain gauge. Both heater and thermometer were epoxy glued onto opposite faces of the sample using Armstrong C-1 epoxy. The method used in the measurement was the standard semidiabatic heat-pulse technique. The contribution to the total heat capacity from the thermometer and the heater, determined in a separate experiment, was 20% and 4% of the total at the lowest and highest temperatures, respectively, and has been subtracted from all the data shown.

Neutron scattering measurements were performed on a 50-g sample of $La_{1.85}Sr_{0.15}CuO_4$ using a triple-axis spectrometer at the High Flux Beam Rector of the Brookhaven National Laboratory. The monochromator and analyzer crystals were pyrolitic graphite, set for their (002) reflections. Energy scans at several fixed momentum transfers (Q) were performed by varying the incident neutron energy. The final neutron energy was fixed at 30.5 meV; a pyrolitic graphite filter before the analyzer eliminated higher order contamination of the scattered beam. The raw data were converted to an unnormalized phonon density of states by subtracting an ω-independent background and then multiplying by $\hbar\omega/[n(\omega)+1]$, where

$$n(\omega)+1=[1-\exp(-\hbar\omega/k_BT)]^{-1} .$$

In Fig. 1 we show the specific heat over the range 2–50 K with the lower-temperature data expanded in the inset. It is clear from the curvature in these data that the lattice specific heat, which dominates over this range, cannot be described by a Debye law with a single cutoff frequency. In addition, the low-temperature C/T data yield a finite intercept of ~2 mJ/mole f.u. K^2, corresponding to a linear term in the specific heat. In contrast, for a pure, single-crystal superconductor one expects exponentially activated behavior at $T \ll T_c$ with a characteristic energy corresponding to the gap value. The observed linear term will be discussed below and compared with the jump in the specific heat at T_c.

In Fig. 2 we show the results of neutron scattering measurements at fixed Q for two different temperatures, 40 and 5 K. These data show, besides an ω^2 background, a distinct peak centered at 10 meV, suggestive of an Einstein or an optical mode possessing weak dispersion near the zone boundary. Data at other momentum transfers in this powder sample show the same feature. We can compare the neutron scattering results to the specific heat by

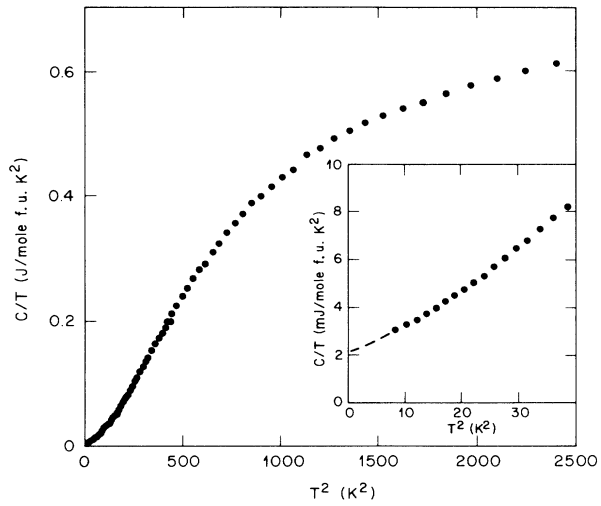

FIG. 1. The specific heat of $La_{1.85}Sr_{0.15}CuO_4$ from 2 to 50 K vs the square of the temperature. The inset shows the low-temperature region and indications of a linear term with a γ of 2 mJ/mole f.u. K^2.

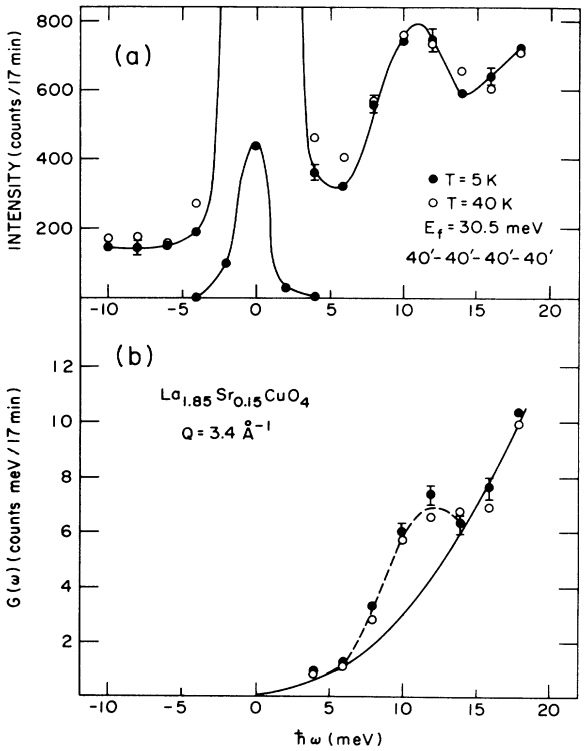

FIG. 2. (a) Neutron scattering spectrum for $La_{1.85}Sr_{0.15}CuO_4$ up to 20 meV for $Q = 3.4$ Å^{-1} at 5 and 40 K. (b) The inelastic part of the spectrum presented in (a) after subtraction of an energy-independent background. The solid line varies as ω^2, and the dashed line indicates the peaking structure near 10 meV.

the following method. One can show that a plot of the lattice contribution to C/T^3 vs $\ln(T/K)$ represents an approximate image of the phonon spectrum $F(\omega)/\omega^2$ vs $\ln(\hbar\omega/4.93k_BT)$.[12] Thus, features in $F(\omega)$ at a particular value of ω show up in C/T^3 at a temperature $T = \hbar\omega/4.93k_B$. In Fig. 3 we show such a plot of C/T^3, illustrating that the non-Debye behavior is a result of the same peak in the density of states as that observed in neutron scattering—indeed the peak position of approximately 23 K corresponds well with the 10-meV neutron value. We thus can parametrize the specific heat using the two main features of the neutron spectrum, namely, the ω^2-background and the 10-meV peak. For this purpose, we allowed the relative weight of the contributions arising from an Einstein mode and an ω^2 background to vary in order to achieve the best fit, also shown in Fig. 3. This is justified by the fact that, in general, different sets of atoms will participate in these qualitatively different types of excitations and, therefore, scattering data contain density-of-states information as well as form-factor corrections, the latter of which will not affect the specific heat.[13] Without accurate knowledge of the modes involved, one can only infer the relative weights of the two contributions. Besides these contributions, we found it necessary to include a 4.3-meV Einstein peak—this is consistent with the neutron data since the peak is so small that it would not be observable at the present level of precision. The inset of Fig. 3 shows the three contributions to the phonon spectrum (drawn to scale) which reproduces the specific heat quite well over the entire range of the measurements. It is interesting to note that the prefactors of the analytic forms for the 10-meV peak and the ω^2 background imply that 3.0 and 1.9 atoms per formula unit, respectively, contribute to the low-frequency motion in this compound. The absence of a contribution from the other two atoms might be taken as a signal of the importance of the linear term, discussed below, or as an indication of higher frequency modes which have already been frozen out at these low temperatures.[14]

Next, the role of these phonons in mediating the superconducting pairing is discussed. The possibility that these modes are strongly coupled to the conduction electrons is suggested by a recent theoretical study of $La_{1-x}Sr_xCuO_4$.[11] In this work it is shown that the optical breathing modes and longitudinal-acoustic modes, both possessing strong electron-phonon coupling, are drastically renormalized as a function of Sr concentration. Evidence for the observability of these strongly coupled modes is suggested by sharp peaks at $\sim$10 meV in the calculated quantity $\alpha^2(\omega)F(\omega)$. These modes and their coupling to the conduction electrons are strongest for $x = 0.15$. For other values of x they shift to higher energies and the coupling becomes smaller. One test of these ideas would be a study of this 10-meV peak as a function of Sr concentration. For $x > 0.15$, the theory predicts that the peak position will move to higher values as more Sr is added —for $x < 0.15$ no prediction is made. We have made specific-heat measurements on $LaCuO_4$, and although we see no change in the peak position, we do find the magnitude of the peak to be about 50% greater than for $x = 0.15$. This result, although consistent with an explanation that the 10-meV mode involves oxygen, and therefore is enhanced by reduction on the La site, does not allow us to determine if the motion is strongly coupled to

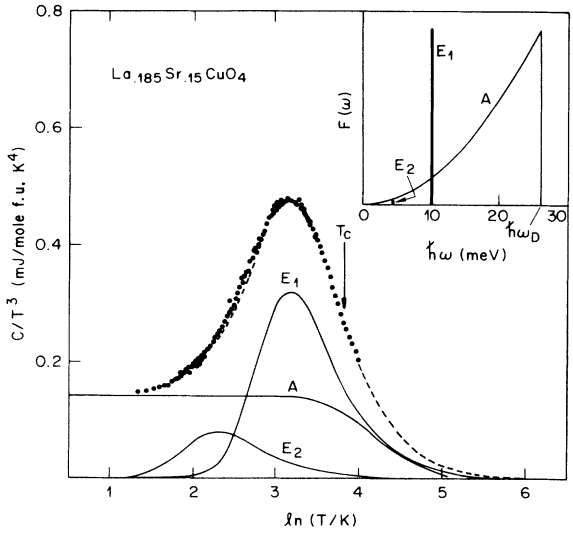

FIG. 3. The specific heat C, divided by T^3 vs the logarithm of the temperature, expressed in kelvin. The peak at 23 K corresponds to an enhanced density of phononic states at energies of 10 meV (115 K). A linear term of 2 mJ/mole K^2 has been subtracted, allowing a conventional phonon spectrum analysis. The continuous lines, labeled A, E_1, and E_2 are contributions from the acoustic and optical branches, as described in the text. The dashed line is the sum of these three contributions and nearly coincides with the experimental points over the range of measurement. The inset shows the phonon spectrum (drawn to scale) used to compute the three contributions. The cutoff frequency for the acoustic branch corresponds to $\Theta_{Debye}=300$ K. Also note the relative unimportance of the lower-energy Einstein mode for the phonon spectrum.

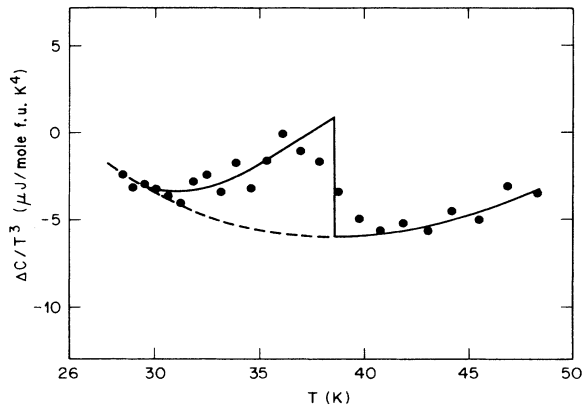

FIG. 4. The specific-heat difference ΔC between the measured values and the results of the fitting procedure as described in the text, in the vicinity of T_c. The curves shown here are guides to the eye and the jump at T_c is estimated to be 10 ± 2 mJ/mole f.u. K^2.

the conduction electrons.

Obviously, these experiments do not cover the entire energy range over which phonons important for superconductivity are expected to lie. The calculations indicate that this range might extend up to energies as high as 80 meV, yet the main contribution to $\alpha^2(\omega)F(\omega)$ comes at energies near 10 meV. Also one cannot rule out the possibility that much of the experimentally observed structure is due to rotational, O c-axis breathing, or La modes,[11,15] all of which are weakly coupled to the conduction electrons.

In this discussion concerning peaking structure in $\alpha^2(\omega)F(\omega)$, we must mention a recent far-infrared (FIR) surface impedance measurement[16] on $La_{1.84}Sr_{0.16}CuO_4$. In this work, a peak in $\alpha^2(\omega)F(\omega)$ is found to lie at 2.9 meV, but no feature is seen at 10 meV. The determination of this energy relies on a prior measurement of the superconducting energy gap $2\Delta_0$, for which a value of $1.8k_BT_c$ is used (obtained in a separate FIR absorption measurement). Recent point contact measurements,[17] in contrast, yield gaps in excess of $2\Delta_0=4k_BT_c$, thus requiring further clarification of the gap values.

In Fig. 4 we show the detailed behavior of the specific heat after subtraction of the total phonon contribution in the vicinity of T_c (as determined by dc magnetization). The jump at T_c is clearly resolved above the scatter and a value of 10 ± 2 mJ/mole f.u. K^2 is obtained, corresponding to a γ of 7.0 mJ/mole K^2. This is in good agreement with both measurements on another sample[18] of the same nominal concentration as well as with various estimates of γ from critical-field and resistivity measurements.[18-20] This value for γ is much larger than the value of 2 mJ/mole f.u. K^2 found at lower temperatures and, if the latter is due to a nonsuperconducting portion of the sample, puts an upper limit of $\sim20\%$ on the fraction of the sample that has not become superconducting, assuming similar densities of states of the nonsuperconducting and superconducting phases.[21] On the other hand, given the novelty of the phenomena present in this compound, and the present state of theoretical speculation, it seems quite possible that the linear term has an intrinsic origin. In particular, the possibility of magnetic,[8] or dense defect modes[22] cannot be ruled out at this stage.

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[13]In general terms, inelastic neutron scattering measures $Q^2\langle g(Q,\omega)\rangle\langle F(Q,\omega)\rangle$, where Q is the momentum transfer and where $\langle g(Q,\omega)\rangle$ and $\langle F(Q,\omega)\rangle$ are the thermal averaged Debye-Waller and structure factors, respectively. In contrast, specific heat measures a quantity similar to $\langle g(Q,\omega)F(Q,\omega)\rangle$, so that a simplistic comparison of relative weights of different modes is not possible between the two techniques. Energy features, however, will survive such thermal averaging procedures.

[14]Although not relevant for the main discussion, we mention one peculiar observation. At one point during the measurements, the sample sat in the calorimeter for $\sim$10 days at room temperature and nominally under vacuum. All the data shown here were obtained after this period and differed from the previous data by an amount that peaked at the same temperature as that shown in Fig. 2, with a height equal to $\sim$25% of the total and approaching zero at the lowest and highest temperatures. The anomaly at T_c was not affected, however, and subsequent cool downs from room temperature produced no further change.

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