RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 18 1 NOVEMBER 1995-II

Anomalous phonon damping and thermal conductivity in insulating cuprates

J. L. Cohn
Physics Department, University of Miami, Coral Gables, Florida 33124

C. K. Lowe-Ma
Chemistry Division, Naval Weapons Center, China Lake, California 93555

T. A. Vanderah
National Institute of Standards and Technology, Gaithersburg, Maryland 20899
(Received 27 June 1995)

We examine the in-plane thermal conductivity (κ_{ab}) for different classes of insulating cuprate crystals, and present measurements for $YBa_2Cu_3O_{6+x}$ and $PrBa_2Cu_3O_{6+x}$ ($x \leqslant 0.11$). An unusual, nonmonotonic temperature (T) dependence of κ_{ab}, previously observed in $La_2CuO_{4+\delta}$, is demonstrated to be a characteristic of the 123 compounds as well. This feature signals the onset of anomalous damping for in-plane, heat-carrying phonons at $T \leqslant 250$ K that is highly sensitive to light oxygen doping in $YBa_2Cu_3O_{6+x}$. Its absence in $Nd_2CuO_{4+\delta}$ and similarity to the behavior of $SrTiO_3$ suggests that the phenomenon in the cuprates is connected with tilt distortions of the CuO polyhedra. We discuss the implications of these results for interpretations of the superconducting-state enhancement of κ_{ab}, widely observed in superconducting compounds.

A long-standing problem in the study of high-temperature superconductors is the uncertain role of lattice vibrations in determining their unusual normal-state properties and superconductivity. Among transport coefficients, the in-plane thermal conductivity (κ_{ab}) (Ref. 1) is a potential probe of phonon interactions and is of particular interest because it can be studied in both superconducting and normal states. However, charge-carrier contributions to κ_{ab} make interpretations of its temperature (T) dependence in superconducting compounds inconclusive. For this reason there is no consensus regarding the origin of the superconducting-state enhancement of κ_{ab}, a prominent feature in $\kappa_{ab}(T)$ that has received considerable attention recently.[2–8] The thermal conductivity of insulating crystals should impose important constraints on analyses of this phenomenon and more generally provide insight into phonon relaxation mechanisms in the cuprates, but the experimental record in this regard[7,9–13] is incomplete. Here we report measurements of κ_{ab} in insulating $YBa_2Cu_3O_{6+x}$ and $PrBa_2Cu_3O_{6+x}$ single crystals ($x \leqslant 0.11$) that offer insight into these issues.

The crystals for this study were prepared by a self-decanting CuO flux method and deoxygenated as described previously.[14] X-ray-diffraction analysis of one of the crystals (No. 1) indicated a c-axis lattice constant, $c = 11.8364(1)$ Å. Using the results of iodometric analyses of polycrystalline samples,[15] this c-axis value indicates $x = 0.05 \pm 0.05$. κ_{ab} was measured using a steady-state technique.[16] For several $YBa_2Cu_3O_{6+x}$ specimens, silver pads were vapor deposited, the crystals were annealed in air at 300–350 °C, and four-probe electrical resistivity and thermopower (TEP) (Ref. 17) were measured with κ_{ab} for the in-plane geometry. The thermal conductivity of one specimen was measured prior to (No. 2) and after (No. 2A) the anneal. By comparing the TEP data with that of polycrystals[18] we infer x values for the annealed crystals (Nos. 2A,3,4) in the range $0.07 \leqslant x \leqslant 0.11$. In the following we refer to $x \approx 0.05$ specimens of $YBa_2Cu_3O_{6+x}$ and $PBa_2Cu_3O_{6+x}$ as YBCO6 and PBCO6, respectively. We use YBCO generically in referring to other stoichiometries.

Figure 1 summarizes κ_{ab} data for a number of insulating cuprate single crystals: $Nd_{1.975}Ce_{0.025}CuO_{4+\delta}$ (NCO),[12] $La_2CuO_{4+\delta}$ (LCO),[11] YBCO6 (No. 1), PBCO6, and nominally fully oxygenated $PrBa_2Cu_3O_{6+x}$ (PBCO7).[19] We note that κ_{ab} for single-crystal Pr_2CuO_4 (PCO) (Ref. 13) is quite similar in magnitude and T dependence to isostructural NCO. Both NCO and PCO exhibit classical dielectric behavior with a sharp peak at low T and weak T dependence at

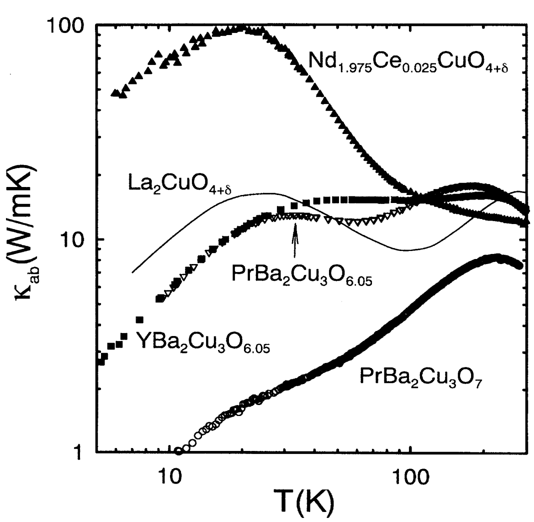

FIG. 1. ab-plane thermal conductivity vs temperature for insulating cuprate crystals. The data are for YBCO6 and PBCO6 (this work); LCO (Ref. 11); lightly Ce-doped NCO (Ref. 12); PBCO7 (Ref. 19).

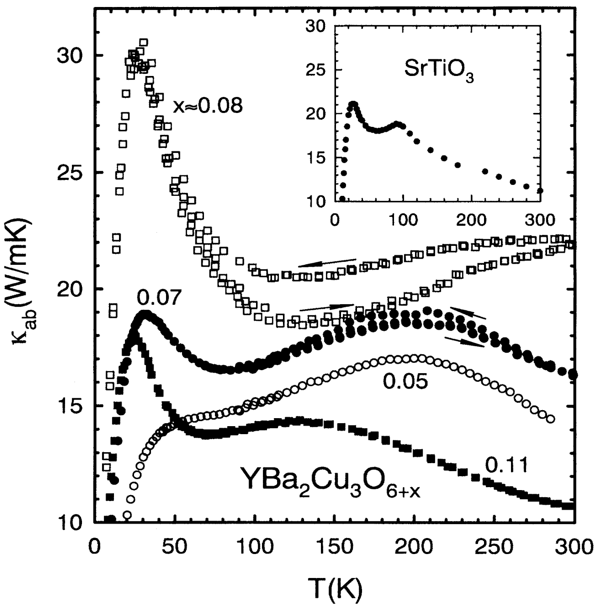

FIG. 2. ab-plane thermal conductivity vs temperature for lightly oxygen-doped YBCO crystals: open circles No. 2 ($x \approx 0.05$); closed circles, No. 2A ($x \approx 0.07, \rho_{ab} = 4.50\ \Omega$ cm); open squares, No. 3 ($x \approx 0.08, \rho_{ab} = 0.30\ \Omega$ cm); solid squares, No. 4 ($x \approx 0.11$, $\rho_{ab} = 0.03\ \Omega$ cm). Inset: κ vs T along the ⟨100⟩ direction in $SrTiO_3$ (Ref. 30).

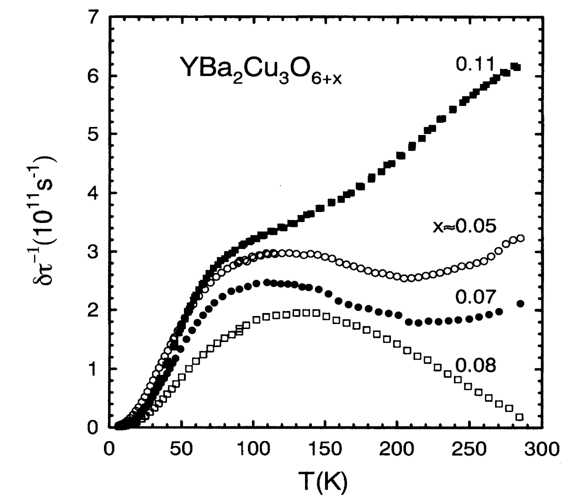

FIG. 3. Additional phonon scattering rate in YBCO relative to NCO, $\delta\tau^{-1} = \tau_{\rm YBCO}^{-1} - \tau_{\rm NCO}^{-1}$. Averaged data (Fig. 2) are employed in the hysteretic region for $x \approx 0.07, 0.08$.

high temperatures, characteristic of phonon-phonon relaxation. No anomalies associated with the antiferromagnetic transition [$T_N \approx 260$–280 K (Ref. 20)] are observed.

For LCO, YBCO6, and PBCO6, κ_{ab} is comparable in magnitude to that of NCO (and PCO) near room temperature, but the T dependence is distinctly nonclassical; an anomalous downturn in κ_{ab} occurs for $T < 200$ K, followed by a minimum at 80–100 K, and a second maximum at 20–30 K. Similar features are observed for PBCO7 though the magnitude of κ_{ab} and the low-temperature peak are substantially suppressed. This anomalous behavior of κ_{ab} signals the onset, for $T < 200$–250 K, of additional phonon damping in these materials that presumably has a common origin. The "double peak" structure in $\kappa_{ab}(T)$ is evidently a result of a competition between this additional scattering, which decreases κ_{ab} with decreasing T, and the usual anharmonic relaxation. Our results for YBCO6 and PBCO6, which have (Ref. 21) $T_N \sim 415$ K and 325 K, respectively, demonstrate that the κ_{ab} anomaly is unrelated to the onset of antiferromagnetic order in these materials. For LCO ($T_N \sim 280$–300 K) it is possible that magnetic ordering plays a contributing role.[9,11] Interestingly, the out-of-plane thermal conductivity (κ_c) for LCO (Ref. 11) and YBCO6 (Ref. 17) show no anomalies, indicating that the additional damping is weaker (relative to other scattering) or absent for phonons propagating along the c axis.

Further insight into the anomaly may be found in our observation that κ_{ab} in YBCO is highly sensitive to oxygen content. In Fig. 2 we present the thermal conductivity of lightly oxygen-doped YBCO crystals. The magnitude of κ_{ab} has a nonmonotonic doping dependence, initially increasing with x and dropping substantially for $x \approx 0.11$. This is most marked at low temperatures where a sharp maximum develops at $T \approx 20$ K, the same temperature at which the conventional dielectric peak is observed in NCO. That over such a narrow range of oxygen content the heat conductivity rises and falls by a factor of 2 is remarkable. Evidently a dramatic change takes place near $x \sim 0.1$. The decrease in κ_{ab} for $x > 0.1$ is consistent with previous results for polycrystal YBCO (Ref. 22) showing a sharp decrease in κ in going from $x \approx 0$ to $x \approx 0.3$, a result attributed to the onset of phonon-carrier scattering. This interpretation is supported by our observation that the $T = 300$ K in-plane electrical resistivity (ρ_{ab}) of these crystals (Fig. 2, caption) decreases by more than two orders of magnitude in going from $x \approx 0.07$ to $x \approx 0.11$. An increase in the carrier density and/or mobility is indicated. The Wiedemann-Franz law implies that electronic heat conduction is negligible for all specimens.

For $x < 0.11$ the data imply a *decrease* with increasing x in the low-temperature phonon scattering. This trend is in sharp contrast to that which would be expected from a simple picture in which the oxygen atoms serve as randomly distributed defects in the CuO_x layers, giving rise to *additional* phonon scattering at a rate proportional to their concentration. This result indicates a more complex role for oxygen in modifying the lattice transport; this is further highlighted by the thermal hysteresis in κ_{ab} that is evident for the crystals with $x \approx 0.07$ and $x \approx 0.08$.

To clarify the temperature and doping dependence of the additional phonon damping we compute effective phonon relaxation rates τ^{-1} from the kinetic theory expression for thermal conductivity $\kappa = (1/3)Cv^2\tau$, where C is the lattice specific heat per volume,[23] and v is the sound velocity.[24] Using the rate for NCO ($\tau_{\rm NCO}^{-1}$) as a reference, we compute the additional scattering rates in the YBCO crystals by subtraction, $\delta\tau^{-1} = \tau_{\rm YBCO}^{-1} - \tau_{\rm NCO}^{-1}$, as shown in Fig. 3. The anharmonic relaxation characterizing NCO is implicitly assumed to be representative of the intrinsic behavior in the other cuprates in the absence of the extra scattering; a reasonable assumption given their very similar phonon spectra.[25] The effects of dispersion and optic-mode contributions to heat conduction tend to reduce the effective phonon velocity at high temperatures, but do not change the qualitative behavior depicted in Fig. 3.

We see that the anomalous scattering for all specimens has a broad maximum near 120 K and decreases systematically with increasing x. The latter trend appears to continue in the $x \approx 0.11$ specimen though the maximum is partially masked by additional scattering with a strong temperature dependence, presumably due to phonon-carrier interactions. Our simplified treatment does not allow for a separation of multiple contributions to $\delta\tau^{-1}$ with any certainty, however it is significant that $\delta\tau^{-1}$ for this specimen approaches that of the $x \approx 0.08$ sample at the lowest temperatures. This suggests that the anomalous scattering is comparable or smaller at $x \approx 0.11$ than at $x \approx 0.08$. Further measurements at higher x are required to confirm this point.

The temperatures of the high-T downturns in κ_{ab} coincide with those of elastic,[26] and Raman[27] anomalies that have been widely reported in many superconducting cuprates. These are generally interpreted as signaling a structural phase transition of first order, though consensus is lacking regarding the mechanism. For YBCO, interpretations have often invoked ferroelectric or antiferroelectric structural rearrangements of chain oxygen atoms. The lightly doped insulators have not been as extensively studied in this context, but dielectric[28] and elastic[29] anomalies have been reported near the same temperature (~ 220 K).

These observations strongly suggest that the κ_{ab} anomaly is another manifestation of this structural modification. Its appearance in LCO, YBCO6, PBCO6, and PBCO7 clearly indicates that the damping mechanism is not peculiar to 123 compounds, nor is it directly related, in the 123 materials, to a specific defect structure of the CuO_x sublattice. It is natural to conclude that the relevant differences between the anomalous κ_{ab} materials and NCO are of a more fundamental structural nature; of particular interest is the possible role of tilt instabilities of the CuO polyhedra in the former materials.

The striking similarity between the κ_{ab} anomalies reported here and that observed in the heat conductivity of $SrTiO_3$[30] at its cubic-tetragonal phase transition near 100 K (Fig. 2, inset) supports the proposition that local distortions of the CuO polyhedra are responsible for this phenomenon in the cuprates. The transition in $SrTiO_3$ is a classic soft-mode phenomenon, characterized by rotations of the TiO_6 octahedra about a cube axis (a zone-boundary mode). The thermal conductivity anomaly for $SrTiO_3$ is attributed to strong resonant damping of acoustic phonons due to interaction with the soft optic branch near the zone center in the low-temperature phase.[31]

Tilts of the CuO_6 octahedra about an in-plane axis are associated with the well-known HTT-LTO phase transition in LCO near 500 K. Neutron-scattering studies[32] indicate that LCO is unstable against further tilts within the LTO phase upon cooling. For YBCO, anomalies in the local structure associated with apical oxygen have been extensively discussed,[33] and quite recently an instability against static in-plane tilts of the CuO_5 pyramids has been identified in the average structure of superconducting compounds.[34] A similar instability possibly occurs in insulating YBCO but has yet to be observed in the structural studies because the distortions occur in sufficiently small (<100 Å in extent), randomly oriented domains that preserve the average tetragonal symmetry. The appearance of thermal hysteresis in κ_{ab} and the elastic properties[26,29] is consistent with the formation of domains and their accommodation by strains.

The decrease in scattering with increased doping in the YBCO crystals may be correlated with known structural changes.[35] In the tetragonal phase, hole transfer from chain fragments in the CuO_x layers to the CuO_2 planes results in a decrease in the apical oxygen-planar Cu bond length and the Ba ion–CuO_x plane distance. Decreases of about 0.01 Å in these distances are inferred for x increasing from 0.05 to 0.11. This implies a reduced coupling between the Ba sublattice and the CuO_5 pyramids, and since Ba vibrations predominate in the low-energy acoustic spectrum, these structural changes could underlie the reduced phonon damping indicated in Fig. 3. An asymmetry in the electrostatic potential at the Ba site, leading to in-plane static displacements of Ba toward the CuO chains, has been identified in YBCO ($x=6.5$) as characteristic of the ortho-II structure.[36] Thus in-plane displacements of Ba toward chain fragments could also play a role in the doping dependence of the damping.

Our results have a direct bearing on interpretations of the normal-state κ_{ab} in superconducting compounds and its enhancement in the superconducting state. It has been argued[3,4,7,37] that a phononic origin of the superconducting-state enhancement is incompatible with the observation that κ_{ab} in the superconductor exceeds that of the insulator. This argument is certainly no longer valid in YBCO for two reasons. First, the κ_{ab} values in lightly doped YBCO (Fig. 2 and Ref. 13) rival or exceed those of untwinned YBCO7 crystals[8,16,37] at all temperatures. Second, our data suggest that the anomalous phonon damping may be weaker in YBCO7. Thus, near the enhancement temperature ($T \sim 40$ K in YBCO7), where phonon-electron scattering is suppressed, the lattice thermal conductivity of superconducting YBCO may exceed that of the insulators.

Furthermore, there is clear evidence that tilts of the CuO polyhedra are coupled to superconductivity.[33,34,38] An abrupt reduction in tilt amplitude for $T<T_c$ is indicated. According to our proposition that tilt distortions give rise to substantial phonon damping, a reduced distortion in the superconducting state should enhance the lattice thermal conductivity.

In summary, our measurements of heat transport in insulating YBCO and PBCO demonstrate that κ_{ab} is substantially greater in magnitude than previously appreciated and highly sensitive to light oxygen doping. The data reveal anomalous phonon damping for $T \leqslant 250$ K that we tentatively attribute to an onset of local tilt distortions of the CuO polyhedra. This phenomenon may play a contributing role in the superconducting-state enhancement of κ_{ab} in superconducting cuprates.

The authors acknowledge C. Uher for helpful discussions, P. Henning for providing data on PBCO7 prior to publication, and D. Litvinov for experimental assistance. The work at the University of Miami was supported, in part, by the UM Research Council.

[1] C. Uher, in *Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1993), Vol. III.

[2] J. L. Cohn *et al.*, Phys. Rev. Lett. **71**, 1657 (1993).

[3] R. C. Yu, M. B. Salamon, and J. P. Lu, Phys. Rev. Lett. **71**, 1658 (1993).

[4] A. S. Alexandrov and N. F. Mott, Phys. Rev. Lett. **71**, 1075 (1993).

[5] B. W. Statt and A. Griffin, Phys. Rev. B **48**, 619 (1993).

[6] W. S. Williams, Solid State Commun. **87**, 355 (1993).

[7] P B. Allen *et al.*, Phys. Rev. B **49**, 9073 (1994).

[8] C. Uher, Y. Liu, and J. F. Whitaker, J. Supercond. **7**, 323 (1994).

[9] D. T. Morelli *et al.*, Phys. Rev. B **39**, 804 (1989).

[10] S. J. Hagen, Z. Z. Wang, and N.-P. Ong, Phys. Rev. B **40**, 9389 (1989).

[11] Y. Nakamura *et al.*, Physica C **185-189**, 1409 (1991).

[12] J. L. Cohn *et al.*, Phys. Rev. B **46**, 12 053 (1992).

[13] A. V. Inyushkin *et al.*, Physica B **194-196**, 479 (1994); A. V. Inyushkin *et al.*, Physica C **235-240**, 1487 (1994).

[14] T. A. Vanderah *et al.*, J. Cryst. Growth **118**, 385 (1992); C. K. Lowe-Ma and T. A. Vanderah, Physica C **201**, 233 (1992).

[15] M. S. Osofsky *et al.*, Phys. Rev. B **45**, 4916 (1992); M. E. Parks *et al.*, J. Solid State Chem. **79**, 53 (1989).

[16] J. L. Cohn *et al.*, Phys. Rev. B **45**, 13 144 (1992).

[17] J. L. Cohn, J. Supercond. **8**, 457 (1995); J. L. Cohn *et al.* (unpublished).

[18] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).

[19] P. Henning *et al.*, J. Supercond. **8**, 453 (1995); similar results have been reported in Ref. 13.

[20] S. Skanthakumar *et al.*, J. Magn. Magn. Mater. **104-107**, 519 (1992).

[21] J. Rossat-Mignod *et al.*, Physica B **169**, 58 (1991); I. Felner *et al.*, Phys. Rev. B **40**, 6739 (1989).

[22] N. V. Zavaritskii, A. V. Samoiov, and A. A. Yurgens, JETP Lett. **48**, 242 (1988).

[23] J. W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993); S. Ghamaty *et al.*, Physica C **160**, 217 (1989); E. Rampf *et al.*, Phys. Rev. B **48**, 10 143 (1993).

[24] We use an average sound velocity, $v = 4\,000$ m/s for both materials, estimated from ultrasonic studies and dispersion curves; D. F. Lee and K. Salama, Mod. Phys. Lett. B **2**, 1111 (1988); L. Pintschovius *et al.*, Physica C **185-189**, 156 (1991).

[25] L. Pintschovius and W. Riechardt, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Singapore, 1994), Vol. IV, p. 295.

[26] Z. Zhao *et al.*, Phys. Rev. B **39**, 721 (1989); V. Müller *et al.*, Solid State Commun. **72**, 997 (1989); Y.-N. Wang *et al.*, Phase Transitions **22**, 9 (1990); H. You, U. Welp, and Y. Fang, Physica C **185-189**, 875 (1991); G. Cannelli *et al.*, Supercond. Sci. Technol. **5**, 247 (1992); M. Kund and K. Andres, Physica C **205**, 32 (1993); W. Ting *et al.*, Phys. Rev. B **47**, 12 197 (1993); Y. N. Huang *et al.*, Phys. Rev. B **49**, 1320 (1994); T. Fukami *et al.*, Physica C **241**, 336 (1995); J. Sugiyama, K. Isawa, and H. Yamauchi, Physica C **242**, 63 (1995).

[27] See review by J. F. Scott, Phase Transitions **22**, 69 (1990), and references therein; D. R. Wake *et al.*, Phys. Rev. Lett. **67**, 3728 (1991).

[28] L. R. Testardi *et al.*, Phys. Rev. B **37**, 2324 (1988).

[29] G. Cannelli, R. Cantelli, and F. Cordero, Phys. Rev. B **38**, 7200 (1988); S. De Brion *et al.*, Europhys. Lett. **12**, 281 (1990).

[30] Y. Suemune *et al.*, J. Phys. Soc. Jpn. **20**, 174 (1965); E. F. Steigmeier, Phys. Rev. **168**, 523 (1968).

[31] H. H. Barrett, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1970), Vol. VI, p. 65.

[32] T. R. Thurston *et al.*, Phys. Rev. B **39**, 4327 (1989); M. Braden *et al.*, Physica C **223**, 396 (1994).

[33] B. H. Toby *et al.*, Phys. Rev. Lett. **64**, 2414 (1990); J. Mustre de Leon *et al.*, *ibid.* **65**, 1675; M. Arai *et al.*, *ibid.* **69**, 359 (1992).

[34] P Schweiss *et al.*, Phys. Rev. B **49**, 1387 (1994).

[35] J. D. Jorgensen *et al.*, Phys. Rev. B **41**, 1863 (1990); R. J. Cava *et al.*, Physica C **165**, 419 (1990); Shaked *et al.*, Phys. Rev. B **51**, 547 (1995).

[36] T. Zeiske *et al.*, Physica C **194**, 1 (1992).

[37] R. C. Yu *et al.*, Phys. Rev. Lett. **69**, 1431 (1992).

[38] C. Meingast *et al.*, Phys. Rev. Lett. **67**, 1634 (1990); M. Braden *et al.*, Phys. Rev. B **46**, 6458 (1993).