Anomalous Dispersion of LO Phonons in $La_{1.85}Sr_{0.15}CuO_4$ at Low Temperatures

R. J. McQueeney,[1] Y. Petrov,[2] T. Egami,[3] M. Yethiraj,[4] G. Shirane,[5] and Y. Endoh[6]
[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[2]*Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
[3]*Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
[4]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
[5]*Brookhaven National Laboratory, Upton, New York 11973*
[6]*Department of Physics, Tohoku University, Sendai 980, Japan*
(Received 26 January 1998; revised manuscript received 28 September 1998)

Inelastic neutron scattering measurements of $La_{1.85}Sr_{0.15}CuO_4$ show that a discontinuity in dispersion develops in the middle of the highest energy LO phonon branch at low temperatures. The result suggests dynamic short range unit cell doubling in the CuO_2 plane along the direction of the Cu-O bond, such as charge ordering on every other row of oxygen. Such charge ordering is related to, but is different from, the stripe charge ordering observed for nonsuperconducting cuprates. [S0031-9007(98)08166-6]

PACS numbers: 74.25.Kc, 63.20.Kr, 74.20.Mn

The question of the influence of the electron-lattice interaction in the normal and superconducting electronic properties of high temperature superconductors remains open. Perhaps the most intriguing experimental evidence of a large and anomalous electron-lattice interaction comes from inelastic neutron scattering experiments on various high temperature superconducting materials [1–6]. A signature of these materials is the strong renormalization of longitudinal high frequency (~80 meV) oxygen bond-stretching phonons in the CuO_2 plane when holes are doped into the insulating compounds. The doping causes a large decrease in the frequency of the zone boundary $(0.5, 0, 0)$ half-breathing phonon mode (15%–20% softening compared to the insulating compound), indicating that there is a strong coupling of these phonons to the doped holes. This effect seems to be ubiquitous, and has been observed in single-crystal inelastic neutron scattering measurements of $La_{2-x}Sr_xCuO_4$ [1], La_2CuO_{4+y} [3], $YBa_2Cu_3O_{6+y}$ [4,5], and even $Ba_{1-x}K_xBiO_3$ [6]. There are also indications of this effect from the observed softening of oxygen phonon bands in inelastic neutron scattering measurements of the phonon density of states in $Pb_2Sr_2(Ca,Y)Cu_3O_8$ [7] and $Li_{1+x}Ti_{2-x}O_4$ [8].

It has proven quite difficult to interpret these results in terms of normal electron-phonon coupling in a metal, especially since the other measured phonon modes are, for the most part, unaffected (especially the oxygen breathing and quadrupole modes). Typical indications of electron-phonon coupling, such as Kohn anomalies, seem to be inconsistent with the wave vector of the affected phonon. The Fermi surface should have strong nesting at $2\mathbf{k}_f$ which is close to $\mathbf{q} = (0.5, 0.5)$, but not at $(0.5, 0)$, as demonstrated by the local-density approximation calculation [9] and ARPES measurements [10].

We have chosen to investigate these phonon phenomena more closely and have discovered that the anomalous nature of the bond-stretching branch is even more mysterious at low temperatures. The sample studied consisted of two single crystals of $La_{1.85}Sr_{0.15}CuO_4$ which were comounted in an aluminum can filled with He exchange gas. Both samples were grown by the floating zone method and were obtained from the same batch. The total size of the sample is approximately $3.8 \times 1.5 \times 0.8$ cm^3. Previous measurements and characterizations attest to the high quality of this sample [11,12].

The experimental scans were performed on the HB-3 triple axis spectrometer at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The spectrometer configuration used the beryllium (002) and pyrolitic graphite (002) reflections as the monochromator and analyzer, respectively. The analyzer angle was fixed when performing inelastic scans, giving a fixed final energy of 14.87 meV. Söller collimators of angular divergence $48'$-$40'$-$80'$-$240'$ were placed along the flight path from source to detector. To reduce higher order Bragg scattering contamination from the analyzer, a pyrolitic graphite filter was placed before the analyzer.

Experimental scans presented here consist of constant-Q energy scans taken in the $(3, 0, 0)$ Brillouin zone, in tetragonal notation ($a = 3.78$ Å). Measurements of the longitudinal bond-stretching phonon branch were made at the reciprocal space positions $(3 + q_x, 0, 0)$. Some off-axis scans were also performed at the reciprocal space positions $(3 + q_x, q_y, 0)$. All scans have energy transfers ranging from 55 to 90 meV.

The experiment described above is simple in principle, but quite difficult in practice. The large incident energy required to measure excitations up to 90 meV is far in the epithermal region of the incident neutron spectrum and the flux is low. For measurement of this particular longitudinal phonon branch, it is best to measure in an odd index Brillouin zone with the largest momentum transfer possible. In our case, the maximum zone attainable was $(5, 0, 0)$. However, spurious scattering, consisting of

 0031-9007/99/82(3)/628(4)$15.00

the (6, 2, 0) Bragg reflection from the sample scattering incoherently from the analyzer, obscured the main phonon branch. In the present paper, results were obtained at about the (3, 0, 0) zone at a significant loss of intensity, but without spurious scattering. Thus, counting rates were extremely low, about 1–5 counts/min.

Figure 1 shows a series of longitudinal scans along the $(3 + q_x, 0, 0)$ direction at $T = 10$ K. In the scan at (3.5, 0, 0), two phonon modes are observed at 58 and 70 meV. Calculations using an empirical lattice dynamical shell model associate the 58 meV phonon with oxygen in-plane Cu-O bond-bending vibrations. The 70 meV peak is associated with the oxygen Cu-O bond-stretching mode also in the CuO_2 plane. It is this 70 meV bond-stretching, half-breathing mode that has strongly softened as compared to the undoped compound. The rising tail at high energy transfer comes from an ambient background (1–2 counts/min) and the slope reflects the increased counting time at high energy transfers.

The remaining scans in Fig. 1 show the development of the phonon dispersion for these two branches while approaching the zone center (3, 0, 0). The frequency of the 58 meV bond-bending branch remains relatively constant through the zone and has a normal decrease of the phonon structure factor while approaching (3, 0, 0). The frequency of the 70 meV branch also remains constant up until (3.25, 0, 0), where the 70 meV phonon disappears and is replaced by a very wide and diffuse feature. At (3.2, 0, 0) a phonon peak reappears at 83 meV, close to the undoped frequency of the phonon branch. We therefore conclude that, at 10 K, the bond-stretching phonon branch is nearly discontinuous at (3.25, 0, 0), with an energy splitting of 13 meV. In addition to this discontinuity, extra peaks exist at 85 meV between (3.25, 0, 0) and (3.5, 0, 0) and at 70 meV between (3.25, 0, 0) and (3, 0, 0). Although these peaks are very weak, they seem to connect smoothly to the broken branch.

All of the longitudinal scans can be fit to a sum of three Gaussians by assuming the time-independent background of ~1.4 counts/min and a small constant energy background (0–4 counts). Figure 1 also shows the fitting curves by solid lines. The dispersion relation is shown in Fig. 2, where the gray shaded circles represent the weak extra modes at low temperatures and the hatched area at (3.25, 0, 0) indicates a broad peak in the intensity.

It was found that the dispersion is strongly dependent upon temperature. While the dispersion remains largely unchanged up to $q_x = 0.1$, the rest of the dispersion is very different between 10 K and room temperature, as constant-Q scans in Fig. 3 and the measured dispersion in Fig. 2 attest. In particular, no peak is seen at 10 K at (3.25, 0, 0), while a peak develops at 76 meV at 300 K. The dispersion at 300 K is largely in agreement with previous measurements on $La_{1.9}Sr_{0.1}CuO_4$, which were made at room temperature [1]. The dispersion changes

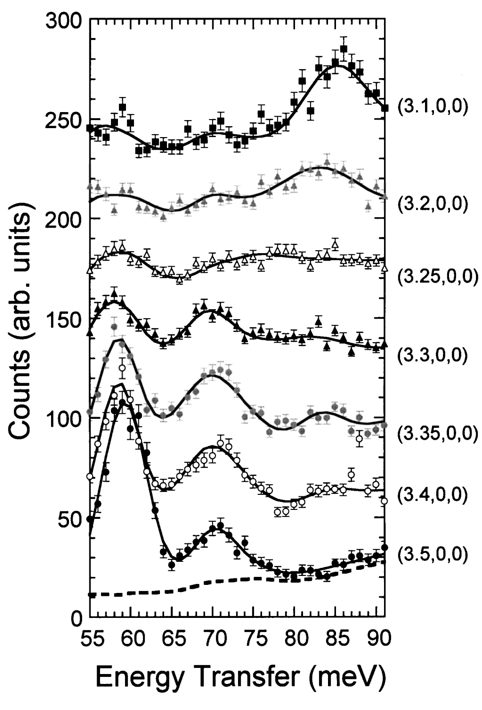

FIG. 1. Seven energy scans along the $(3 + q_x, 0, 0)$ direction at 10 K are shown, each successively displaced by 35 counts. Two prominent branches can be tracked from the zone boundary (3.5, 0, 0) point, the in-plane oxygen bond-bending mode at 58 meV and the oxygen bond-stretching mode at 70 meV. The bond-stretching branch experiences a discontinuity at (3.25, 0, 0), jumping to 85 meV as the zone center is approached. Solid lines indicate fits as described in the text. The dashed line for (3.5, 0, 0) is the background obtained from the counting time for each point, assuming a time-independent count rate of 1.4 counts/min.

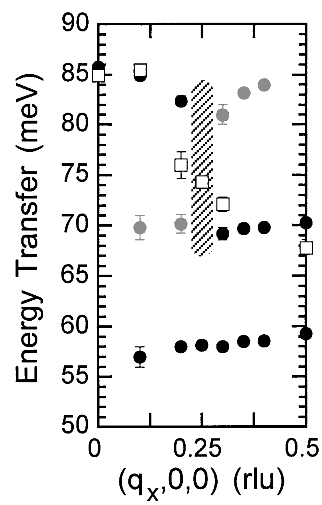

FIG. 2. The dispersion relation of the upper two longitudinal optic branches along $(q_x, 0, 0)$ as obtained from the Gaussian fits. The 10 K results are filled circles and room temperature results are empty squares. The gray shaded circles indicate the frequency of the weak extra branches seen at 10 K. The hatched area at (3.25, 0, 0) indicates a broad and ill-defined phonon peak.

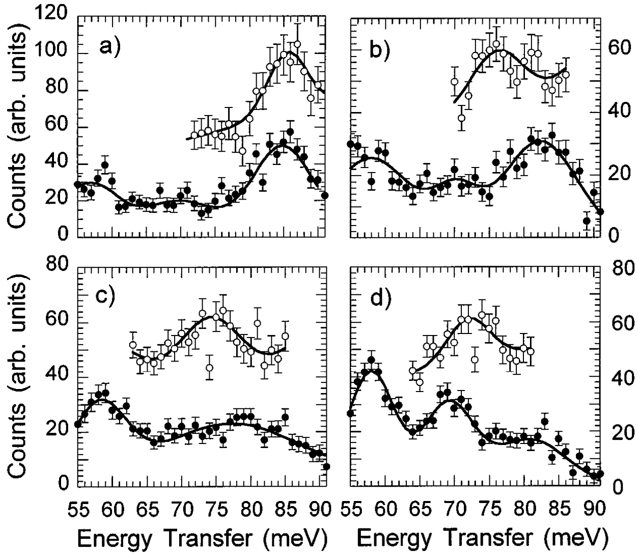

FIG. 3. Comparison of the background subtracted constant-Q energy scans at 10 K (filled circles) and room temperature (empty circles) at (a) (3.1, 0, 0), (b) (3.2, 0, 0), (c) (3.25, 0, 0), and (d) (3.3, 0, 0). Room temperature results are offset by 35 counts.

little between 10 and 50 K and therefore does not appear to be related to the superconducting transition ($T_c = 37$ K).

In addition to the longitudinal scans, several scans were made off axis along $(3.3, q_y, 0)$ and $(3.25, q_y, 0)$. The $(3.3, q_y, 0)$ scans are shown in Fig. 4. They indicate a narrow dispersionless region up to $q_y = \pm 0.1$ and gradual dispersion to the (3.3, 0.3, 0) phonon mode, which connects to the quadrupolar mode at (3.5, 0.5, 0). The

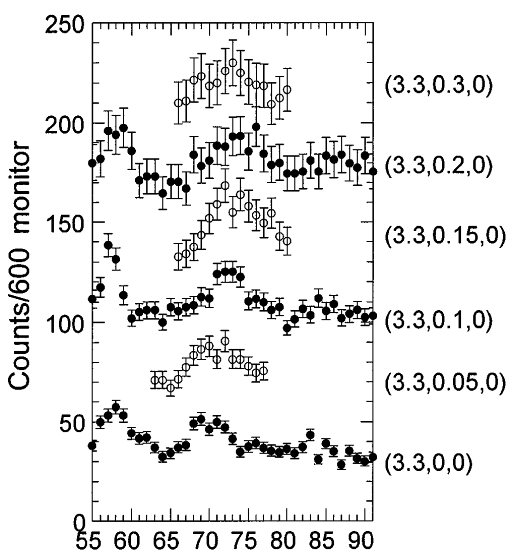

FIG. 4. Six energy scans along the $(3.3, q_y, 0)$ direction at 10 K are shown, each successively displaced by 35 counts. The branch along q_y eventually connects to the quadrupole branch at (3.3, 0.3, 0).

(3.25, 0, 0) and (3.25, 0.2, 0) scans made at 10 K (not shown) show some indication that the broad feature at $q_y = 0$ is narrowing to a well-defined phonon mode near 75 meV as q_y is increased.

The results on the oxygen LO mode presented here are characterized by two remarkable features. One is the apparent discontinuity of dispersion at (0.25, 0, 0), and the other is the flatness of the phonon dispersion from (0.25, 0, 0) to (0.5, 0, 0). These features have, in fact, been already observed in $YBa_2Cu_3O_7$ [4,5], and $Ba_{0.6}K_{0.4}BiO_3$ [6], but collected little attention, and their temperature dependence has not been studied thus far.

The behavior of cuprates has been discussed initially, assuming perfect periodicity in the lattice and electronic structures. However, it became recognized that the strong electron-electron interaction may lead to phase separation of spin and charge [13–15]. A possible manifestation of such phase separation is the spin/charge stripe formation which has been observed at least in the nonsuperconducting cuprates with the charge density x close to $\frac{1}{8}$, in terms of the magnetic and lattice satellites in the elastic neutron scattering measurement [16]. It has been assumed that similar stripes exist even in the superconducting phase but they are dynamic, since similar incommensurate magnetic scattering has been observed in inelastic neutron scattering measurements. The magnetic periodicity of the current sample, as determined by inelastic magnetic neutron scattering, is approximately $8a$. This would result in a charge periodicity of $4a$ in the stripe model, with a wave vector of (0.25, 0, 0) Such a charge density would create a new Brillouin zone boundary and a gap in the phonon dispersion at (0.125, 0, 0).

However, the discontinuity observed here is at (0.25, 0, 0). Since the softening of the oxygen LO phonons near (0.5, 0, 0) is clearly related to the presence of the doped holes, it can be safely argued that the

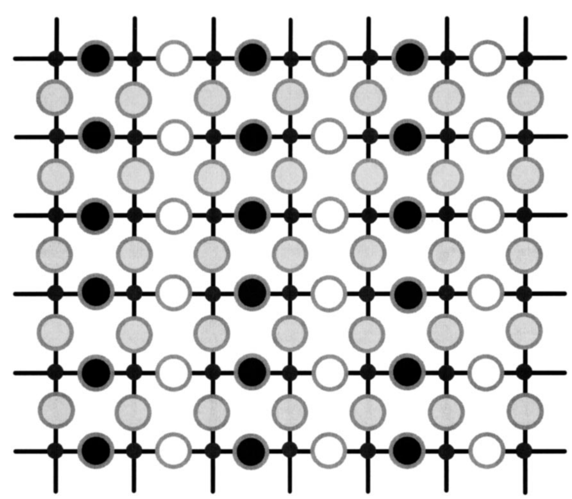

FIG. 5. Schematic oxygen charge distribution in the model of the CuO_2 plane used in calculating the dispersion shown in Fig. 6. The light shaded circles indicate lower electron density.

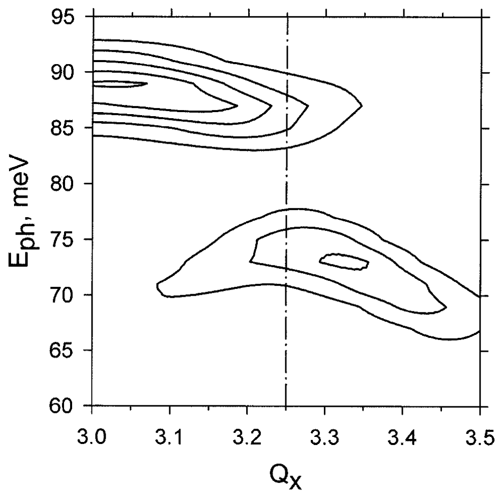

FIG. 6. Contour plot (each 15% of the maximum) of the scattering intensity for the $(Q_x, 0, 0)$ LO phonon mode calculated with the spring model, assuming that the oxygen-Cu interaction parameter was softened by 20% and the oxygen-oxygen parameter by 10% for the oxygen charge with $\lambda = 2a$. The calculated phonon peaks were broadened with a Gaussian with a the full width of 7 meV to simulate the experimental resolution.

discontinuity at $(0.25, 0, 0)$ must also be intimately connected with the presence of charges. We propose that the discontinuity at $(0.25, 0, 0)$ is due to charge ordering with the periodicity of $2a$ and the wave vector of $(0.5, 0, 0)$. Indeed, a simple spring model assuming the weakening of the spring constant due to a charge modulation on oxygen in the CuO_2 plane with the periodicity of $2a$, shown schematically in Fig. 5, accounts for the observed features of the oxygen LO phonon dispersion observed here remarkably well (as shown in Fig. 6). Similar models with the charges on Cu or with charges on O with the periodicity of $4a$ do not reproduce the observed dispersion at all. It should be noted, however, that this charge ordering must be dynamic, since a superlattic diffraction corresponding to such ordering has never been reported, including our own search. The charge ordering also is most probably short ranged, since the absence of dispersion of the 70 meV mode suggests localization. From the extension of the flat dispersion, $0.25 < q_x < 0.75$ and $-0.1 < q_y < 0.1$, the coherence lengths of the localized phonon are estimated to be $5a \times 2a$, or 20×8 Å in the a-b plane. It is interesting to note that the same coherence lengths were detected in $YBa_2Cu_4O_8$ by the pulsed neutron pair-density function study [17].

As the origin of the dynamic charge density modulation, the Hubbard-Peierls instability [18,19] is still a possibility, but needs further studies. Regardless of the exact origin, the observed phonon dispersion strongly suggests that we have to consider seriously the possibility of a new local dynamic charge ordering that is strongly interacting with the lattice [20], and is different from the spin/charge stripes.

The authors are grateful to J. B. Goodenough, A. R. Bishop, J. Tranquada, V. Emery, J. Zaanen, H. Mook, E. Mele, and M. Tachiki for useful discussions. R. J. McQueeney was supported by the U.S. Department of Energy under Contract No. W-7405-ENG-36 with the University of California. The work at the University of Pennsylvania was supported by the National Science Foundation through DMR96-28134. HFIR is operated by the U.S. Department of Energy. Measurements were made at Oak Ridge National Laboratory, which is managed by Lockheed Martin Energy Research under Contract No. DE-AC05-96OR22464 for the Department of Energy.

[1] L. Pintschovius *et al.*, Physica (Amsterdam) **185C–189C**, 156 (1991).
[2] L. Pintschovius and W. Reichardt, in *Physical Properties of High Temperature Superconductors IV*, edited by D. Ginsberg (World Scientific, Singapore, 1994), p. 295.
[3] L. Pintschovius and M. Braden, J. Low Temp. Phys. **105**, 813 (1996).
[4] W. Reichardt *et al.*, Physica (Amsterdam) **162C–164C**, 464 (1989).
[5] W. Reichardt, J. Low Temp. Phys. **105**, 807 (1996).
[6] M. Braden *et al.*, J. Supercond. **8**, 1 (1995).
[7] R. Currat *et al.*, Phys. Rev. B **40**, 11 362 (1989).
[8] F. Gompf, B. Renker, and H. Mutka, Physica (Amsterdam) **180B–181B**, 459 (1992).
[9] H. Krakauer, W. E. Pickett, and R. E. Cohen, Phys. Rev. B **47**, 1002 (1993).
[10] Z.-X. Shen and D. S. Dessau, Phys. Rep. **253**, 1 (1995).
[11] K. Yamada *et al.*, Phys. Rev. Lett. **75**, 1626 (1995).
[12] R. J. McQueeney *et al.*, Phys. Rev. B **54**, R9689 (1996).
[13] D. Poilblanc and T. M. Rice, Phys. Rev. B **39**, 9749 (1989).
[14] J. Zaanen and O. Gunnarson, Phys. Rev. B **40**, 7391 (1989).
[15] V. J. Emery, S. A. Kivelson, and H. Q. Lin, Phys. Rev. Lett. **64**, 475 (1990).
[16] J. M. Tranquada *et al.*, Nature (London) **375**, 561 (1995).
[17] T. R. Sendyka *et al.*, Phys. Rev. B **51**, 6747 (1995).
[18] S. Ishihara, T. Egami, and M. Tachiki, Phys. Rev. B **55**, 3163 (1997).
[19] Y. Petrov and T. Egami, Phys. Rev. B **58**, 9485 (1998).
[20] A. Perali *et al.*, Phys. Rev. B **54**, 16 216 (1996); C. Castellani, C. Di Castro, and M. Grilli, Los Alamos archive depository, cond-mat/9702112.