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Anomalous dispersion of LO phonons in $La_{1.85}Sr_{0.15}CuO_4$

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The dispersion of the highest energy LO phonon branch in $La_{1.85}Sr_{0.15}CuO_4$ in the (100) direction has been reinvestigated by high-resolution inelastic scattering. In contrast to what has been recently reported by McQueeney *et al.* [Phys. Rev. Lett. **82**, 628 (1999)], we find that the dispersion is continuous throughout the Brillouin zone. Our results are in conflict with the idea of a short-range unit-cell doubling in the CuO_2 plane existing on a time scale which is long compared to that of the LO frequencies. On the other hand, the strong softening and broadening of LO bond-stretching phonon modes observed upon doping might be taken as a precursor phenomenon to stripe charge ordering which has been observed in nonsuperconducting cuprates. [S0163-1829(99)51946-2]

Inelastic neutron-scattering experiments on high-temperature superconductors have provided clear evidence of a large electron-lattice coupling.[1] In particular, the highest-energy longitudinal optic vibrations at wave vector $(\pi,0)$ (in square planar notation) soften and broaden strongly as holes are doped into the insulating parent compounds. This effect has been studied in detail by measurements on single-crystal $La_{2-x}Sr_xCuO_{4+\delta}$ (Refs. 2 and 3) and $YBa_2Cu_3O_{6+x}$.[4,5] Also powder measurements on Bi-based cuprates[6] indicate a strong doping induced softening of high-frequency modes. Therefore, it is reasonable to assume that this frequency renormalization is a general phenomenon within the class of cuprate superconductors. Interestingly, a similar effect has been observed in the noncuprate high-T_c compound $Ba_{1-x}K_xBiO_3$,[7] but not in the low-T_c oxides Sr_2RuO_4 (Ref. 8) and $Sr_{1-x}Nb_xTiO_3$.[9] In this paper, we want to discuss whether the experimental results are not only indicative of a strong electron-phonon coupling, but also of a dynamic short-range unit-cell doubling in the CuO_2 plane, as has been recently suggested by McQueeney *et al.*[10] This hypothesis was based on evidence of a discontinuity in the dispersion of the highest energy LO phonon branch in $La_{1.85}Sr_{0.15}CuO_4$. We reinvestigated this branch with a much higher resolution. We found that features in the data of Ref. 10 which were taken as a signature of a discontinuity in the dispersion can be fully understood as a resolution effect. We were led to a different physical picture than that proposed in Ref. 10: There is no evidence for a unit-cell doubling existing on a time scale which is long compared to that of the LO frequencies, but $La_{1.85}Sr_{0.15}CuO_4$ seems to be close to a charge ordered phase with about the same periodicity as observed in nonsuperconducting cuprates.[11]

The sample used for the present study was a $La_{1.85}Sr_{0.15}CuO_4$ single crystal of volume ~ 0.5 cm^3 and mosaic spread 0.7°. We emphasize that Petit *et al.*[12] observed a magnetic gap of about 3.5 meV on this sample ($T_c^{onset} = 38$ K), very similar to what has been observed by Yamada *et al.* [13] on a high-T_c sample, but in contrast to the results reported on lower T_c samples. The neutron measurements were performed on the 2T spectrometer at the ORPHEE reactor at the Laboratoire Léon Brillouin. In order to achieve a high resolution, the copper (220) reflection was used as monochromator. Pyrolitic graphite (002) was used as an analyzer with E_F fixed at $\nu = 3.55$ THz and a pyrolitic graphite filter placed before the analyzer. Both the monochromator and the analyzer crystals were horizontally and vertically focusing. Typical dimensions of the resolution ellipsoid projected onto the $Q_x - E$-plane can be seen in Fig. 2 (middle). The sample was mounted in an aluminum can with an (010)-axis (in tetragonal notation, $a_o = 3.78$ Å) vertical.

The results presented here were derived from a series of constant-Q energy scans in several Brillouin zones, i.e., at wave vectors $(h-\zeta, 0, z)$ with $z = 0, \pm 1, \pm 2, \pm 3$ and with $0 \leqslant \zeta \leqslant 0.5$. In this way, we were able to maximize the scattering intensity (large Q's, favorable inelastic structure factors) to cover the full Q range between the Γ and the Z point[15] and, very importantly, to achieve focusing in q-energy space for the whole branch investigated (see the discussion below). Moreover, a comparison of results taken at symmetry-equivalent points in reciprocal space [e.g., at (4.7, 0, 2) and at (4.7, 0, −2)] greatly helps to isolate spurious contributions to the scattering intensity. Finally, wave vectors with $Q_z = \pm 1, \pm 2, \pm 3$ are advantageous for the study of the highest-energy branch since the structure factors of the next lowest LO branch around 14 THz are strongly reduced compared to the measurements with $Q_z = 0$ (as chosen in Ref. 10). This facilitates the separation of the contributions of the two branches (see, e.g., Fig. 1, top). The energy interval covered by the scans was chosen very large in order to get a good estimate of the background. The background counting rate as a function of energy and momentum transfer was fitted to the entire set of scans.

Typical scans are shown in Fig. 1. A contour plot of the background corrected intensities is shown in Fig. 2 (top). The peak positions and linewidths evaluated from the data are shown in Fig. 2 (middle) and Fig. 2 (bottom), respectively. There are two features which we consider as quite remarkable: first, the dispersion is extremely steep at

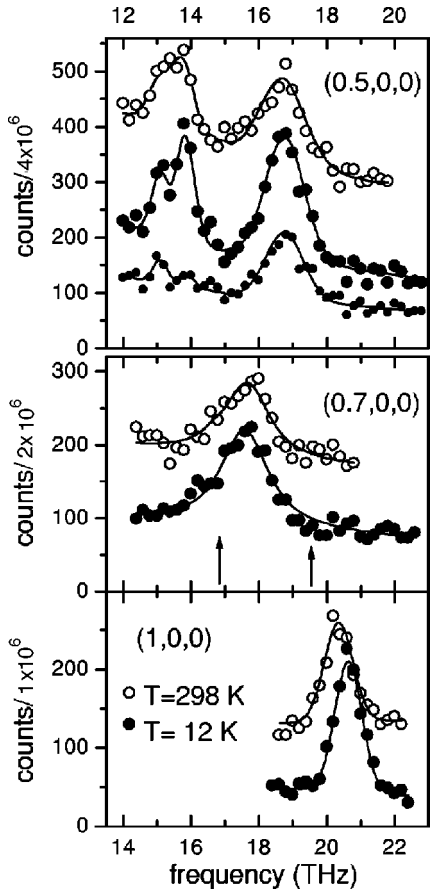

FIG. 1. Constant-Q scans taken at $T=12$ K (full symbols) and 298 K (open symbols). The lines were obtained by fitting Gaussian (top and bottom) or Voigt (middle) profiles to the data. Top (large symbols): The sum of scans taken at $Q=(4.5, 0, 0)$, $(4.5, 0, 1)$, and $(4.5, 0, 2)$. Top (small symbols): the individual scan taken at $Q=(4.5, 0, 2)$ with half the monitor count. Middle: The scans taken at $Q=(4.7, 0,2)$. The arrows denote peak positions deduced from a scan at $Q=(3.3, 0, 0)$ by McQueeney *et al.*[10] Bottom: The scans taken at $Q=(5, 0, 0)$.

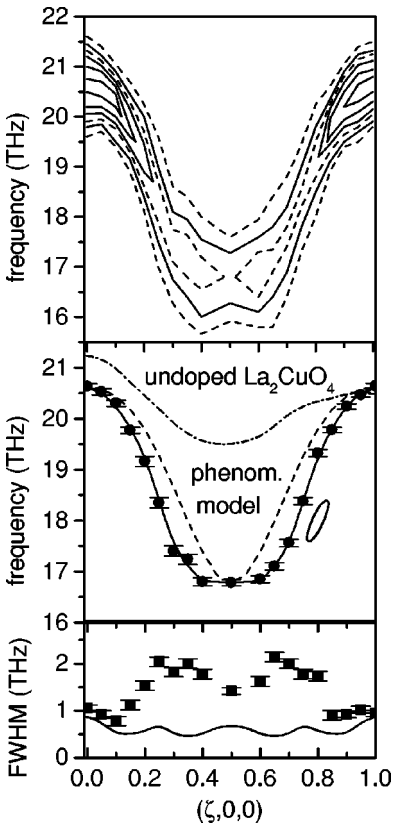

FIG. 2. Top: Contour plot (full lines: steps of 40 counts/monitor 10^6, broken lines: steps of 20 counts/monitor 10^6) of the scattering intensity for the highest Δ_1 branch as observed in scans at $Q=(5-\zeta, 0, 1)$ (left part) or $Q=(5-\zeta, 0, 2)$, respectively. Middle: the frequencies of the Δ_1 phonons as determined by fitting a Gaussian line shape to the data. The full line is a guide to the eye. The dashed line is the result of a phenomenological model designed to reproduce the anomalously low frequency of the Δ_1 phonon at $\zeta=0.5$. The ellipse denotes the projection of the resolution ellipsoid onto the ζ-ν plane. Note that in the measurements up to $\zeta=0.5$ the slope of the ellipse was opposite to that shown here. The dashed-dotted line depicts the frequencies observed in undoped La_2CuO_4. Bottom: linewidths of the Δ_1 phonons as determined by fitting a Gaussian line shape to the observed profiles. The solid line depicts the instrumental resolution including focusing effects.

$\zeta\approx0.25$. Second, the observed linewidths peak at $\zeta\approx0.3$ (resp. 0.7) rather than at the zone boundary. (We note that the peaks are broad but not asymmetric as has been claimed in Ref. 14.) These observations are reminiscent of what has been reported in Ref. 10, but there are nevertheless important qualitative and quantitative differences. There is a qualitative difference in that our data do not show any signature of a doubling of the unit cell. At each wave vector, we find just one peak as expected for a single, continuous branch rather than two (see, e.g., Fig. 1, middle). This means that the contour plot of our data is very different from the contour plot calculated with a model assuming a modulation of the oxygen charge with $\lambda=2a$ shown in Ref. 10. There is a quantitative difference between our data and those of McQueeney *et al.*[10] in that the linewidths observed in our experiment are considerably smaller. This difference is, however, fully understandable as a resolution effect: it is not only that the resolution in energy of the spectrometer used in Ref. 10 is about 80% larger than that of our setup, but the large linewidths observed in Ref. 10 are also attributable to the fact that the measurements were carried out in a different Brillouin zone, i.e., at $(3+\zeta, 0, 0)$ instead of $(5-\zeta, 0, l)$: neutron spectrometers of the type used in Ref. 10 or in the present study show pronounced focusing or defocusing effects depending on the slope of the dispersion curve in respect to the orientation of the resolution ellipsoid. As can be seen in Fig. 3, going from $(5-0.25, 0, 2)$ to $(3+0.25, 0, 2)$ leads to a substantial broadening of the phonon line, apart from a drastic loss in intensity due to the lower Q. As a consequence, the pronounced broadening observed at $\zeta=0.25$ in Ref. 10 is fully compatible with a continuous dispersion and a moderate intrinsic broadening (see the lowest curve in Fig. 3).

It was found in Ref. 10 that the dispersion is strongly dependent upon temperature, whereby only the low-temperature data, not the room-temperature data, speak in favor of a short-range unit-cell doubling. Such a temperature dependence, if confirmed, would make it difficult to attribute the unusual line shapes found in Ref. 10 completely to resolution effects. However, we emphasize that no unusual temperature dependence was observed in our experiment (examples are shown in Fig. 1): the reduction in phonon

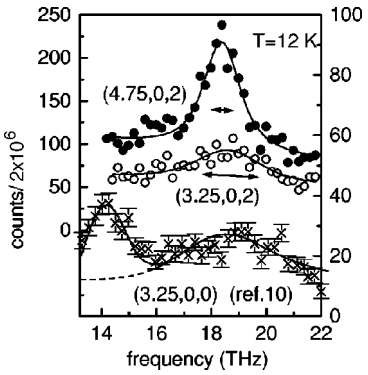

FIG. 3. Scans taken at $Q=(4.75, 0, 2)$ (full circles) and $Q=(3.25, 0, 2)$ (open circles) at $T=12$ K (left-hand scale). The horizontal arrows depict the instrumental resolution including focusing effects. The lines show fits of the intensity profiles assuming the same Lorentzian broadening for the two scans. For the sake of comparison, data reported by McQueeney *et al.*[10] for $Q=(3.25, 0, 0)$ are shown also (crosses, right-hand scale). The lines were computed from the intrinsic phonon properties deduced from our data and the experimental parameters of Ref. 1 as explained in the text. Note that the absence of the 14 THz peak in our data is due to the choice of $Q_z=2$ instead of $Q_z=0$.

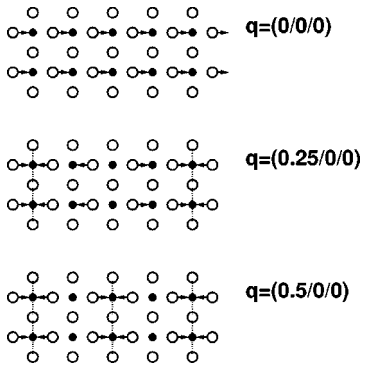

FIG. 4. Polarization patterns of the LO bond-stretching modes for $q=(0, 0 0)$, $(0.25, 0 0)$, and $(0.5, 0, 0)$ within a CuO_2 plane. The filled circles indicate the Cu positions and open circles the oxygen positions with their displacements. The perpendicular pointed lines represent the rows where a localization of positive charges is favored by the oxygen displacements.

intensity between $T=12$ K and 298 K can be explained by the Debye-Waller factor; a slight shift ($\sim 1\%$) to lower frequencies as well as a slight Lorentzian broadening are attributable to anharmonic effects. In summary, none of the arguments evoked in Ref. 10 to support the picture of dynamic unit-cell doubling is confirmed by our experimental results. The absence of a splitting in the phonon branch basically means that there is no sizeable superstructure existing on a time scale which is long compared to that of the LO frequencies. The term *dynamic* charge order used in Ref. 10 is somewhat misleading in that the proposed model is a quasistatic one in the sense that a frozen-in charge order was assumed for the calculation of the phonon dispersion.[16]

The strong softening and broadening of the LO phonons with doping [see Fig. 2 (middle)] is nevertheless indicative of a tendency towards a charge order. The highest LO branches in all perovskite compounds are of bond-stretching character, which makes them susceptible to a redistribution of charges. The polarization patterns of the bond-stretching modes under discussion are illustrated in Fig. 4, showing the displacements for $q=(0, 0, 0)$, $(0.25, 0, 0)$, and $(0.5, 0, 0)$. The zone-center mode is associated with an uniform displacement of the oxygens and thererefore it cannot be related to a charge ordering; however, the displacement pattern of the mode at $q=0.5$ induces rows of Cu sites with two short Cu-O distances separated by rows with two long distances. The latter arrangement will favor a localization of positive charges on the rows with short Cu-O distances, however not necessarily on the Cu-sites themselves. Therefore, the strong softening of the $q=0.5$ phonon can be seen as a precursor phenomenon towards a charge ordered phase with periodicity $2a$.

However, inspection of the data shown in Fig. 2 shows that it is not really the $(\pi,0)$ phonon ($\zeta=0.5$) which shows the strongest phonon self-energy effects but phonons of longer wavelengths. This conclusion is based on the very steep dispersion at $\zeta\approx 0.25$ which is not expected from a simple model designed to reproduce the softening of the $(\pi,0)$ phonon [as shown by the dashed line in Fig. 2 (middle)]. Further, and more importantly, the maximum of the intrinsic phonon linewidth is not observed at $\zeta=0.5$ but rather at $\zeta\approx 0.3$.[17] This means that coupling of the LO phonons to the electrons is strongest for $\zeta=0.25, \ldots, 0.3$, which corresponds to a stripe pattern with periodicity $4a$ to $3a$ (see Fig. 4), i.e., close to what was observed in the charge ordered stripe phase in nonsuperconducting cuprates.[11]

One might ask to what extent the effects observed in $La_{1.85}Sr_{0.15}CuO_4$ can be explained by density-functional theory within the local-density approximation (LDA). We note that the total frequency drop between Γ and $\zeta=0.5$ is well reproduced by frozen phonon calculations by Rojewski[18] ($\nu_{calc}=21.0$ THz and 16.8 THz for $\zeta=0$ and 0.5, respectively). Unfortunately, there are no results for intermediate ζ values nor for the phonon linewidth to allow a more detailed comparison. Furthermore, the origin of phonon anomalies in La_2CuO_4 has been investigated in a series of papers by Falter and co-workers starting from a LDA electronic band structure.[19–23] They obtain phonon anomalies as a consequence of long-range, nonlocal electron-phonon interaction effects of monopole charge-redistribution type which are strongly enhanced when going from the insulating to the metallic state. In their most recent papers,[22,23] the overall dispersion of the highest-energy phonon branch in the $(1, 0, 0)$ direction is calculated in good agreement with experiment ($\nu_{calc}=20.1$ THz and 17.2 THz at $\zeta=0$ and 0.5, respectively). However, this theory does not reproduce the exact shape of the LO phonon branch observed in the experiment; instead, it gives a shape as calculated by our phenomenological model (depicted by the broken curve in Fig. 2, middle).

In summary, our data do not support a short-range unit-cell doubling in the CuO_2 plane of $La_{1.85}Sr_{0.15}CuO_4$ existing on a time scale which is long compared to that of the LO frequencies. The data are, however, consistent with the idea that $La_{1.85}Sr_{0.15}CuO_4$ is close to a stripe order phase with a periodicity close to that observed in nonsuperconducting related compounds.

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[1] For a review, see L. Pintschovius and W. Reichardt, in *Neutron Scattering in Layered Copper-Oxide Superconductors*, edited by A. Furrer, Physics and Chemistry of Materials with Low-Dimensional Structures Vol. 20 (Kluwer Academic Publishers, Dordrecht, 1998) p. 165.
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[15] We note that the point (3,0,0) was incorrectly labeled in Ref. 10 as the zone center but is a *Z* point.
[16] In Ref. 10, the charge order was assumed to be dynamic to be compatible with the absence of superlattice diffraction peaks. We note that the absence of superlattice diffraction peaks sets an upper limit on the charge order lifetime which is very long compared to the inverse LO phonon frequency.
[17] Note that a deconvolution of the total linewidth to account for instrumental broadening enhances the ratio of the intrinsic linewidth observed at $\zeta \approx 0.3$ ($\Delta\nu \approx 1.8$ THz) and at $\zeta = 0.5$ ($\Delta\nu \approx 1.2$ THz), respectively.
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