Pronounced In-Plane Anisotropy of Phonon Anomalies in $YBa_2Cu_3O_{6.6}$

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The dispersion of the Cu-O bond-stretching and bond-bending vibrations in $YBa_2Cu_3O_{6.6}$ has been studied by high resolution inelastic neutron scattering. While the behavior of the bond-bending vibrations can be well accounted for by a simple potential model, the bond-stretching vibrations show a highly anomalous behavior. The displacement pattern of the most anomalous phonons is in principle consistent with dynamic charge stripe formation. However, charge stripes would have to extend along the *a* axis and not the *b* axis as inferred from the magnetic fluctuations by Mook *et al.* [Nature (London) **404**, 729 (2000)].

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It has been repeatedly suggested by theory [1,2] that the charge distribution in the CuO_2 planes of the high temperature superconductors is inhomogeneous, involving an array of metallic stripes acting as domain walls for the antiferromagnetic background. The most compelling experimental support for this picture has come from neutron diffraction results for $La_{1.45}Nd_{0.4}Sr_{0.15}CuO_4$ by Tranquada *et al.* [3,4] which yielded evidence for static stripes at low temperatures. Static charge ordering, however, seems to compete with superconductivity [4]. Charge ordering in superconducting samples is assumed to be dynamic in nature which poses an enormous problem for an experimental verification of this hypothesis. Phonon measurements appear as a promising technique because dynamic charge stripe formation should reveal itself by producing pronounced anomalies; i.e., phonons with a displacement pattern closely related to the charge stripe wave vector should have anomalously low energies, similar to what has been observed as precursor phenomenon to charge-density wave order in one-dimensional metals [5]. For this reason, we have carried out a detailed study of the dispersion of longitudinal optic branches involving Cu-O bond-stretching vibrations in $YBa_2Cu_3O_{6.6}$ (O6.6). O6.6 was chosen out of the YBCO family because incommensurate magnetic fluctuations are documented best for just this compound [7–9]. The wave vector of the phonon anomalies, if they are present at all, has to be 2 times the wave vector of the magnetic fluctuations if they are to be seen as fingerprints of a stripe phase putting an important constraint on the interpretation of the data. Moreover, and very importantly, recent inelastic neutron scattering measurements on a partially detwinned sample by Mook *et al.* [9] have shown that the magnetic fluctuations in O6.6 are one dimensional. This implies that charge stripe order will be one dimensional as well, and hence phonon anomalies are expected essentially for one direction only. Thus, O6.6 is a particularly well-suited system to check whether or not the phonon behavior is consistent with the stripe phase picture.

Inelastic neutron scattering measurements were performed on a twinned single crystal grown using the top-seed melt texturing method. The sample of size 1.3 cm^3 was cut from an as-grown crystal to achieve a low mosaic spread (1.3°). Annealing led to a composition of $YBa_2Cu_3O_{6.6}$ with a superconducting transition temperature $T_c \approx 60$ K with a (magnetic) 10%–90% width of 2.5 K. We note that the observed T_c corresponds very well to that reported for O6.6 after aging [10]. We observed superlattice peaks related to oxygen order for both the ortho II and the ortho III phases as has to be expected from the established phase diagram of $YBa_2Cu_3O_x$ [11]. Further, we observed incommensurate magnetic fluctuations very similar to what is reported in the literature [9]. Extensive measurements were performed on this sample for two orientations with its [001] axis or its [010] axis vertical to obtain redundant information to check against spurious effects. The experiments were carried out on the 1T triple-axis spectrometer at the ORPHEE reactor of the Laboratoire Léon Brillouin at Saclay, France. The (220) reflection of a Cu crystal was used to monochromatize the incident neutrons in order to achieve high resolution. [$\Delta E = 1.8(2.8)$ meV (FWHM) for an energy transfer of 45 (70) meV.] Achieving high resolution was crucial in this experiment in order to distinguish between the dispersion of the optic branches along the *a* and the *b* directions despite the twinning of the sample. Pyrolithic graphite (PG) (002) was used as analyzer crystal. Both crystals were horizontally and vertically focusing. A PG filter was placed into the final beam to suppress higher order contaminations. Residual second order scattering was controlled by scans with different final energies in the energy window of the filter from 12.8 to 15 meV. All measurements were performed at $T = 10$ K.

As mentioned above, our measurements focused on the highest energy longitudinal bond-stretching vibrations because these are expected to couple most strongly

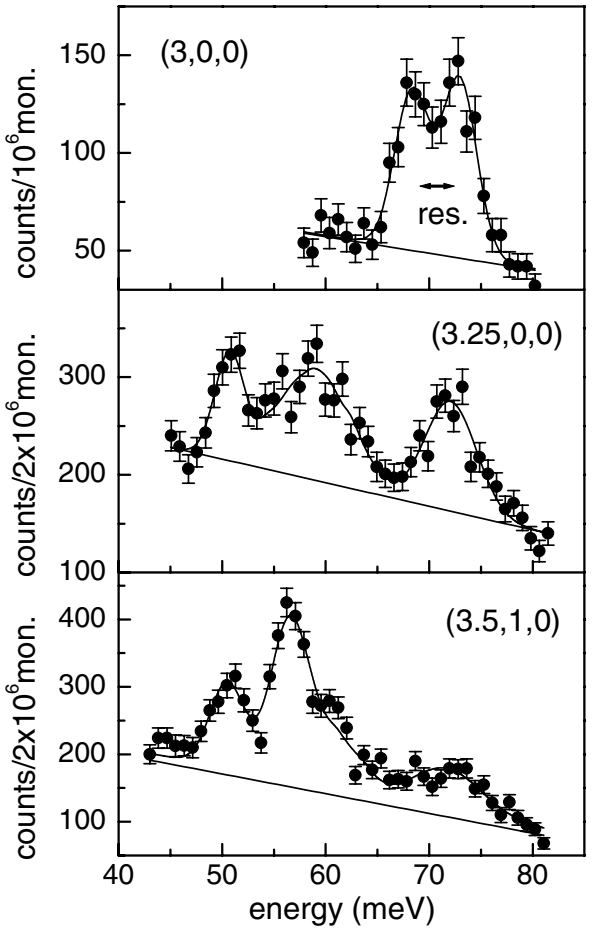

FIG. 1. Typical energy scans performed on $YBa_2Cu_3O_{6.6}$ at $T = 10$ K. A monitor count of 10^6 corresponds to an average counting time of 9 min per point. Dashed lines indicate the estimated background scattering.

to dynamic charge stripes. However, the longitudinal bond-bending modes were studied in detail as well for the following reasons (displacement patterns of bond-stretching vibrations and of bond-bending vibrations are depicted in Fig. 6 below): (i) Close to the zone boundary, they are so high in energy that they are practically degenerate with some bond-stretching modes. Hence, an assignment of the phonon peaks cannot be made without a detailed knowledge of both types of vibrations. (ii) Mook *et al.* [9,12] reported an anomalous broadening of bond-bending phonons in O6.6 which they related to charge fluctuations.

Representative raw data are shown in Fig. 1. The observed frequencies of phonons with Δ_1 symmetry are summarized in Fig. 2b. For sake of comparison, Fig. 2a shows the dispersion of the corresponding phonon branches as calculated from an empirical interatomic potential model [13]. The assignment of the high energy phonon peaks to the $[\zeta 00]$ $(= a)$ or the $[0\ \zeta 0]$ $(= b)$ direction was based on the observation that constant E-scans through the steeply dispersive branch across the nominal $(3, 0, 0)$ reciprocal lattice point were centered at (0,3,0) rather than at (3,0,0) (Fig. 3). Our assignment is further corroborated by the

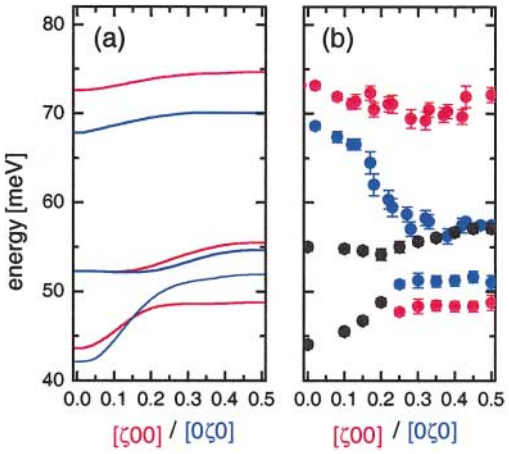

FIG. 2 (color). Dispersion relation of high energy longitudinal optic phonons in $YBa_2Cu_3O_{6.6}$ with Δ_1 symmetry. (a) Dispersion curves calculated from an interaction potential model [13]. The differences between the $[\zeta 00]$ and the $[0\zeta 0]$ directions shown in red and blue, respectively, are due to the orthorhombicity of the structure. The branches above 65 meV correspond to in-plane copper oxygen bond-stretching vibrations. The branches starting at 52 meV and at about 43 meV are associated with apical oxygen vibrations along c and with in-plane copper oxygen bond-bending vibrations, respectively. For $\zeta > 0.25$, there is considerable mixing of eigenvectors of these two types of vibrations. (b) Experimental results obtained by high resolution inelastic neutron scattering on a twinned single crystal. Black symbols denote phonon peaks where the splitting between $[\zeta 00]$ and $[0\zeta 0]$ behavior could not be resolved.

fact that at the zone center — where electron-phonon coupling effects are probably small — the phonons polarized along a are expected to be higher in frequency than those polarized along b because of the smaller Cu-O distance similar to what was observed by optical measurements on detwinned samples of O6.95 [14] (Fig. 2a). In contrast, the phonon peaks at $E \approx 50$ meV could not be assigned unambiguously to the a or the b direction. Here the assign-

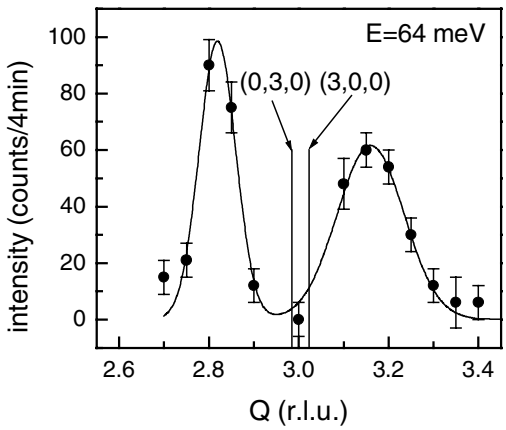

FIG. 3. Background-corrected intensities versus momentum transfer for an energy transfer of 64 meV deduced from a series of constant-Q scans. Actual counting times varied between 8 and 20 min. The vertical lines denote the positions of the (3,0,0) and (0,3,0) reciprocal lattice points observed with the same instrumental configuration.

ment was guided by the model calculations (cf. Figs. 2a and 2b).

Evidently, there is no clue for an anomalous behavior in the dispersion of the lower energy branches of bond-bending character. Further, we emphasize that we did not observe any anomalous line broadening in these branches in contrast to what was reported previously [12] (Fig. 4a). Using very high resolution, we do observe a splitting of the phonon lines for $q \geq 0.25$ r.l.u. (Fig. 4b) reminiscent of what has been reported in [9], but there is no need to invoke an electronic effect to explain this splitting because the potential model predicts a sizable energy difference between the a and the b directions for structural reasons. We point out, however, that the absence of anomalous behavior in these branches is not at all surprising because they are related to Cu-O bond-bending vibrations. The displacement pattern of these phonons does not involve a modulation of the Cu-O distance and therefore is not easily associated with charge stripe formation (see Fig. 6b below). Rather, dynamic stripes should strongly couple to longitudinal bond stretching vibrations because an inhomogeneous charge distribution will lead to a modulation of the copper-oxygen bond length.

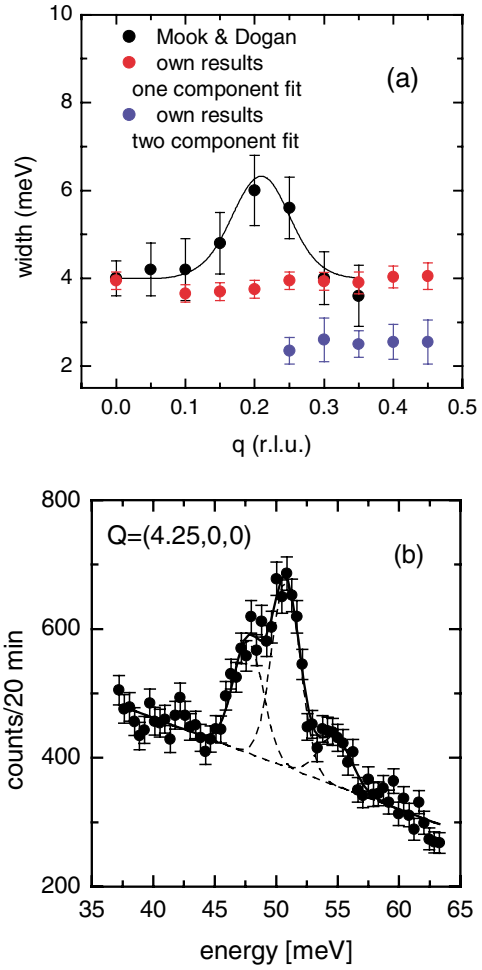

FIG. 4 (color). (a) Linewidths of longitudinal optic phonons with bond-bending character as observed in our own work and as reported in [12]. The plotted values correspond to the definition of the width used in [12] which is related to the commonly used full width at half maximum (FWHM) by $w = \mathrm{FWHM}/\sqrt{2 \times \ln 2}$. For $q \geq 0.25$ r.l.u., we are able to show that the phonon groups are, in fact, composed of two lines (apart from a further component related to a higher energy branch) which are each only slightly broader than the instrumental resolution of 1.8 meV. (b) An example of a phonon group which can be decomposed into three narrow lines. For a twinned sample, one expects to see two pairs of lines, one for each of the domains: a strong component around 50 meV and a weak component around 55 meV (see Fig. 2a). The splitting of the two lines around 55 meV is too small to be resolved in the measurement. The scan was made with a final energy $E_f = 15.1$ meV and $E_f = 13.2$ meV for energy transfers $E \leq 42.6$ meV and $E \geq 42.6$ meV, respectively, to avoid second order scattering.

Indeed, Fig. 2b demonstrates that the bond-stretching vibrations in O6.6 do show a highly anomalous behavior. We note that even in the a direction, although there is very little dispersion, the zone boundary phonons are about 5 meV lower in energy than in $YBa_2Cu_3O_6$ [15] indicating some degree of renormalization due to an interaction with the conduction electrons. However, the very rapid drop of frequencies for phonons propagating along the b direction at halfway to the zone boundary is certainly the most anomalous feature [16]. For $q > 0.25$ r.l.u., the peaks related to the bond-stretching vibrations are so low in energy that they cannot be separated in energy from those related to bond-bending vibrations making an assignment of phonon peaks and an exact determination of frequencies difficult. In this respect, it is helpful to study the corresponding branches of Δ_4 symmetry, i.e., branches where the corresponding atoms in the Cu-O_2 bilayer move out-of-phase instead of in-phase as for the phonons of Δ_1 symmetry. Here bond-bending ($E < 53$ meV) and bond-stretching ($E > 53$ meV) phonons are not close in energy at the zone boundary which allows an unambiguous assignment (Fig. 5b). Comparison of Figs. 2b and 5b shows that the results for the Δ_4 branches corroborate our interpretation of the data for the Δ_1 branches.

Additional measurements along the (110) direction have shown that the zone boundary frequency of the bond-stretching phonons is not halfway between the values for the a and the b directions, but slightly higher than in the a direction, and so the b direction is really distinguished in this respect. Further, the shape of the dispersion curves suggests that the phonons with wave vectors about (0,0.25,0) are the most anomalous ones. The displacement pattern of these phonons is depicted in Fig. 6a. Evidently, such a displacement pattern is compatible with dynamic charge stripe formation with a period of about 4b, and so it is tempting to interpret the anomalously low energy of these phonons as a precursor phenomenon to formation of a striped phase. At first glance, this seems to fit nicely to the striped-phase interpretation of the magnetic fluctuations in O6.6 proposed by Mook *et al.* [9]. However, these authors concluded from the one-dimensional nature of the magnetic fluctuations that the dynamic charge stripes extend along the b axis, whereas our phonon results suggest that dynamic charge stripes extend along the a axis. This

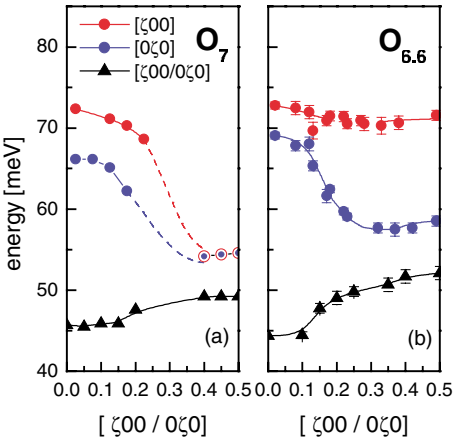

FIG. 5 (color). Dispersion relation of longitudinal optic phonons with Δ_4 symmetry in $YBa_2Cu_3O_x$. Phonon branches above and below $\sim$53 meV are associated with Cu-O bond-stretching and Cu-O bond-bending vibrations, respectively. Δ_4 symmetry means that the atomic displacements in the CuO2 bilayer are out of phase. (a) Results reported by Reichardt [15] for $x = 7$. The assignment of the high energy branches to the $[\zeta 00]$ or $[0\zeta 0]$ directions, respectively, was not yet proposed in [15] but appears to be highly plausible in view of our present results. (b) Results of the present study for $x = 6.6$.

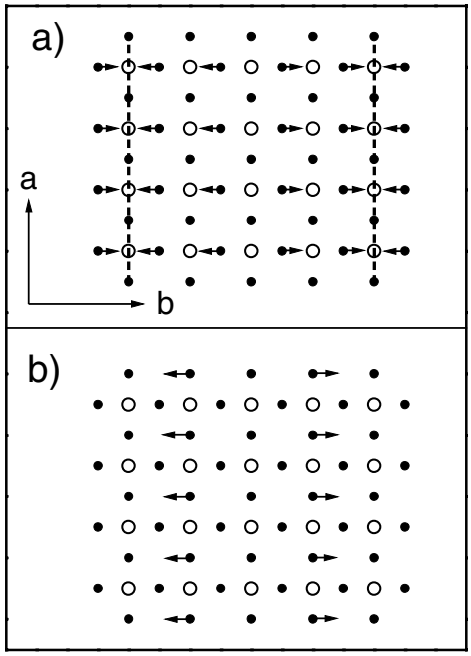

FIG. 6. Displacement patterns of in-plane polarized longitudinal optic phonons in $YBa_2Cu_3O_{7-x}$ for $q = (0, 0.25, 0)$. The phonons of interest involve primarily displacements of Cu (circles) and O atoms (full dots) in the CuO_2 planes. Therefore, the other atoms are not shown here. (a) Bond-stretching vibrations with a period of four lattice constants propagating along the b axis. The dashed lines denote positions where an extra charge will be dynamically accumulated on the Cu atoms due to the displacements of the neighboring O atoms. (b) Bond-bending vibrations with a period of four lattice constants. Displacements of this type will not lead to a nonuniform charge distribution.

This inconsistency strongly argues against the striped-phase interpretation of the inelastic neutron scattering results obtained on O6.6. Therefore, our results do not support the existence of a dynamic striped phase, and so the demonstration of dynamic charge fluctuations by microscopic probes, let alone their possible effect on superconductivity, remains an open issue. On the other hand, our results support the idea that high-T_c superconductivity correlates with a strong electron-phonon coupling [17]. Numerous measurements of the phonon density of states have shown [18,19] that high-frequency phonons in superconducting compounds are significantly renormalized in comparison to those in their insulating parent compounds. This finding fits well to the interpretation of angle-resolved photoemission spectroscopy data given by Lanzara *et al.* [20] who ascribe a kink in the quasiparticle dispersion of several high-T_c compounds in the energy range 50-80 meV as due to a strong electron-phonon coupling. Our results for O6.6 show that the phonon anomalies in this compound are about as pronounced as in O7 in the b direction but are much weaker in the a direction. Whatever the role of the phonons for the high T_c is, there is apparently some correlation between the strength of the electron-phonon coupling and T_c in $YBa_2Cu_3O_x$.

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