Giant phonon anomalies in the bond-stretching branches in Ba$_{0.6}$K$_{0.4}$BiO$_3$

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The dispersion of the longitudinal bond-stretching (BS) branches in superconducting Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO) studied by inelastic neutron scattering reveals giant phonon anomalies. In the [110] and [111] directions these branches even split close to the middle of the zone, in contradiction to any harmonic lattice dynamical model with cubic symmetry. The additional low energy branch in the [111] direction ends at the R-point with a frequency near 10.5 THz representing a doping induced renormalization of a breathing type vibration by about 40%, the strongest observed so far in any superconductor.

BKBO merits special interest since it exhibits by far the highest $T_c$ among the non-cuprate perovskite superconductors [1, 2]. The pure compound exhibits charge order between Bi$^{5+}$ and Bi$^{3+}$ associated with a breathing distortion of the lattice, i.e. alternating BiO$_6$-octahedra with short (Bi$^{5+}$) and long (Bi$^{3+}$) Bi-O-bond distances. The Bi-O bond distances reflect directly the latter configuration was used in most cases in order to fix the internal energy was fixed either to 3.55 THz or 7.37 THz; the (111) monochromator and a PG-(002) analyzer. The first scan was performed on the triple-axis spectrometer 1Ta using a Cu(111) monochromator and a PG-(002) analyzer. The final energy was fixed either to 3.55 THz or 7.37 THz; the latter configuration was used in most cases in order to avoid higher order contamination. Samples were cooled to $\sim$11K to minimize background; only a few comparative scans were performed at higher temperature.

Along the [100]-direction the BS branch connects to the linear breathing mode at the zone boundary, $X$. In figure 1 we show scans on these modes for $q=(0\ 0\ 0)$ to $X$, $Q=(5\ 0\ 0)$ to $(4.5\ 0\ 0)$ ($Q$ denotes the scattering vector with $Q=q+\tau$ where $q$ is within the first Brillouin zone and $\tau$ a reciprocal lattice vector). In agreement with our previous report, the branch drops down in frequency near $q=(0.25\ 0\ 0)$, see Fig. 1. In addition to the frequency softening along [100] the modes are strongly broadened close to X. The improved statistics also permits a quantitative analysis of the intensity: the upper part of figure 1 clearly demonstrates, that the integrated intensity continuously decreases when approaching X in the range $(0.3\ 0\ 0)$ to $(0.5\ 0\ 0)$, i.e. in the range where frequency is almost constant. The fact that this behavior is seen in two configurations (and also for other Q-values not shown) excludes an experimental artifact. The loss of intensity towards X may suggest that some spectral weight is split off and shifted to even lower energy.

Figure 2 and 3 present the scans recorded on the BS branches in the [110] and [111] directions. Along [110] the scans were obtained by comparing and adding the results at many different Q-values. Along [111], all scans were performed at $Q=(4-x\ 1+x\ 1+x)$ which allows direct comparison of intensity. Additional measurements were also done along [111] in many different Brillouin zones in order to establish the dispersion unambiguously. In both directions we find an unexpected splitting: upon increase of $x$ in $q=(x\ 0\ 0)$ and in $q=(x\ 0\ 0)$ the unique peak at $\Gamma$ develops first a shoulder for $x=0.1$–0.2 and then shows intensity continuously decreases when approaching X in the range $(0.3\ 0\ 0)$ to $(0.5\ 0\ 0)$, i.e. in the range where frequency is almost constant. The fact that this behavior is seen in two configurations (and also for other Q-values not shown) excludes an experimental artifact. The loss of intensity towards X may suggest that some spectral weight is split off and shifted to even lower energy.
interpretation that the split off intensities are of BS character is further corroborated by intensity checks. When comparing the total intensity of the split peaks with that of the BS mode at $\Gamma$ and with those of the BB modes at $M$ and $R$, respectively, we find good agreement with calculated structure factors by a lattice dynamical model, whereas the upper better-defined peaks account only for about half of the expected intensity.

Figure 4 shows the dispersion of the BS branches in [110] and [111] directions deduced from a two peak analysis of the experimental spectra. The upper branches agree well with our former results [4, 5]. In the [110]-direction the additional branch is close to the low frequency plateau of the [100] branch. In the [111] direction the lower branch exhibits continuous softening through the zone, ending near 10.5 THz at $R$. However, it cannot be excluded that even the additional branch is split, with an upper branch with reduced slope and a dispersion-less feature near 10.5 THz. The interpretation of the additional spectral weight is severely hampered by the strong intensities from the LO branches with BB character. Whereas in the [111] direction this branch stays below 9 THz the situation is much less favorable for the [100] and [110] directions. Here the corresponding branches rise from below to beyond 10 THz near the zone boundaries. For this reason we cannot exclude that near $X$ and $M$ some of the intensity in the 10 THz region has to be attributed to BS vibrations. It appears interesting to note that in the closely related compound BaBi$_{0.25}$Pb$_{0.75}$O$_3$ a dispersion-less additional intensity has been found just at this energy [14].

Two groups have examined the phonon density of states upon doping [15, 16]: there is a strong doping induced shift of spectral weight from the region above 15 THz towards the region 10–13 THz. This behavior agrees qualitatively with the bending down of the BS branch along [100] and the additional low frequency intensities displayed in figure 4. The simulation of the phonon density of states with the lattice dynamical model indicates that the observed spectral shift cannot be explained by the bending down of the [100]-branch alone, which provides additional support for the identification of the split intensities to be of BS character.

The temperature dependence of the BS intensities has been studied at (0.4 0 0), $X$ and $R$ on the crystal with the

FIG. 1: Scans on the BS modes in the [x00] direction at $Q=(5-x0)$ with low a) and high b) resolution. Dispersion of the BS mode along [100], c), and q-dependence of the FWHM, d); the inset in d) shows an elongation pattern of the 1D-breathing mode at $q=(0.50)$ for a single BiO$_2$-layer; closed circles denote Bi- and open ones O-ions.

FIG. 2: Scans on the BS modes in [110] direction, scans at different equivalent Q-values have been added, $E_f=5.37$ THz; arrows indicate the positions of the modes. The inset shows an elongation pattern of the planar breathing mode at $q=(0.50)$ for a single BiO$_2$-layer; closed circles denote Bi- and open ones O-ions.
FIG. 3: Scans on the BS modes in [111] direction at $Q=(4-x, 1+x, 1+x)$, $E_f=7.37$THz; arrows or horizontal bars indicate the positions of additional intensity; thin lines show the background.

superconducting transition at $T_c=29.5$ K. We observe no difference in position or peak width between 10, 36 and 120 K, whereas the phonons become significantly broadened upon heating to room temperature. The absence of an anomaly at $T_c$ does not contradict the expected strong electron phonon coupling, since the phonon frequencies are much higher than the superconducting gap.

Obviously, the two branches in figure 4 cannot be explained by any model based on harmonic lattice dynamics and ideal cubic perovskite symmetry. The split dispersion might arise from a folding back of the zone boundary frequencies to the Γ-point. In principle the rotation distortion present in these crystals might cause such behavior; however, lattice dynamical calculations within the symmetry of this distortion show that there is no influence of the rotation on the BS modes, and, in particular, there are no gaps at the zone-boundary of the superstructure. Since Ba/K-mixing may in principle cause splittings in the phonon dispersion, we have analyzed these effects by superlattice calculations with the Ba and K randomly distributed; details of these calculations are described in Ref. [13]. The simulated spectra yield an influence for the BB branches, but there is no sizeable effect on the BS branches: this finding reflects the orientation of the Ba/K-O interaction perpendicular to the Bi-O-bonds.

The renormalization of the BS frequencies can be attributed to electron lattice interaction. LDA band structure calculations indeed predicted some frequency softening induced by doping [17, 18]; however, the agreement is at most qualitative and the splitting of the BS branches is not explained at all. The observed much stronger effects indicate that ab initio LDA calculation [8] severely underestimates the electron phonon coupling for the BS modes. The strength of the renormalization and the splitting in the BS branches must be directly related to the bond distances and, hence, to some inhomogeneity or fluctuation of charge. For example, the three-dimensional breathing mode at $R$ is associated with oscillating octahedral volumes. If the charge in the octahedra is oscillating in phase – i.e. positive charge is always going to the smaller octahedron –, the phonon frequency becomes reduced similar to the reduction of a longitudinal polar frequency by screening. One may consider specific charge fluctuations to screen the linear and planar breathing modes too. However, such screening of BS displacements requires at least a partial localization of the charges on a time scale determined by the inverse phonon frequency. Dynamic charge-phonon coupling may explain a continuous dispersion along [100], but, the split dispersion suggests some charge inhomogeneity on a time scale larger than the inverse phonon frequency. Evidence for some local variation of the Bi-O-bond distance, and hence charge inhomogeneity, has been found in EXAFS-experiments [19] and in the anisotropic Debye-Waller factors [13]. One should emphasize the strong frequency broadening of all renormalized modes. The FWHM of the mode at $X$ indicates a phonon life-time of the order of the vibration period; the even broader signals in the split-of branches along [110] and [111] demonstrate that the character of these excitations is quite different to that of a harmonic phonon mode. One may speculate, that also the spatial extension of these excitations is reduced.

The observations in BKBO may be compared with other metallic perovskites. The shooting down of the BS branch in [100] is observed in manganates [8], in both cuprate systems studied, La$_{1.85}$Sr$_{0.15}$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-\delta}$ [7], and in nickelates [9]. In manganates,
cuprates and the bismuthates the step-like form of the dispersion is extremely anomalous, and the similarity between these systems is striking. The step near $q=(0.25 0 0)$ suggests an underlying cell-doubling. McQueeney et al. [20] have tried to explain the dispersion in La$_{1.85}$Sr$_{0.15}$CuO$_4$ by such a superstructure; however, recent studies did not reveal the expected discontinuity in the dispersion [21]. We think that the step-like shooting down in all these perovskites arises from a dynamic charge lattice coupling. The [100] BS modes appear to be exceptional due to their particular displacement pattern: the metal-ions with close oxygens are connected via metal-oxygen-metal bonds, see figure 1. This displacement pattern further yields a pronounced coupling to the charge on the oxygen. Furthermore, this configuration requires only little reduction of the kinetic energy of the charges involved in the screening, since the metal-oxygen-metal paths will favor metallic behavior even in a frozen-in phase. For the displacement patterns of the BS branches along the other directions, the cations with short bonds are not connected by metal-oxygen paths; therefore, the screening of the displacements by some charge displacement requires sizeable reduction of kinetic energy.

The outstanding renormalization along [110] and [111] found in the bismuthate does not have an analogy in the superconducting cuprates [7]. One may note that the spectral weight of the frequency shifts is essentially enhanced by the additional renormalization along [110] and [111], since these directions show high multiplicities of 12 and 8 respectively. Therefore, the spectral weight of the BS mode renormalization in BKBO, which may be taken as a measure of the electron phonon coupling, is essentially larger than that found in the cuprates, rendering a superconducting mechanism based on coupling to BS modes [22] much more likely for BKBO. The distinct behavior along [110] and [111] between manganates and bismuthates on one side and the cuprates on the other side, is further reflected in different charge-ordering schemes appearing upon substitution [3, 6, 11]: cuprates exhibit only one-dimensional stripe-type order [10]. Finally, we note that a split dispersion is observed for the first time in BKBO, but should represent a characteristic feature for perovskites with inhomogeneous charge distribution.

In conclusion, we have reported on the dispersion of the phonons are strongly coupled to some charge fluctuations in BKBO. Comparing BKBO to La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_7$, which exhibit similar or higher superconducting transition temperatures, the spectral shift due to the BS phonon anomalies in BKBO is substantially larger.

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