Comment on "Renormalization of Phonons in a (Y/Pr)$Ba_2Cu_3O_7$ Superlattice Investigated by Raman Spectroscopy"

In a recent Letter Li *et al.* [1] have investigated the vibrational modes of thin-period superlattices of the type (YPrY)$Ba_2Cu_3O_7$ (2 Y by 1 Pr). They found an additional mode beside those found in [2] for 8 by 8 and 7 by 14 superlattices. They interpreted it as admixture of an even-parity $PrBa_2Cu_3O_7$ mode with a normally Raman-inactive mode in $YBa_2Cu_3O_7$. This new mode, with a substantial wave vector if viewed in the original Brillouin zone of bulk $YBa_2Cu_3O_7$, does not exhibit the superconductivity-induced frequency shifts found for $\mathbf{q} = 0$ phonons and predicted for $\mathbf{q} \neq 0$ phonons by a theory of Zeyher [3]. We point out here that the supposed admixture of even-parity phonons to odd phonons in $YBa_2Cu_3O_7$ leads to predictions about the Raman intensities which are in contradiction with the experimental results of [1].

The admixture of modes in a superlattice was obtained by Li *et al.* from a lattice-dynamical calculation. One can also find this admixture directly from experiments by considering the frequency shift from the bulk values to the superlattice values assuming that the interaction across the bulk unit cells can be represented by a number V. Symmetrizing the bulk Pr Raman frequency (306 cm^{-1}; 100 K) [2] and Y ir frequency (314 cm^{-1}; 100 K) [4] with respect to the superlattice frequencies (299 and 309 cm^{-1}; from Fig. 3 of Ref. [1]), we express the shifted frequencies as eigenvalues of the exactly diagonalized matrix

$$\begin{pmatrix} \frac{\Delta\omega_0}{2} & V \\ V & -\frac{\Delta\omega_0}{2} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \omega_\pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix}, \qquad (1)$$

$$\omega_\pm = \pm\sqrt{(\Delta\omega_0/2)^2 + V^2}, \qquad (2)$$

where α, β are the two coefficients of admixture to the superlattice mode and $\Delta\omega_0$=314–306 cm^{-1}. The eigenstates of the superlattice are $\alpha\,|\mathrm{Pr}\rangle_g + \beta\,|\mathrm{Y}\rangle_u$ with the bulk eigenmodes of B_{1g} symmetry in $PrBa_2Cu_3O_7$ ($|\mathrm{Pr}\rangle_g$) and of B_{1u} symmetry in $YBa_2Cu_3O_7$ ($|\mathrm{Y}\rangle_u$). The coefficients α and β may be obtained from (1):

$$\alpha = V, \qquad \beta_\pm = \Delta\omega_0/2 \pm \sqrt{(\Delta\omega_0/2)^2 + V^2}. \qquad (3)$$

The admixture of $|\mathrm{Pr}\rangle_g$ is thus determined by V, which we can deduce from the experiment and Eq. (2). We obtain $V = 3.0$ cm^{-1} with $\Delta\omega_0/2 = 4.0$ cm^{-1} and the symmetrized superlattice frequencies $\omega_\pm = \pm\ 5$ cm^{-1} and thus, the *normalized* eigenvectors, $\alpha = 0.32$ and $\beta_+ = 0.95$ for one mode and $\alpha = 0.95$ and $\beta_- = -0.32$ for the other.

The Raman intensity I of the superlattice modes is proportional to the square of the eigenvector contribution of the Raman-active modes, i.e., $I \sim \alpha^2$, independently of β, since $|\mathrm{Y}\rangle_u$ is not Raman active by symmetry in the bulk. The relative strength of these two modes becomes $I(309\ cm^{-1})/I(299\ cm^{-1}) = (0.32/0.95)^2 = 0.11$; i.e., the higher-frequency superlattice mode should be much smaller than the lower one. The admixture estimated by Li *et al.* from their model is actually quite a bit lower (17%) and would make this ratio even smaller. Experimentally, however, the two peaks are nearly equal [Fig. 2(b) of [1]]. If anything, the higher-frequency one appears slightly larger. These relative intensities are incompatible with the estimated small admixture and thus the assignment to a nearly zone-boundary mode of the $YBa_2Cu_3O_7$ unit cell is unfounded. The conclusions concerning renormalization effects of phonons away from $\mathbf{q} = 0$ should be treated with caution.

A further point is raised by the comparison of the bulk-ir data and neutron scattering measurements. The ir results which show a clear softening of the B_{1u} mode at 315 cm^{-1} are well established [4–8]. Near $\mathbf{q} = 0$ neutron measurements [9] show, in fact, self-energy effects nearly as large. The small decrease from 0.6% to 0.4% in $\Delta\nu/\nu$ was attributed to a finite q resolution in neutron spectroscopy [9]. There is thus no contradiction between these two types of measurements regarding the self-energy effects.

It remains to suggest a possible origin of the double-peak feature observed by Li *et al.* [1] at low temperatures. One possibility is a structural defect which may occur significantly for thin superlattices: upon switching the material the chain oxygen site may be rotated by 90° from the previous layer. Such an interface-specific defect could give rise to a splitting of the Pr-like Raman mode. For very thin layer superlattices the density of such defects could be high.

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