Superconductivity-Induced Phonon Softening in $YBa_2Cu_3O_7$ Observed by Inelastic Neutron Scattering

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Inelastic neutron scattering yielded the first information on superconductivity-induced frequency shifts for $q \neq 0$ phonons in $YBa_2Cu_3O_x$. For branches starting from the Raman-active mode at 340 cm^{-1} (10.2 THz), the shifts were found to decrease only slowly with increasing momentum transfer ($x=7.0$) or even exhibit a maximum at finite q ($x=6.92$) when going along the [100] and [010] directions. They were independent of q in the [001] direction. The shifts were much smaller for the A_u mode at 307 cm^{-1} and the E_u mode at 343 cm^{-1} and for $q \neq 0$ phonons related to these modes.

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On cooling below T_c, significant changes in phonon frequencies, phonon linewidths, and oscillator strengths were observed in $YBa_2Cu_3O_x$ by Raman scattering [1–4]. These effects are considered to reflect the opening of the gap via a strong electron-phonon coupling. The mode at 340 cm^{-1}, which involves the out-of-phase vibrations of the oxygen atoms in the planes (see Fig. 1), has attracted particular interest because it shows the largest effects. According to the theory of Zeyher and Zwicknagl [5], this mode is outstanding not because it has a larger than average electron-phonon coupling, but because its energy is presumably closest to the gap energy 2Δ. Attempts have been made to derive quantitative estimates of the electron-phonon coupling constant λ from the observed frequency shifts under the simplifying assumption that the zone center modes are typical for all phonons throughout the Brillouin zone (BZ). Values of $\lambda \approx 1$ have been obtained in this way [2,5]. Although larger values of λ are required to fully explain $T_c = 92$ K, already a coupling strength of $\lambda \approx 1$ will be of considerable importance for the superconducting properties and cannot be neglected.

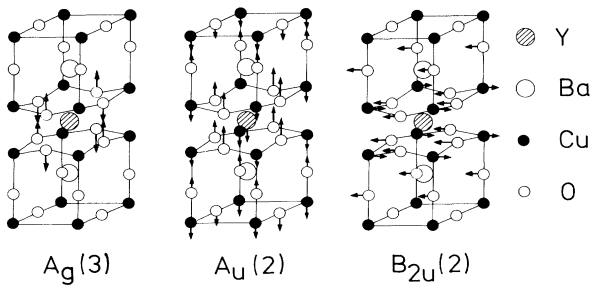

FIG. 1. Displacement pattern of three $q=0$ phonons in $YBa_2Cu_3O_7$. Left: A_g mode at 340 cm^{-1} (10.2 THz); middle: A_u mode at 307 cm^{-1} (9.2 THz); right: B_{2u} mode at 347 cm^{-1} (10.4 THz).

For simple reasons of phase space, $q=0$ phonons cannot be taken as representative for the whole spectrum. Inelastic neutron scattering allows in principle a search for superconductivity-induced phonon self-energy effects in the whole BZ but the small size of available single crystals has not allowed such measurements so far. In this paper we report the first observation of superconductivity-induced frequency shifts in $YBa_2Cu_3O_x$ by inelastic neutron scattering. Branches starting from the 340 cm^{-1} mode were investigated along the [100] and [010] and the [001] directions up to the zone boundary. Several other phonons with a similar energy were also investigated to see how much the frequency shifts depend on the vibrational pattern.

The sample was a single crystal with a volume of 0.3 cm^3 and a mosaic width of $\sim 1°$. Its "porous" microstructure allowed us to change the oxygen content between 6.0 and 7.0 with good homogeneity. The variation in x after each thermal treatment was determined from the difference in weight. The absolute values were deduced from measurements of T_N in the antiferromagnetic phase. The sample was investigated first with an oxygen content $x=6.92$ and later with $x=7.0$. As had to be expected, the crystal was twinned with about equal size of the two domains. Hence, the [100] and [010] directions were superimposed.

The neutron measurements were carried out on the 2T triple-axis spectrometer located at a thermal beam tube of the ORPHEE reactor at Saclay. This instrument was equipped with horizontally and vertically curved Cu(111) and PG(002) crystals as monochromator and analyzer, respectively, to maximize the scattering intensity. The crystal was mounted in a helium cryostat with a ⟨100⟩ axis vertical. Whereas the mounting support gave little contribution to the background in the first run ($x=6.92$), the situation was much worse in the second run ($x=7.0$) for some scattering configurations. Unfortunately, this

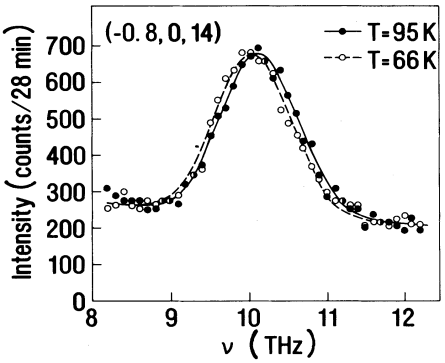

FIG. 2. Examples of phonon groups observed above and below T_c in $YBa_2Cu_3O_{6.92}$. Lines are the result of fits with a Gaussian line shape.

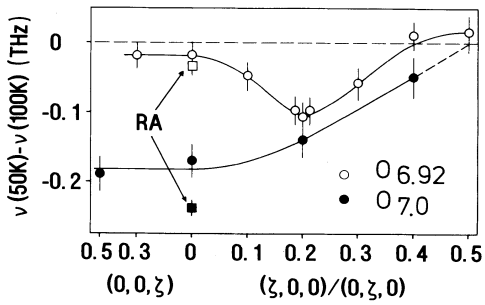

FIG. 4. Frequency shifts observed in $YBa_2Cu_3O_{6.92}$ and $YBa_2Cu_3O_{7.0}$ for phonons related to the 340 cm^{-1} A_g mode vs momentum transfer. Lines are a guide to the eye. The Raman results were taken from Ref. [1]. The full and open squares refer to $x=7.0$ and 6.87, respectively.

could not be remedied, in order not to disturb investigations of the magnetic scattering done on the same sample.

The first measurements were made on the sample with $x=6.92$ for the A_g mode at 340 cm^{-1} ($\nu=10.2$ THz) to allow a comparison with the Raman results. Subsequent measurements were carried out for several q values in the [100] and [001] directions. The largest frequency shift between 100 and 50 K was observed for $q\approx(0.2,0,0)$. As can be seen from Fig. 2, the data could be very well fitted with a Gaussian line shape which allowed determination of frequency shifts with an accuracy of $\Delta\nu \approx 0.02$ THz. No significant change in linewidth was found. This was not unexpected as the instrumental resolution (FWHM ≈ 1 THz) did not allow us to determine reliably as small a change in linewidth as was reported from Raman experiments [1–4].

In order to check that the observed frequency shifts were induced by the onset of superconductivity in our sample, we measured the frequency for $q=(0.2,0,0)$ at several temperatures above and below T_c. The frequency shift occurred in a narrow temperature range below T_c, thus confirming its relation to the occurrence of superconductivity (see Fig. 3).

The results are summarized in Fig. 4. The three values given for $q\approx(0.2,0,0)$ were obtained with different total momentum transfer. As a result of a small offset in the sample alignment, the three measurements did not correspond to exactly the same q value. The good agreement between these three frequency shifts is a further confirmation that the observed effects were not spurious.

After loading the sample to $O_{7.0}$, the measurements were repeated for the same branches as before. As mentioned above, the sample holder gave a bigger contribution to the background in this case (see Fig. 5). Nevertheless, frequency shifts could be evaluated with sufficient accuracy. As can be seen from Fig. 4, they were not only larger than in $O_{6.92}$, but also showed a different q dependence. For both O concentrations, the shifts were independent of q_z.

Having found a rather large frequency shift for the A_g mode, we decided to investigate further phonons with frequencies close to the presumed gap value of $YBa_2Cu_3O_7$, i.e., $2\Delta\approx 9.5$ THz (316 cm^{-1}) [2]. The displacement patterns of the investigated Γ-point modes are shown in

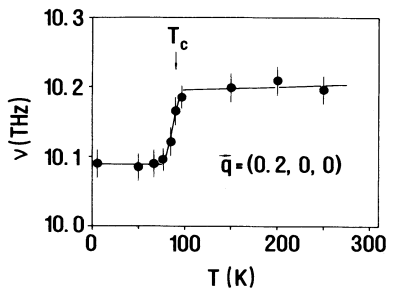

FIG. 3. Frequency of a phonon with $q=(0.2,0,0)$ in $YBa_2Cu_3O_{6.92}$ vs temperature. The line is a guide to the eye.

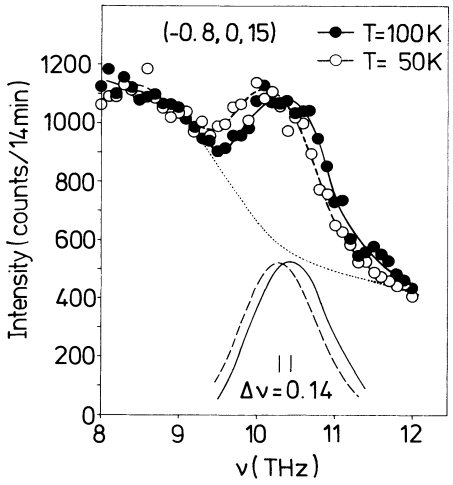

FIG. 5. Phonon groups observed in $YBa_2Cu_3O_{7.0}$ above and below T_c. The corresponding mode is the same as in Fig. 2. The background was determined by a measurement at $Q=(0,0,15)$, where the structure factor for the A_g phonon is zero.

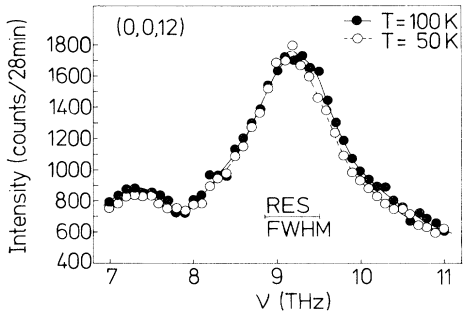

FIG. 6. Constant-q scans above and below T_c for $YBa_2Cu_3O_7$ showing the A_u mode at 9.2 THz.

Fig. 1. For the A_u mode at $\nu=9.2$ THz and related phonons with wave vectors $q=(0.1,0,0)$ and $(0.2,0,0)$, a scattering configuration could be used which gave a high signal-to-background ratio resulting in small statistical errors. The maximum shift $\Delta\nu/\nu=(0.4\pm0.1)\%$ was observed at $q=0$ (see Fig. 6). This value is somewhat smaller than found by infrared spectroscopy ($\Delta\nu/\nu\approx0.6\%$ [6]), which may be due to the finite q resolution in the neutron measurements and a rapid decrease of the shifts with increasing q. We found that for $q=(0.2,0,0)$, the shift was already within experimental error.

For $q=0$ the phonon linewidth was much larger than the resolution with a slight decrease below T_c. The linewidth decreased with increasing q, becoming resolution limited at $q=(0.2,0,0)$.

Additional measurements were performed for the E_{2u} mode at 10.4 THz and a related mode at $q=(0.15,0,0)$ and $\nu=11.4$ THz. Here, the experimental conditions were rather unfavorable, leading to a considerably larger error bar for the frequency shifts. The frequencies observed at 50 and 100 K agreed with each other within the error bar, which was $\Delta\nu/\nu\approx\pm0.5\%$ and $\pm0.3\%$ for $q=0$ and 0.15, respectively. We note that there are no optical data to compare with: All modes polarized within the basal plane are so strongly screened by the free carriers that they are unaccessible to optical measurements.

Raman investigations have shown that the superconductivity-induced frequency shifts decrease strongly when going from $O_{7.0}$ to $O_{6.85}$ [1,7]. Our results for the A_g mode show the same trend. To get quantitative agreement with the Raman results we have to assume a slightly lower oxygen content ($\Delta x\approx-0.05$) than deduced from our analysis, which we think is within the experimental uncertainty. So far, no convincing explanation has been given for the strong reduction of the frequency shifts with x in a range where T_c remains constant. Zeyher and Zwicknagl [5] predicted a drastic diminution of phonon self-energy effects if the inverse impurity scattering rate becomes equal to or larger than 2Δ. If oxygen vacancies act as scattering centers, this might explain the reduction of the frequency shifts with decreasing x. However, it would not explain why the line broadening observed below T_c by Raman scattering in O_7 is not just reduced on oxygen depletion, but instead a line narrowing is found for $x\leq6.90$ [7]. Such a change of sign can be explained within the framework of the theory of Ref. [5] only by the assumption that the gap value increases substantially with decreasing x, for which no plausible reason can be given, as T_c remains the same. Our results for $x=6.92$ show that it might be misleading to consider $q=0$ phonons only, as we found a very small frequency shift at $q=0$, but substantial shifts for $q\neq0$.

Two recent theoretical papers deal with self-energy effects of $q\neq0$ phonons: Zeyher [8] assumed a cylindrical Fermi surface and predicted a strong, monotonous reduction of superconductivity-induced changes with increasing momentum transfer. On the other hand, Marsiglio [9] considered the case of a nested Fermi surface at half-filling and found a strong enhancement of phonon self-energy effects for certain large wave vectors related to the Fermi surface topology. From our experimental findings, in particular from the observation of a maximum at finite wave vectors in $O_{6.92}$, we conclude that the assumption of a simple cylindrical Fermi surface for $YBa_2Cu_3O_x$ cannot hold. Nesting seems to be important, and the different q dependences of the frequency shifts found for $O_{6.92}$ and $O_{7.0}$ possibly reflect a change in the topology of the Fermi surface.

We find it puzzling that frequency shifts for phonons related to the A_u and B_u modes are much smaller than for the A_g mode. It is true that the theory in its simplest form gives nonzero effects for $q=0$ only for Raman-active phonons [8]. However, extensions of the theory by allowing for interband transitions revealed that infrared-active phonons may show effects of similar size like Raman-active phonons [10]—in agreement with experiment [6]. In particular, we are surprised by the absence of a large effect for the E_u mode: The frequencies of the E_u and the A_g modes are nearly the same, and intuitively we had expected that in-plane elongations (like for the E_u mode) would give a stronger electron-phonon coupling than out-of-plane elongations (like for the A_g mode).

In summary, we report inelastic neutron scattering measurements which allowed exploration of superconductivity-induced phonon frequency shifts in $YBa_2Cu_3O_x$ as a function of phonon wave number. Branches starting from the Raman-active mode at 340 cm^{-1} show substantial effects over a large part of the BZ. Comparison with existing theories [8,9] indicates that an understanding of the observed q dependence has to await calculations based on realistic band structures.

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