Copper isotope effect in Raman scattering on superconducting $YBa_2Cu_3O_{7-x}$

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Results of Raman scattering studies on the natural isotope superconductor $YBa_2Cu_3O_{7-x}$ and the heavy isotope superconductor $YBa_2{}^{65}Cu_3O_{7-x}$ are presented. The phonon at 148.6 cm^{-1} is down-shifted by 1.8 cm^{-1} in $YBa_2{}^{65}Cu_3O_{7-x}$ whereas the position of the phonon at 112.5 cm^{-1} remains unchanged. This conclusively relates the phonon mode at 148.6 cm^{-1} to the vibration of Cu(2) atoms and suggests that the phonon at 112.5 cm^{-1} is independent of Cu vibrations.

During the past two years there has been intensive research on Raman scattering in the high-temperature superconductor $YBa_2Cu_3O_{7-x}$.[1-12] Oxygen isotope studies[1,2] have demonstrated the existence of a small but nonzero isotope shift in the transition temperature (T_c) and have also helped identify the oxygen-coupled vibrations in the Raman spectrum.[1-3] Raman studies on the closely related semiconducting structure $YBa_2Cu_3O_{6+x}$ have revealed the effect of oxygen vacancies on the phonon spectrum of the superconductor.[4-6] Early Raman and infrared measurements on sintered ceramic samples of $MBa_2Cu_3O_{7-x}$ (where M=Y or a rare-earth element) led to extensive speculation on the identity of the optic modes. Recent polarized Raman studies on single crystals of $YBa_2Cu_3O_{7-x}$ have revealed the vibrational symmetry of these optic phonons.[7-9] This new information, coupled with the earlier results on sintered ceramics and lattice dynamic calculations, has led to a consensus in many of the mode assignments.[7-9]

In this paper we present results on Raman scattering in the natural isotope superconductor $YBa_2Cu_3O_{7-x}$ and the heavy isotope superconductor $YBa_2{}^{65}Cu_3O_{7-x}$. Our studies show that the phonon at 148.6 cm^{-1} is down-shifted by 1.8 cm^{-1} in $YBa_2{}^{65}Cu_3O_{7-x}$, whereas the position of the phonon at 112.5 cm^{-1} remains unchanged. This provides strong evidence that the phonon at 148.6 cm^{-1} is due to the vibration of Cu(2) atoms and that the vibrational mode at 112.5 cm^{-1} does not involve Cu atoms. It is necessary to reexamine an earlier discussion[10] on the coupling of superconducting gap excitations with low-energy phonons in view of the results presented in this paper.

The $YBa_2Cu_3O_{7-x}$ sample was prepared[1] by solid-state sintering of 99.999% purity CuO (naturally abundant isotope), Y_2O_3, and $BaCO_3$. The $YBa_2{}^{65}Cu_3O_{7-x}$ sample was made using isotope enriched (99.61% ^{65}Cu) ^{65}CuO in the same furnace and under the same sintering conditions as the $YBa_2Cu_3O_{7-x}$ sample. We found no measurable isotope shift for T_c, which was 92 K for both samples. The procedure for obtaining the Raman spectra has been reported elsewhere.[4] To further suppress the laser background, the spectra in Figs. 1 and 2 were obtained using an additional third spectrometer stage. The 5145-Å line of an Ar-ion laser of intensity 12 W/cm^2 was used to excite the spectra in Fig. 1. To further improve the signal-to-noise ratio in Fig. 2, the laser excitation intensity was increased to 20 W/cm^2, but no sample heating effects were observed. The experimental uncertainty in the repeatability of spectral positions with our spectrometer is ± 0.2 cm^{-1}.

The Raman spectra in the high-energy phonon region of $YBa_2{}^{65}Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$ are typical of high-quality single-phase material prepared by the sintering technique.[4,5] Polarization Raman measurements[7-9] on single crystals of $YBa_2Cu_3O_{7-x}$ have determined the vibrational symmetries of the phonons at 338, 443, and 505 cm^{-1}. Oxygen isotope studies have shown these modes to be oxygen-coupled vibrations.[1,3] We observe no detectable Cu isotope shift for these modes, consistent with the much higher mass of Cu compared to O. The phonon at 505 cm^{-1} has been assigned to the stretching mode of O(4) against Cu(1) and the phonons at 338 and 443 cm^{-1} to the out-of-phase and in-phase bending modes in the Z direction of O(3) and O(2) atoms situated in the O(2)-Cu(2)-O(3) planes.[7-9] In a polarized Raman study at low temperatures of a single crystal $YBa_2Cu_3O_{7-x}$, Cooper *et al.*[10] have demonstrated evidence for the strong coupling between the phonons at 116 and 335 cm^{-1} with superconducting gap excitations.[11] The phonon at 335 cm^{-1} is observed to soften[10,12] and to show a strong resonance below T_c, whereas the phonon at 116 cm^{-1} showed a decreasing antiresonance below T_c.[10] Since the superconductivity in high-T_c oxides has been associated[6] with conduction in the O(2)-Cu(2)-O(3) planes, one would expect a strong electron-phonon coupling with the Cu(2)

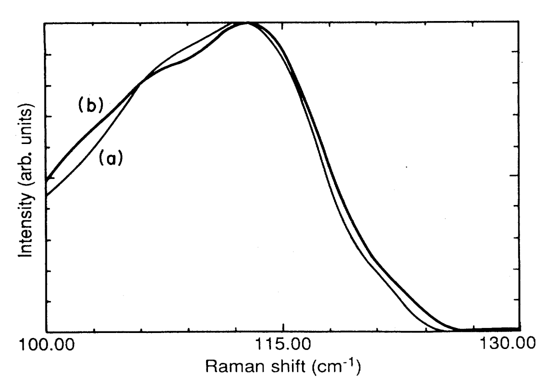

FIG. 1. Raman spectrum at T=293 K in the region of the 112 cm^{-1} phonon for (a) $YBa_2Cu_3O_{7-x}$ and (b) $YBa_2{}^{65}Cu_{7-x}$.

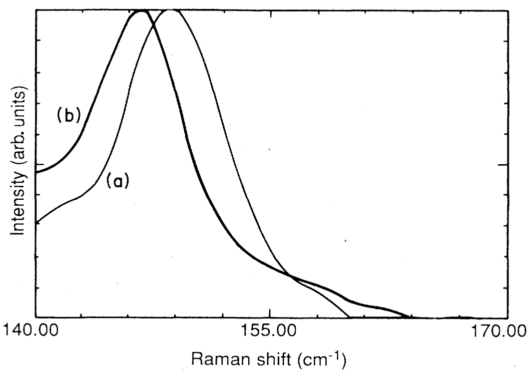

FIG. 2. Raman spectrum at $T=293$ K in the region of the 148 cm^{-1} phonon for (a) $YBa_2Cu_3O_{7-x}$ and (b) $YBa_2{}^{65}Cu_{7-x}$.

breathing mode. On this basis, the phonon at 116 cm^{-1} has been attributed[10] to Cu(2) vibrations along Z and the much narrower mode[7,10] at 150 cm^{-1} which exhibited a weak coupling, to Ba(Z) vibrations.[10] The phonon at 150 cm^{-1} does not show an oxygen isotope shift.[1,2] It has been implicated with Ba vibrations along Z.[7,8,10] Studies based on infrared and Raman measurements coupled with lattice-dynamic calculations attribute this phonon to Cu(2) vibrations along Z.[6,7] Thus, there exists a conflict regarding the assignment of the low-frequency phonon modes. In any attempt at narrowing down existing theories of the superconductivity mechanism in high-T_c oxides, it is crucial to determine if the phonon at 150 cm^{-1} is indeed a Cu(2) breathing mode, since if this were true, then the weak coupling of this mode to gap excitations would be a puzzle. To resolve this issue, we have performed high-precision Cu isotope Raman measurements in the low-energy phonon region.

The phonon reported[10] at 116 cm^{-1} (at low temperature) occurs at lower energies in our measurements since it is performed at room temperature. In Fig. 1 this phonon, which appears at 112.5 cm^{-1} in $YBa_2Cu_3O_{7-x}$, shows no systematic down shift in $YBa_2{}^{65}Cu_3O_{7-x}$, whereas Fig. 2 shows the phonon at 146.8 cm^{-1} in $YBa_2{}^{65}Cu_3O_{7-x}$ to be systematically down shifted from the one at 148.6 in $YBa_2Cu_3O_{7-x}$. The theoretically calculated down shift is 1.65 cm^{-1}; the discrepancy between experimental and theoretical values is within our experimental uncertainty. This new evidence, together with its vibrational symmetry,[7-9] relates the phonon at 146.8 cm^{-1} to the Cu(2) vibration in the Z direction. It also shows that the phonon at 112.5 cm^{-1} does not involve Cu vibrations. Figure 1 indicates a weak shoulder on the low-energy side of the phonon at 112.5 cm^{-1}. This could be caused by the ir-active mode predicted[9] at 109 cm^{-1}, which could become Raman active owing to the presence of defects.

To conclude, we have performed a Cu isotope Raman investigation on $YBa_2Cu_3O_{7-x}$. A precise comparison of the Raman lines in the low-energy spectrum of the natural and heavy isotope superconductor indicates an isotope shift for the mode at 148.6 cm^{-1} but none for the mode at 112.5 cm^{-1}. This conclusively identifies the phonon at 148.6 cm^{-1} with the Cu(2) breathing mode and suggests that the vibrational mode at 112.5 cm^{-1} does not involve Cu. From these results and measurements[10] on Raman scattering from superconducting gap excitation, we infer that the modulation of the Cu($d_{x^2-y^2}$)–O(p) orbital overlap by Cu(2) breathing mode vibrations, manifests no evidence of strong electron-phonon coupling.

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