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Raman study of the copper isotope effect in $YBa_2Cu_3O_{7-\delta}$

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Raman spectra of isotopically pure $YBa_2{}^{63}Cu_3O_{7-\delta}$ and $YBa_2{}^{65}Cu_3O_{7-\delta}$ were taken at room temperature and at 20 K. We find that at room temperature the phonon line at 151 cm^{-1} shows a shift in frequency of 2.0 ± 0.3 cm^{-1} with Cu isotopic substitution, while the phonon at 116 cm^{-1} does not shift within the experimental accuracy (0.05 ± 0.3 cm^{-1}). Similar values are also obtained at 20 K. This proves that the phonon line at 151 cm^{-1} has predominantly Cu character and that the coupling between the Ba and Cu sublattice vibrations is very weak. Fits to the experimental data with a coupled two-mode model yield a value for the Ba admixture of the 151 cm^{-1} phonon of less than 20% and only a weak renormalization of the bare Ba and Cu phonon frequencies.

I. INTRODUCTION

With the microscopic origin of superconductivity in the high-T_c copper oxides still unknown, isotopic substitution studies play an important role in the determination of the influence of lattice vibrations on the superconducting and normal-state properties of these materials. In the case of oxygen substitution, a change of the critical temperature T_c with isotopic substitution can be observed and has been reported by many groups.[1,2] Raman spectra have been used to identify oxygen related phonons by their isotope shifts.[3–5] These shifts are quite large because of the high frequencies of the oxygen phonons and the large relative mass difference between ^{16}O and ^{18}O. For example, the 500 cm^{-1} A_g phonon in $YBa_2Cu_3O_{7-\delta}$ is observed to shift by almost 30 cm^{-1} upon $^{16}O/^{18}O$ substitution.[4]

There are only a few reports on isotopic replacement studies for elements other than oxygen. In fully oxygenated $YBa_2Cu_3O_{7-\delta}$ neither Cu nor Ba replacements result in an observable change of T_c,[3,6–9] although recent results indicate that this is different in oxygen-reduced samples.[10] In Raman experiments on a natural $YBa_2Cu_3O_{7-\delta}$ (69% ^{63}Cu, 31% ^{65}Cu) and a heavy isotope $YBa_2{}^{65}Cu_3O_{7-\delta}$ superconductor, Mascarenhas *et al.*[9] showed that only the 150 cm^{-1} phonon shifted with Cu substitution, whereas the nearby 115 cm^{-1} phonon remained unchanged within the experimental accuracy, and thus concluded that the 150 cm^{-1} phonon is a pure copper vibration. They did not attempt to give an estimate of the maximum Ba admixture still possible within their experimental accuracy. This result is in contrast to linear muffin-tin orbital LMTO calculations of Rodriguez *et al.*,[11] which predict a strong mixing of the Ba and Cu vibrational modes. From this theory an isotopic shift of both phonon lines with $^{63}Cu/^{65}Cu$ substitution is therefore expected. In order to determine an upper limit for the strength of the coupling between the Ba and Cu vibrations we performed Raman measurements on isotopically pure samples of $YBa_2{}^{63}Cu_3O_{7-\delta}$ and $YBa_2{}^{65}Cu_3O_{7-\delta}$.

II. THEORY

Two vibrational modes in a solid can be coupled and renormalized by mutual interaction, provided they have the same symmetry properties and approximately the same energy. This is the case for the two A_g lattice vibrations of the Ba and the Cu sublattice in $YBa_2Cu_3O_{7-\delta}$. In a simple harmonic model, the equations of motion for two coupled oscillations are

$$m_1\ddot{x}_1(t) = -k_1x_1(t) - k_{12}x_2(t),$$
$$m_2\ddot{x}_2(t) = -k_{12}x_1(t) - k_2x_2(t),$$

where m_j, x_j, and k_j ($j = 1,\ldots,2$) denote mass, amplitude, and force constant of the vibration and k_{12} the force constant of the coupling. Using the standard ansatz $x_j(t) = x_je^{i\omega t}$ one is immediately led to a 2×2 eigenvalue problem $K\vec{x} = \lambda\vec{x}$:

$$\begin{pmatrix} \frac{k_1}{m_1} & \frac{k_{12}}{m_1} \\ \frac{k_{12}}{m_2} & \frac{k_2}{m_2} \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \omega^2 \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \tag{2.1}$$

yielding the renormalized frequencies

$$\omega_{1/2} = \sqrt{\frac{1}{2}\left(\Omega_1^2 + \Omega_2^2\right) \pm \frac{1}{2}\sqrt{\left(\Omega_1^2 - \Omega_2^2\right)^2 + \frac{4k_{12}^2}{m_1m_2}}}, \tag{2.2}$$

where $\Omega_1 = \sqrt{k_1/m_1}$ and $\Omega_2 = \sqrt{k_2/m_2}$ are the unrenormalized frequencies of the two vibrations. For a discussion of the eigenvectors it is convenient to transform Eq. (2.1) into $M^{1/2}KM^{-1/2}M^{1/2}\vec{x} = \lambda M^{1/2}\vec{x}$ where

$$M^{1/2} = \begin{pmatrix} \sqrt{m_1} & \\ & \sqrt{m_2} \end{pmatrix}. \tag{2.3}$$

The resulting eigenvalue equation

$$\begin{pmatrix} \frac{k_1}{m_1} & \frac{k_{12}}{\sqrt{m_1m_2}} \\ \frac{k_{12}}{\sqrt{m_1m_2}} & \frac{k_2}{m_2} \end{pmatrix} \begin{pmatrix} \sqrt{m_1}x_1 \\ \sqrt{m_2}x_2 \end{pmatrix} = \omega^2 \begin{pmatrix} \sqrt{m_1}x_1 \\ \sqrt{m_2}x_2 \end{pmatrix} \tag{2.4}$$

has the advantage that it yields orthogonal eigenvectors for the two renormalized states. Subsequent results will

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be given in terms of these new eigenvectors.

The experimental determination of the coupling constants is as follows: Replacing m_1 by a different isotope results in slightly different renormalized frequencies ω_1' and ω_2' for the Cu and Ba vibrations. For zero coupling, ω_2 will be unchanged, while ω_1 will exhibit the "full isotopic shift," according to $\omega_1/\omega_1' = \sqrt{m_1'/m_1}$. For nonzero coupling, however, both phonons will be shifted partially. Thus measuring the renormalized frequencies in a $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ and a $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$ sample, respectively, leads one to a set of four experimental values sufficient to solve for the three unknown theoretical parameters k_1, k_2, and k_{12}. This problem, in principle being overdetermined, is most conveniently solved by a least-squares fit of the theoretically expected to the experimentally determined frequencies.

III. EXPERIMENT

In a first step isotopically pure elemental $^{63}\mathrm{Cu}$ (99.98% purity) and $^{65}\mathrm{Cu}$ (99.96% purity)[12] were oxidized to CuO. Ceramic pellets of $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ and $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$ were then produced using standard solid-state techniques.[13,14] Both samples exhibit fairly broad superconducting transitions with an onset at 88 K and a width (10–90 %) of 3 K, as determined by superconducting quantum interference device (SQUID) measurements. No isotopic shift of T_c was detected. The superconducting volume fractions are 0.16 and 0.25 for $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ and $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$, respectively. Raman spectra at room temperature and at 20 K were recorded using a DILOR *XY* spectrometer equipped with a liquid nitrogen cooled charge-coupled device (CCD) detector. Slits were set for a spectral width of 1.6 $\mathrm{cm^{-1}}$ half width at half maximum (HWHM) as determined by measuring the laser line. The samples were measured in a near-backscattering configuration using 5 mW from the 514.5 nm line of an $\mathrm{Ar^+}$ ion laser. For absolute wavelength calibration and to correct for small drifts of the spectrometer during the experiment, we used a weakly visible laser plasma line at 77 $\mathrm{cm^{-1}}$. We estimate that the absolute error in the position of the measured peaks is less than 1 $\mathrm{cm^{-1}}$. Deviations in Raman shifts between any two spectra are less than 0.1 $\mathrm{cm^{-1}}$. Since at 514.5 nm the spatial distance between two pixels on the CCD allows us to take only one data point every 1.5 $\mathrm{cm^{-1}}$, we always recorded three spectra with slightly shifted spectrometer positions. The combination of these three measurements results in a spectrum with effectively one data point every 0.5 $\mathrm{cm^{-1}}$, from which phonon peak positions could be more accurately fitted.

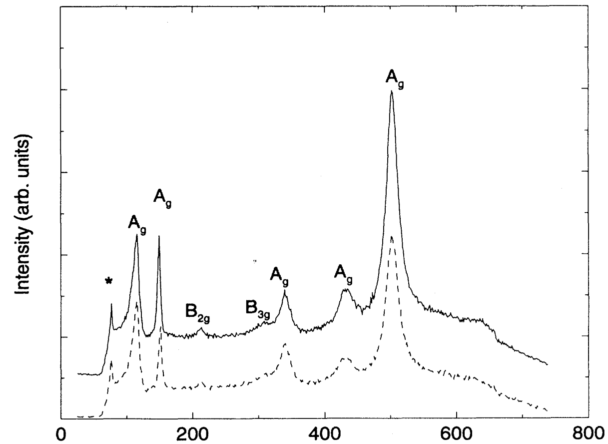

FIG. 1. Raman spectra of $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ (dashed line) and $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$ (solid line) at room temperature. The upper spectrum is lifted for clarification.

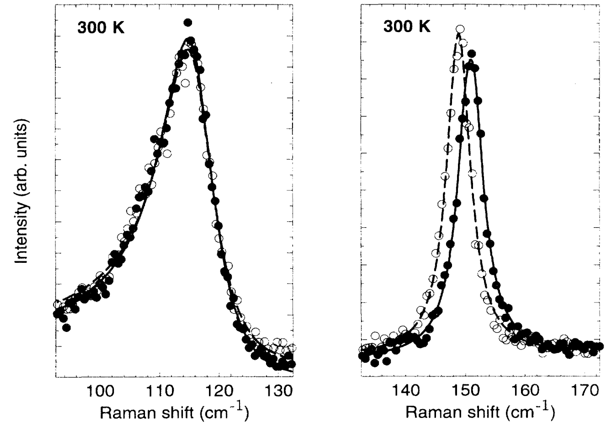

FIG. 2. Ba- and Cu-like A_g phonons of $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ (closed circles) and $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$ (open circles) at room temperature. The solid and dashed lines represent fitted Fano and Lorentzian profiles using Eqs. (3.2) and (3.1).

Figure 1 shows room-temperature Raman spectra of $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ and $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$. Five A_g phonons (115, 150, 340, 430, and 500 $\mathrm{cm^{-1}}$), a B_{2g} (210 $\mathrm{cm^{-1}}$), and a B_{3g} (310 $\mathrm{cm^{-1}}$) phonon[15,16] are clearly visible in both samples, in addition to an $\mathrm{Ar^+}$ laser plasma line at 77 $\mathrm{cm^{-1}}$ and some weak features above 500 $\mathrm{cm^{-1}}$, indicating the presence of small amounts of the impurity phase $\mathrm{BaCuO_2}$.[17,18] From the position of the three oxygen related A_g phonons at 340, 430, and 500 $\mathrm{cm^{-1}}$ we conclude that both materials are fully oxygenated,[19] with $\delta = 0 \pm 0.05$. These phonons are not expected to shift with $^{63}\mathrm{Cu}/^{65}\mathrm{Cu}$ substitution, and indeed no such

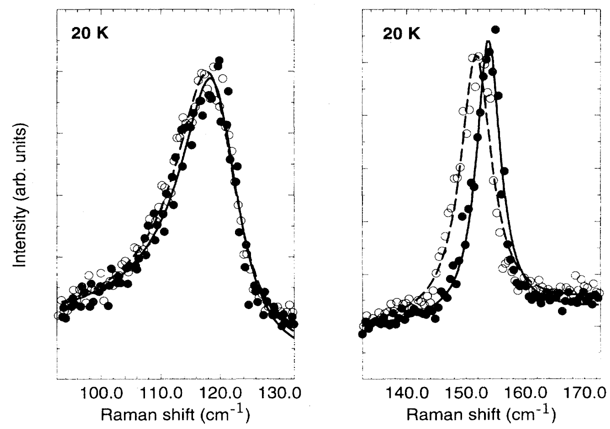

FIG. 3. Phonons of $\mathrm{YBa_2{}^{63}Cu_3O_{7-\delta}}$ (closed circles) and $\mathrm{YBa_2{}^{65}Cu_3O_{7-\delta}}$ (open circles) at 20 K. The solid and dashed lines represent fitted Fano and Lorentzian profiles using Eqs. (3.2) and (3.1).

TABLE I. Phonon parameters of $YBa_2{}^{63}Cu_3O_{7-\delta}$ (^{63}Cu) and $YBa_2{}^{65}Cu_3O_{7-\delta}$ (^{65}Cu) as determined by Fano (lower-frequency phonon) and Lorentzian (upper-frequency phonon) line fits to the experimental spectra. ω_0: center frequency, Γ: width (HWHM), q: asymmetry parameter (Fano fit only). Experimental uncertainties are given in parentheses. The values of Γ include the spectral slit width of 1.6 cm^{-1} (HWHM).

	Lower-frequency phonon			Higher-frequency phonon	
	ω_0 (cm^{-1})	Γ (cm^{-1})	q	ω_0 (cm^{-1})	Γ (cm^{-1})
^{63}Cu, 300 K	116.05(0.15)	4.34(0.2)	−5.47(0.3)	150.91(0.15)	2.50(0.1)
^{65}Cu, 300 K	116.00(0.15)	4.42(0.2)	−5.45(0.3)	148.90(0.15)	2.38(0.1)
^{63}Cu, 20 K	119.60(0.30)	4.72(0.2)	−5.93(0.6)	153.81(0.20)	2.44(0.15)
^{65}Cu, 20 K	118.99(0.30)	5.35(0.4)	−6.24(0.6)	151.72(0.20)	3.17(0.15)

shift is found within the experimental accuracy.

In Fig. 2 the two spectral regions around 115 and 150 cm^{-1} are displayed on an enlarged scale. Closed symbols correspond to data taken on $YBa_2{}^{63}Cu_3O_{7-\delta}$ and open symbols to data taken on $YBa_2{}^{65}Cu_3O_{7-\delta}$. It is evident that the 151 cm^{-1} phonon experiences a frequency shift with $^{63}Cu/^{65}Cu$ substitution, whereas the phonon at 116 cm^{-1} does not change its position. Least-square fits of the data to Lorentzian profiles for the upper-frequency phonon,

$$L(\omega) = \frac{S}{(\omega - \omega_0)^2 + \Gamma^2} + m_0\omega + b_0, \tag{3.1}$$

and Fano profiles[20] for the lower-frequency phonon,

$$F(\omega) = \frac{S}{q^2\Gamma^2} \frac{[q\Gamma + (\omega - \omega_0)]^2}{(\omega - \omega_0)^2 + \Gamma^2} + b_0, \tag{3.2}$$

as shown by the solid and dashed lines in Fig. 2, yield an isotopic shift of 1.99 ± 0.30 cm^{-1} for the 151 cm^{-1} mode, and 0.05 ± 0.30 cm^{-1} for the 116 cm^{-1} line. Note that Γ represents the HWHM of the Lorentzian line shape from Eq. (3.1), which is also obtained from Eq. (3.2) in the limit $|q| \to \infty$. Figure 3 shows the same spectral regions measured at 20 K. Again it can be seen that the higher-frequency phonon experiences a considerable isotope shift (2.09 ± 0.40 cm^{-1}), while the change of the lower-frequency phonon is close to the detection limit (0.61 ± 0.60 cm^{-1}). It should be noted that the accuracy of the low-temperature data is not as good, due to a reduced laser power to prevent sample heating. The results of the fits at room temperature and at 20 K are summarized in Table I.

The parameters k_1, k_2, and k_{12} were determined by simultaneous least-squares fits of the theoretically predicted isotopic shifts for both phonons using Eq. (2.2). With these force constants other quantities like the unrenormalized phonon frequencies and the Ba/Cu content of the renormalized phonons can be calculated. Table II contains a summary of the fitted values for k_1, k_2, and k_{12} at 300 and 20 K as well as the phonon frequencies calculated using Eq. (2.2). Finally, in Table III the bare and the renormalized frequencies are listed as well as the calculated eigenvectors for $YBa_2{}^{63}Cu_3O_{7-\delta}$ at both room temperature and 20 K.

IV. DISCUSSION

Any coupling between the Ba and Cu sublattice vibrations in $YBa_2Cu_3O_{7-\delta}$ will lead to a partial isotope shift of both observed phonon frequencies. The fact that the "Ba" phonon hardly shifts while the "Cu" phonon exhibits essentially the full expected isotopic shift of 2.35 cm^{-1} immediately implies that the coupling between the two vibrations is quite weak and that the renormalized phonons have almost pure "Ba" (116 cm^{-1}) and "Cu" (151 cm^{-1}) character. From Table III we conclude that the Ba admixture to the 151 cm^{-1} vibration is on the order of 10%. To obtain an estimate for the possible error of the determined values of k_1, k_2 and k_{12} several least-squares fits were performed with the value of k_{12} fixed. At room temperature, fits to the data within the experimental accuracy could only be achieved for $k_{12} \leq 19.6$ N/m. This leads to an upper limit for the Ba admixture of the 151 cm^{-1} phonon of 18.0%. At 20 K, the fits could be achieved for $k_{12} < 22.7$ N/m, yielding a slightly higher upper limit (27.1%) for a possible Ba admixture of the higher-frequency phonon. Thus, the coupling is considerably weaker than predicted by Rodriguez *et al.*[11] They find a value for the Ba content of the 151 cm^{-1} phonon of ≈ 55%, which is definitely excluded by our experiment.

TABLE II. Fitted force constants and theoretically calculated phonon frequencies for $YBa_2{}^{63}Cu_3O_{7-\delta}$ and $YBa_2{}^{65}Cu_3O_{7-\delta}$ as obtained from a least-squares fit of Eq. (2.2) to the experimentally determined frequencies.

Temperature	Force constants (N/m)			Phonon frequencies (cm^{-1})	
	k_1	k_2	k_{12}		
^{63}Cu, 300 K	81.5(−3.1/+2.8)	116.3(+6.6/−6.1)	14.9(+4.7/−8.8)	116.12 ± 0.08	150.96 ∓ 0.10
^{65}Cu, 300 K				115.94 ∓ 0.09	148.85 ± 0.11
^{63}Cu, 20 K	81.2(−2.8/+3.0)	130.2(+6.1/−6.5)	20.2(+2.5/−4.2)	119.48 ± 0.08	153.72 ∓ 0.10
^{65}Cu, 20 K				119.11 ∓ 0.09	151.81 ± 0.11

TABLE III. Bare and renormalized frequencies, eigenvectors, and Ba content of the $YBa_2{}^{63}Cu_3O_{7-\delta}$ phonon at room temperature and at 20 K.

Temperature	Bare freq. (cm^{-1})	Renorm. freq. (cm^{-1})	Eigenvector	Ba content
300 K	148.0(−2.8/ + 2.1)	151.0 ∓ 0.1	$\begin{pmatrix} 0.952(-0.047/+0.041) \\ 0.306(+0.119/-0.187) \end{pmatrix}$	0.09 ± 0.09
	119.8(+3.4/ − 3.2)	116.1 ± 0.1	$\begin{pmatrix} -0.306(+0.119/-0.187) \\ 0.952(-0.047/+0.041) \end{pmatrix}$	0.91 ∓ 0.09
20 K	147.8(−2.6/ + 2.7)	153.7 ∓ 0.1	$\begin{pmatrix} 0.899(-0.046/+0.046) \\ 0.437(+0.084/-0.109) \end{pmatrix}$	0.19 ± 0.08
	126.7(+2.0/ − 3.1)	119.5 ± 0.1	$\begin{pmatrix} -0.437(+0.084/-0.109) \\ 0.899(-0.046/+0.046) \end{pmatrix}$	0.81 ∓ 0.08

V. CONCLUSION

We performed Raman-scattering experiments on isotopically pure $YBa_2{}^{63}Cu_3O_{7-\delta}$ and $YBa_2{}^{65}Cu_3O_{7-\delta}$ ceramics at room temperature and 20 K. From the observed isotopic shifts of the two Raman-active A_g phonons at 116 cm^{-1} and 151 cm^{-1} we determine room-temperature values of $k_1 = 81.5$, $k_2 = 116.3$, and $k_{12} = 14.9$ N/m for the force constants of these coupled vibrations. The Ba admixture of the 151 cm^{-1} vibration is limited to less than 27% at both temperatures, a value that can serve as a test for future theoretical calculations of the phonon frequencies of $YBa_2Cu_3O_{7-\delta}$.

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