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Effects of Ca substitution on the phonon anomalies in the Raman scattering of $YBa_2Cu_4O_8$

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Abstract. We report on the temperature dependence of the frequencies and linewidths in the phonon Raman scattering for $Y_{1-y}Ca_yBa_2Cu_4O_8$ system ($y = 0-0.15$). The phonon anomalies above T_c of the frequencies are observed for the out-of-phase O(2)-O(3) A_g ($\sim$ 340 cm^{-1}) and O(4) A_g ($\sim$ 500 cm^{-1}) modes, and these onset temperatures decrease with increasing Ca content. These features are consistent with the spin-gap behaviors associated with Ca doping reported previously. Furthermore, we find that the smaller gap exists near or just above the Ba phonon frequency at $\sim$ 100 cm^{-1} in the undoped samples and its energy increases with Ca doping.

PACS. 74.25.Gz Optical properties – 74.62.Dh Effects of crystal defects, doping and substitution – 74.72.Bk Y-based cuprates

1 Introduction

The anomalous temperature-dependent behaviors of the Raman active phonons below and above T_c in high-T_c superconductors have attracted much attention [1,2]. The anomalies below T_c are interpreted in terms of the superconductivity-induced phonon self-energy effect which provide us information about the superconducting gap [3–5]. Generally, when the temperature decreases below T_c, the superconducting gap opening affects the frequencies and linewidths of the phonons whose frequencies are close to the gap frequency. The phonons which couple to the electronic system are to soften and sharpen if they are situated below the superconducting gap 2Δ, while the phonons above 2Δ should harden and broaden. On the other hand, the anomalies above T_c are considered to be due to a coupling between the phonon and the magnetic excitations by a spin gap. Because, the onset temperatures of the above-phonon anomalies are similar to the temperature at which several experiments have indicated an opening of the spin gap.

The unique temperature-dependent behaviors of the NMR [6–9], resistivity [10], infrared conductivity [11], electric thermopower [12] and heat capacity [13] in the Y systems above T_c have been interpreted in terms of the opening of the spin-gap in the spin charge spectrum. The spin-gap is strongly correlated with hole concentration [14] and decreases to zero in the overdoped side near the hole concentration of $n = 0.19$. In the Y1:2:4 system, the carrier(hole) concentration can be varied by substituting Ca^{2+} for Y^{3+}. Element-substitution studies are made without complications from oxygen deficiency effects in the Y1:2:4 system which has a fixed oxygen stoichiometry. NMR measurements [9] suggest that the spin gap temperature decreases with increasing Ca content in Y1:2:4.

In the Y1:2:4 and underdoped Y1:2:3 systems, the anomalies in the temperature behavior of the phonons have been observed well above T_c, whose onset temperature corresponds closely to the spin-gap opening one [15–18]. Recently, Mori *et al.* [19] observed a phonon softening above T_c in experiments carried out on the Ca doped Y1:2:4. However, the correlation between phonon anomalies temperature above T_c and hole concentration is not clear.

In this paper, we report on the temperature dependence of the frequencies and linewidths in the phonon Raman scattering for $Y_{1-y}Ca_yBa_2Cu_4O_8$ system ($y = 0-0.15$). The phonon anomalies above T_c of the frequencies were observed for the out-of-phase O(2)-O(3) A_g ($\sim$ 340 cm^{-1}) and O(4) A_g ($\sim$ 500 cm^{-1}) modes. The onset temperature of the phonon anomalies above T_c decreases with increasing Ca content. This is consistent with the NMR measurements [9] in which the spin gap temperature decreases with increasing Ca content. We also found that a smaller gap existing near or just above the Ba phonon frequency ($\sim$ 100 cm^{-1}) in the undoped samples increases with Ca doping.

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2 Experimental details

Samples of $Y_{1-y}Ca_yBa_2Cu_4O_8$ with $y = 0$ to 0.15 were prepared by the conventional solid-state reaction method and a high-oxygen-pressure technique using a hot isostatic pressing apparatus in a mixed gas environment Ar + 20%O_2 (O_2-HIP). Y_2O_3, CaO, $BaCO_3$ and CuO powders were mixed to nominal compositions of $Y_{1-y}Ca_yBa_2Cu_4O_8$. Powder mixtures were calcined at 860 ℃ for 12 h in air and then repeatedly sintered at 880–920 ℃ for 12 h several times with intermediate grindings. Sintered ceramics were finally treated by O_2-HIP at 1 000–1 100 ℃ for 40 h under an oxygen partial pressure of 20 MPa.

For characterization of superconducting properties, the DC magnetic susceptibility was monitored by a SQUID magnetometer under the "field cooling" condition at an external field of 10 Oe.

Raman spectra were measured at various temperatures in the backscattering configuration. The 514.5-nm line of an Ar-ion laser was used for excitation. The incident laser beam from the Ar laser was focused on the sample surfaces with a diameter of about 8 μm and the power density was kept around 150 W/cm^2 to avoid heating effects. The temperatures were verified by using Stokes to anti-Stokes ratios of the spectral densities. The scattered light was detected with a Jasco NR-1800 triple monochromator and a CCD (charge-coupled-device) detector. The samples were mounted on the cold finger of a liquid-He cryostat and the temperature was measured with a thermocouple placed near the sample.

3 Results and discussion

3.1 Magnetization

Field-cooled magnetization (Meissner) data below and near T_c for samples with y between 0 to 0.15 are shown in Figure 1. All samples show a typical superconducting transition with a relatively narrow transition width. T_c increases monotonically as the Ca doping level is increased. The inset of Figure 1 shows the T_c plotted as a function of Ca concentration y in $Y_{1-y}Ca_yBa_2Cu_4O_8$. The plotted values of T_c were determined by magnetic susceptibility.

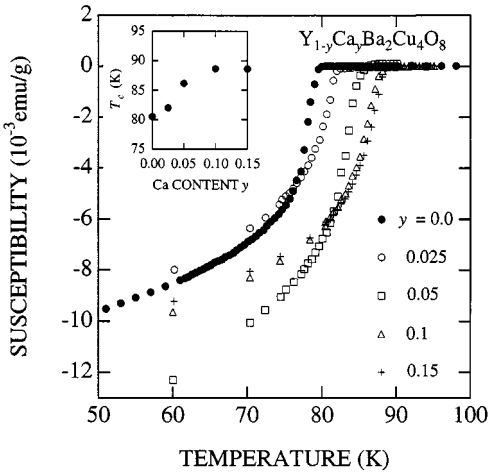

Fig. 1. The temperature dependence of the field-cooled magnetization (Meissner) data of $Y_{1-y}Ca_yBa_2Cu_4O_8$ samples with y from 0 to 0.15 in a magnetic field of 10 Oe. Inset: Superconducting transition temperature T_c plotted as a function of Ca concentration y in $Y_{1-y}Ca_yBa_2Cu_4O_8$. The plotted values of T_c are determined by magnetic susceptibility.

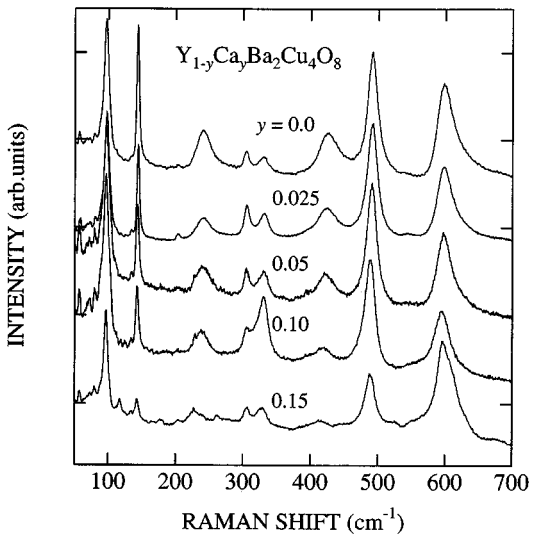

Fig. 2. Room temperature Raman spectra for $Y_{1-y}Ca_y$ $Ba_2Cu_4O_8$.

3.2 Raman spectra

In Figure 2 Raman spectra at room temperature for $Y_{1-y}Ca_yBa_2Cu_4O_8$ are shown. Nine main peaks are observed in all of the spectra. For the pure $YBa_2Cu_4O_8$ with $y = 0$, these peaks have been previously assigned to the vibration modes of Ba A_g ($\sim$ 100 cm^{-1}), Cu(2) A_g ($\sim$ 150 cm^{-1}), O(1) B_{2g} ($\sim$ 210 cm^{-1}), Cu(1) A_g ($\sim$ 250 cm^{-1}), Cu(1) B_{3g} ($\sim$ 310 cm^{-1}), out-of-phase O(2)-O(3) A_g ($\sim$ 340 cm^{-1}) (B_{1g} in tetragonal notation), in-phase O(2)-O(3) A_g ($\sim$ 430 cm^{-1}), O(4) A_g ($\sim$ 500 cm^{-1}) and O(1) A_g ($\sim$ 600 cm^{-1}) [20]. There are no peaks from impurity phases such as CuO, $BaCuO_2$ and CaO. Raman spectra for doped samples which resemble undoped ones suggest that Ca doping hardly affect the lattice dynamics. There are no signs of peaks from impurity phases or phonon scattering induced by structural disorder for $y \leq 0.01$. For increasing Ca substitution, although spectrum variation is rather small, we can find variations in the frequency shift and the linewidth of the Raman peaks.

As Ca content increases from 0 to 0.1, $\sim$ 250 and $\sim$ 450 cm^{-1} phonon frequencies decrease by 5 and 6 cm^{-1}, respectively. However the frequencies of other modes appear to be almost constant with increasing y. The absence of any shift in Ba mode with Ca doping also indicates that Ca atoms preferentially occupy Y sites.

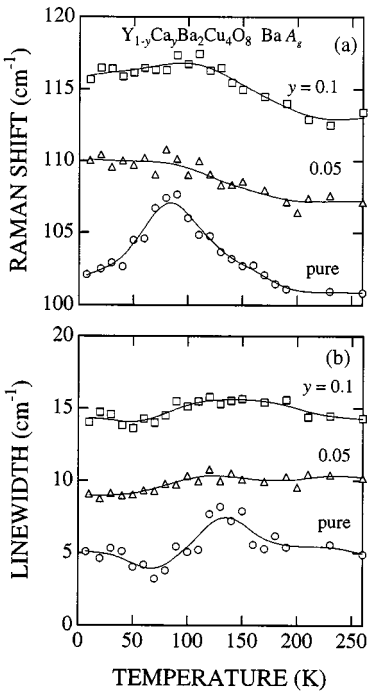

Fig. 3. Temperature dependence of the (a) frequency and (b) linewidth of the Ba mode for $Y_{1-y}Ca_yBa_2Cu_4O_8$. The curves are offsets by (a) 12, 6, 0 cm^{-1} and (b) 10, 5, 0 cm^{-1} from top to bottom. The solid lines are guides to the eye.

The linewidth of the O(4) phonon (~ 600 cm^{-1}) for the $y = 0.15$ sample is approximately 20% larger than that for the other four samples. Furthermore we find that several new peaks appear below ~ 300 cm^{-1}. These results also indicate that Ca can be doped onto Y site with a solubility limit approaching 10% in Y1:2:4.

3.3 Phonon anomalies below T_c

The temperature dependencies of the (a) frequencies and (b) linewidths of the Ba vibrational mode in $Y_{1-y}Ca_y$ $Ba_2Cu_4O_8$ are summarized in Figure 3. Values for the frequencies and linewidths of the Ba mode were obtained by fitting the corresponding Ba mode feature to a Fano profile [1] with a linear background.

Above T_c this mode displays the normal slight shift to higher frequencies. Below T_c, however, this mode displays an abrupt mode softening for all samples. The largest shift is observed in pure Y1:2:4 sample in which the frequency softens by approximately 5.5 cm^{-1} between T_c and 10 K. Our results show that Ca significantly suppress the magnitude of the superconductivity-induced phonon softening of the Ba vibrational mode at ~ 100 cm^{-1}.

The linewidth shows an unusual increase from room temperature down to about 130–150 K, then decreases rapidly to reach a minimum around T_c, where it starts to increase slightly again. The largest broadening is observed in pure sample. For this sample the linewidth broadens by approximately 2.5 cm^{-1} between T_c and 10 K.

Heyen *et al.* [21] observed the phonon anomalies below T_c in a Y1:2:4 single crystal and used the Zeyer-Zwicknagl (ZZ) theory [3] to interpret these anomalies. They suggested the presence of two superconducting gaps; one gap close to the Ba phonon (~ 100 cm^{-1}, *i.e.*, $2\Delta_1/kT_c \sim 2.3$) attributed to the CuO chain bands, and another one close to the out-of-phase O(2)-O(3) phonon (~ 340 cm^{-1}, *i.e.*, $2\Delta_2/kT_c \sim 6.5$) attributed to the CuO_2 plane bands. The large softening of the Ba mode may be explained by a very strong coupling to the lower gap $2\Delta_1$ with an energy only slightly higher than the Ba mode frequency. This is because the dependence of the frequency on temperature appears to be normal in the Cu(2) phonon at about 150 cm^{-1}.

It turns out that the decrease in the magnitude of softening between T_c and 10 K with increasing the dopant content is explained quite well by the ZZ model [3]. The main prediction of the ZZ theory which is based on the strong electron-phonon coupling is as follows: the phonon peaks with energies below 2Δ soften and do not change in the width, while those with energies above 2Δ harden and broaden. In addition, the most remarkable change should occur for $\omega \sim 2\Delta$. If the value of $2\Delta_1$ varies with the Ca-doping level, the temperature dependencies of frequency and linewidth for a certain phonon should be changed with doping. According to this prediction, the reduced softening upon cooling of the phonon at ~ 100 cm^{-1} for two samples with Ca content $y > 0.05$ suggests the presence of the gap at higher energies. The change in magnitude of the linewidth below T_c with increasing dopant content can also be fitted to the ZZ prediction. Note that the results on the scaling of the superconducting gap with T_c do not rule out the possibility of a *d*-wave gap in large gap of YBCO systems.

It is also noted that, as regards to the effect of the reduction of T_c on the Raman-active phonon self-energies, complemented results have been observed for Pr-substituted $YBa_2Cu_4O_8$ [22] and $YBa_2(Cu_{1-x}M_x)_4O_8$ (M = Ni and Zn) [23]. In these systems the smaller gap was observed near or just above the Ba phonon frequency at ~ 100 cm^{-1} in the undoped samples and its energy decreases with doping.

3.4 Phonon anomalies above T_c

The temperature dependencies of the frequencies of the out-of-phase O(2)-O(3) A_g (~ 340 cm^{-1}) and O(4) A_g (~ 500 cm^{-1}) are shown in Figures 4 and 5, respectively. The oxygen phonon parameters of these lines were obtained by fitting Lorentzian line shapes with linear backgrounds. In the pure sample both phonons exhibit a hardening in the range from room temperature down to $T \cong 160$ K, as may be consistent with the normal anharmonic model [24]. Below $T \cong 160$ K down to $T \cong T_c$, these phonon frequencies are almost independent of temperature. Then a small softening of ~ 2 cm^{-1} occurs below T_c. We find that the onset temperature of the phonon anomalies above T_c appears to decrease and the plateau disappears with increasing Ca content. On the other hand,

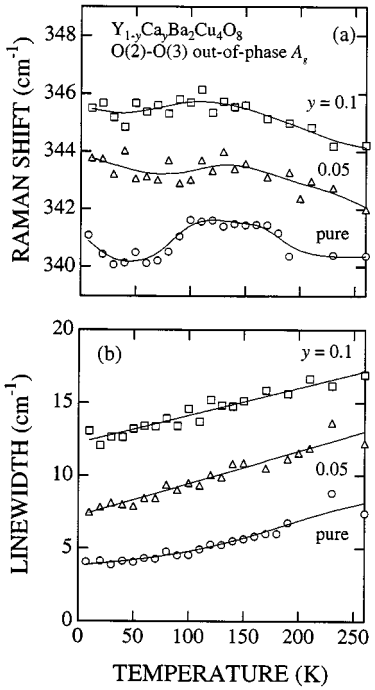

Fig. 4. Temperature dependence of the (a) frequency and (b) linewidth of the out-of-phase O(2)-O(3) mode for $Y_{1-y}Ca_y$ $Ba_2Cu_4O_8$. The curves are offsets by (a) 4, 2, 0 cm^{-1} and (b) 8, 4, 0 cm^{-1} from top to bottom. The solid lines are guides to the eye.

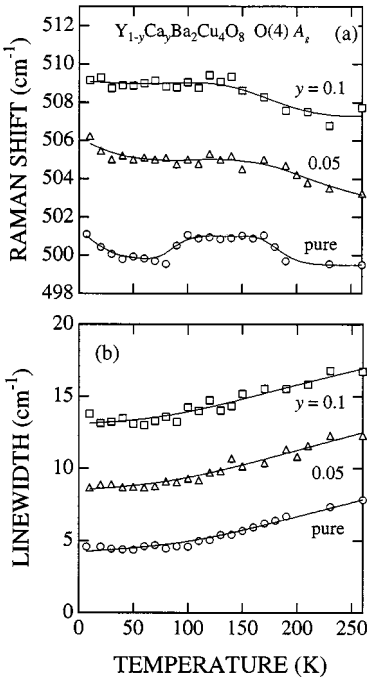

Fig. 5. Temperature dependence of the (a) frequency and (b) linewidth of the O(4) mode for $Y_{1-y}Ca_yBa_2Cu_4O_8$. The curves are offsets by (a) 8, 4, 0 cm^{-1} and (b) 8, 4, 0 cm^{-1} from top to bottom. The solid lines are guides to the eye.

the temperature dependence of the phonon linewidth appears to follow the expected behavior for the normal anharmonic model for all samples.

The anomalies that are observed well above T_c cannot be understood within the framework of superconducting-induced phonon self-energy effects [2]. The softenings of the phonon frequency above T_c have been reported so far for underdoped superconductors such as Y1:2:4 and oxygen deficient Y1:2:3 [2]. This result led a number of authors to suppose that the phonon anomalies above T_c are due to the opening of a spin-gap or pseudo-gap which is observed in NMR, neutron, photoelectron spectroscopy measurements, etc. [6–9]. Machi *et al.* [6] revealed from NMR measurements for $Y_{1-y}Ca_yBa_2Cu_4O_8$ that the spin-gap temperature T_s of about 160 K in undoped crystals becomes 140 K and 130 K by 5% and 7.5% Ca doping, respectively. Above Ca doping effect on the phonon anomaly is consistent with that on the spin-gap energy in Y1:2:4: the temperature where the softening occurs decreases with increase of Ca doping.

At present it is not clear what the microscopic mechanism could be suitable for a coupling of spin systems with certain phonons. It has been suggested that the ordinary electron-phonon coupling mechanism could lead to a spin-phonon coupling, if the part of the Fermi surface to which the phonons couple is modified by spin excitations [16]. The recent theory by Normand, Kohno and Fukuyama (NKF) within an extended $t-J$ model [25,26] suggests that the Raman active out-of-phase oscillatory motion of the planar oxygen atoms could couple to the spin system through a phonon modulation of the superexchange interaction between neighboring Cu atoms. The magnitude of the phonon shift is then dependent on the degree of buckling of the CuO_2 plane.

The theory predicts that both the frequency and linewidth change around the spin-gap temperature. However, no anomalies were observed above T_c for the linewidth of the out-of-phase O(2)-O(3) phonon. There are several factors which contribute to the width of phonon lines. The crystalline defects and impurity phases may play important roles for linewidth. The broadening of linewidth due to spin-phonon coupling suggested by NKF theory may be obscured by these crystalline imperfections, especially in polycrystalline samples used in our measurements.

Furthermore, it is not clear why the anomaly of the O(4) modes should occur, since this phonon seems not to be related with superexchange interaction in the CuO_2 plane. One possible approach is taken in the phonon hybridization. Theoretical calculations for Y1:2:3, which consider the electron-phonon coupling, suggest that the apical O(4) motion is strongly hybridized with the out-of-phase O(2)-O(3) mode [27,28]. Y1:2:4 is structurally similar to Y1:2:3 and may have the same phonon hybridization. Therefore it is possible that both the Ba and out-of-phase O(2)-O(3) mode affect spin excitations through the hybridization of the atomic vibrations.

It should be noted that Mori *et al.* [19] also observed the temperature dependence of the frequencies and linewidths in the phonon Raman scattering for the Ca doped Y1:2:4. Their results where the phonon softening

above T_c was not observed are in slightly contrast to our results. These discrepancies may be caused by the difference of sample characteristics: The recent theory such as NKF model suggests that the coupling would be highly sensitive on the microscopic structures such as the amount of buckling of the CuO_2 planes. In the present case the Raman spectrum does not change at least up to 10% Ca substitution, which indicates that the Ca substitution does not affect on the structural property. The phonon anomalies observed above T_c may be due to the opening of spin-gap as expected by NKF theory.

4 Summary

We report on the temperature dependence of the frequencies and linewidths in the phonon Raman scattering for $Y_{1-y}Ca_yBa_2CuO_8$ system ($y = 0-0.15$). The phonon anomalies above T_c of the frequencies for the out-of-phase O(2)-O(3) A_g ($\sim$ 340 cm^{-1}) and O(4) A_g ($\sim$ 500 cm^{-1}) were observed. The onset temperature of the phonon anomalies above T_c decreases with increasing Ca content. The phonon anomalies observed above T_c may be due to the opening of spin-gap. We also observed that the smaller gap $2\Delta_1$ is near or just above the Ba phonon frequency ($\sim$ 100 cm^{-1}) in undoped samples and its energy increases with Ca doping.

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