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Inelastic light scattering studies of overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin film

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The vibrational and magnetic Raman excitation spectra were examined in overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films. Below T_c, certain phonons in undoped $YBa_2Cu_3O_{7-\delta}$ (YBCO) show strong self-energy effects, which gradually vanish with increasing Ca concentration into the overdoped regime. The observed B_{1g} symmetry two-magnon excitation peak near 2900 cm^{-1} in YBCO is significantly broadened, weakened, and shifts to the lower frequency with increasing Ca content, indicating the effective value of magnetic superexchange energy decreases and that the life time of the magnons becomes shorter with increasing hole concentrations.

1 Introduction

While the Raman data in the underdoped region of the phase diagram of cuprates have been extensively studied [1], the Raman-scattering experimental results in the overdoped region are rare. In this paper, we report Raman-scattering measurements of $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films as a function of temperature and doping. The partial substitution of Y^{3+} by Ca^{2+} introduces additional hole carriers into the CuO_2 planes and allows the YBCO systems access far into the overdoped regime [2]. Our goal is to examine light scattering data on the low- and high-frequency excitation spectra and focus particularly on evidence for anomalous electron-phonon coupling and magnetic scattering in overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films.

2 Experimental

The 400 nm-thick $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ films were deposited on $SrTiO_3$ (001) substrates by using pulsed laser ablation method and in a process optimized to obtain high oxygen contents [3]. All the samples were structurally characterized by x-ray diffraction, which showed their *c*-axis orientation. The superconducting transition determined by dc resistivity measurements showed these samples with nominal Ca contents of $x = 0.0$, 0.10, 0.20, and 0.30 to be successively optimally doped (onset $T_c = 92$ K, $\Delta T_c = 2$ K), slightly overdoped ($T_c = 89$ K, $\Delta T_c = 5$ K), mediately overdoped ($T_c = 86$ K, $\Delta T_c = 6$ K), and heavily overdoped ($T_c = 75$ K, $\Delta T_c = 7$ K), respectively.

Temperature-dependent Raman spectra were performed using a cold finger cryostat and a Dilor XY 800 triple spectrometer equipped a liquid nitrogen cooled charge-coupled device array detector. The samples were excited with 1 W/cm^2 of the 514.5 nm photons from an Ar^+ ion laser. The spectral resolution with these instruments was typically less than 1 cm^{-1}.

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3 Results and discussion

The room-temperature optical reflectance spectra of all samples have been measured over a wide frequency range (40-55000 cm^{-1}), as shown in Fig. 1. The general shape of these spectra displays a metallic character. Moreover, calculations of the effective number of carriers from the optical conductivity and the fits to the reflectance indicate that the Ca doping increases the carrier concentrations in the CuO_2 plane. Interestingly, this trend becomes saturated in the high Ca-doped (x = 0.3) sample. It should be emphasized that the observed changes in the optical spectra of all samples studied are not created by the oxygen vacancies, nor is it due to the inhomogeneity of the films. These data were reproducibly observed at three different spots on the samples using a specially designed microscopy coupled with optical spectrometer for the spot (10×10 μm^2) measurements.

Figure 2 shows the room temperature low-frequency Raman spectra of x = 0.10 sample in a number of *a-b* plane scattering geometries. The five observed Raman-active phonons at ~ 117, 147, 339, 450, and 510 cm^{-1} have symmetries (point group D_{4h}) A_{1g}(Ba), A_{1g}(Cu(2)), B_{1g}(O(2)-O(3)), A_{1g} (O(2)+O(3)), and A_{1g}(O(4)), respectively. Their overall characters are in good agreement with those reported previously [4, 5]. In order to investigate the effects of Ca doping on the phonon properties in $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films, we fit the phonon peaks using three Lorentzian and two Fano profiles [8]. Additionally, the electronic background is taken to be a quadratic form. First, we notice that the 117 cm^{-1} phonon, involving the *c*-axis vibrations of the Ba atoms, becomes hardening and broadening by the Ca doping (> 20 %), suggesting the possibility of a Ca substitution on both the Y and Ba sites at high Ca concentrations [6]. Second, the 339 cm^{-1} mode involving the planar oxygen vibrations exhibits a lineshape change with increasing Ca content. This reveals the coupling parameter of the electronic continuum excitations to the 339 cm^{-1} phonon increases, making it more asymmetric. The behavior of both these modes, then, reflects not only a changing structure at a Ca content higher than 20 % but most importantly Ca doping increases the carrier concentrations in the CuO_2 planes.

Among the Raman-active phonons in YBCO, the Fano-coupled Ba and planar oxygen modes exhibit possible self-energy effects in the superconducting state. The temperature dependences of the fitting parameters (frequency ω and linewidth γ) in the x = 0.0 and 0.20 samples reveal two important changes when the superconducting gap opens: (i) the Ba mode exhibits a discontinuity of the hardening at T_c. The linewidth narrows with a cusp occurring at T_c; and (ii) the planar oxygen phonon mode exhibits a large softening and an enhancement of the linewidth below T_c. Notably, these superconductivity-induced phonon anomalies become weak with increasing Ca concentrations, suggesting the interactions of certain optical phonons with the superconducting quasiparticles are reduced in the overdoped regime.

The high-frequency part of B_{1g} Raman-scattering spectra at room temperature is shown in Fig. 3(a) as a function of Ca concentrations. The spectrum of YBCO exhibits a band peaked at ~ 2900 cm^{-1} and is assigned to scattering by two-magnon [7]. This peak maximum position shifts upon Ca doping to lower frequency, until it weaken into a very broad peak in x = 0.30 sample. Once again, it should be emphasized that the observed changes in the Raman spectra of all samples are not due to the increased defect densities. These data were reproducibly observed at three different spots on the samples using the micro-Raman setup with a spatial resolution of 1 μm.

To quantitatively study the changes of the two-magnon Raman-scattering with Ca doping, we fit the peak using Heisenberg model of antiferromagnetism [8]. The resulting fitting parameters (superexchange energy J and magnon's linewidth Γ) are shown in Fig. 3(b). With increased Ca doping, one first observes the J value shifts monotonically downward in energy. The generation of additional holes in the CuO_2 planes due to the partial replacement of Y^{3+} by Ca^{2+} are believed to form singlets with holes that would otherwise form local antiferromagnetic order [8]. This screens the effective spin moment on the doped Cu site and leads to a reduction of the spin superexchange energy in the vicinity of holes. Second, the two-magnon peak strongly broadens by the Ca doping. One can understand this by noting that the hole doping into the CuO_2 planes reduces the antiferromagnetic correlation length and the time interval during which the size of the antiferromagnetic aligned Cu spin cluster exceeds the three lattice constant limit. As a result, the two nearest-neighbor Cu spin-flip excitations lose intensity and become overdamped.

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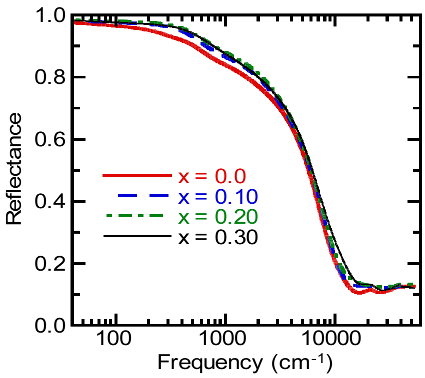

Fig. 1 The optical reflectance spectra of four samples at 300 K.

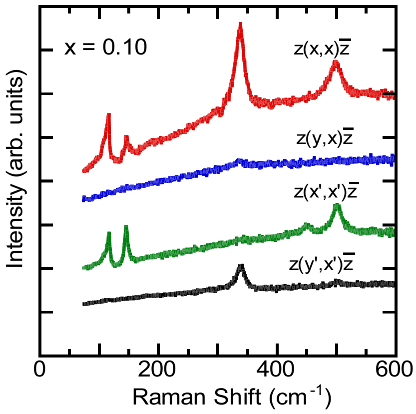

Fig. 2 Room temperature Raman-scattering spectra of x = 0.10 sample with green (514.5 nm) excitation in various scattering geometries [tetragonal representation] including:(x,x)[A_{1g}+B_{1g}], (y,x)[B_{2g}], (x',x')[A_{1g}+B_{2g}], and (y',x') [B_{1g}]. The Raman-scattering response was obtained by dividing the measured spectra by Bose-Einstein thermal factor.

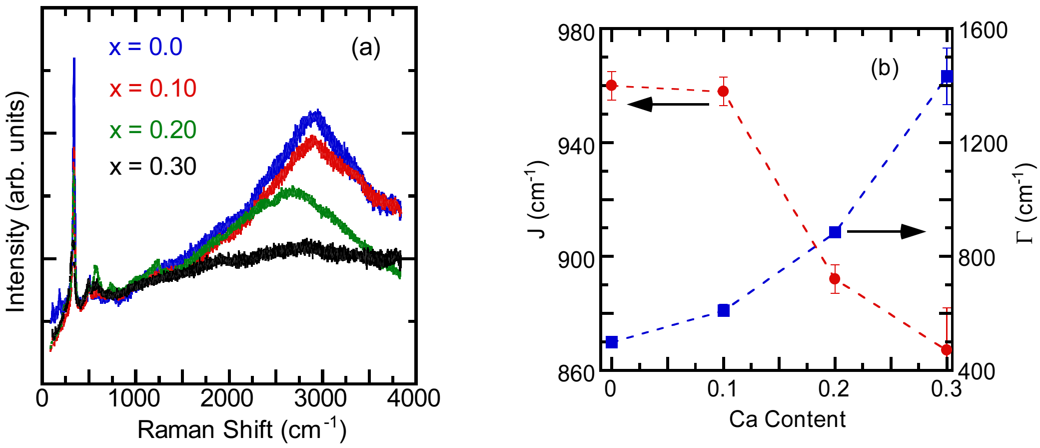

Fig. 3 (a) RT B_{1g} two-magnon Raman-scattering spectra of four samples studied with blue-green (488.0 nm) excitation. (b) The doping dependence of the superexchange energy J and linewidth Γ of the two-magnon peak.

4 Summary

In summary, we have studied the Raman-scattering response of overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films. With increased Ca concentrations, the observed superconductivity-induced phonon anomalies become weak, indicative of a reduced phonon-superconducting-gap interaction at higher doping level. The two-magnon scattering also disappears upon Ca doping, suggesting that the antiferromagnetic correlation length is less than twice the lattice parameter in the overdoped phase regime.

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