Subpicosecond time-resolved studies of coherent phonon oscillations in thin-film $YBa_2Cu_3O_{6+x}$ ($x<0.4$)

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We report the results of the first time-resolved observation of impulsively generated coherent optical phonon oscillations in the semiconducting cuprate compound $YBa_2Cu_3O_{6+x}$ ($x<0.4$). The oscillations, which were probed through time-resolved transmissivity modulation, had a period of 237 fs at room temperature, corresponding to a Raman active mode of A_{1g} symmetry at 142 cm^{-1}. No oscillations were observed in the superconducting form of Y-Ba-Cu-O either above or below T_c. The amplitude, frequency, and linewidth of this mode were measured over a temperature range from ~7 K to room temperature.

Studies of the phonon spectra of $YBa_2Cu_3O_x$ (YBCO) compounds can yield important knowledge regarding the mechanism of superconductivity in high T_c materials. Recently, it has been shown that femtosecond pump-probe experiments can be used to induce and time-resolve coherent optical phonons in semiconductors[1] and metals[2] using pulses of light that are short in duration compared to the characteristic periods of the lattice vibrations. These oscillations are generated and detected in a type of impulsive-stimulated Raman scattering (ISRS) experiment which utilizes two optical pulses. This type of time-domain technique offers advantages over frequency-domain techniques with regard to bandwidth resolution and signal-to-noise.[2] In a previous publication concerning the carrier heating dynamics in various high T_c compounds, pronounced oscillations were found in the transient transmissivity profile of a nonsuperconducting $YBa_2Cu_3O_{6+x}$ ($x<0.4$) sample.[3] These oscillations were postulated to be the result of coherent phonons. In this letter we definitively identify these oscillations as being the result of optical phonons and time resolve them over a temperature range from ~7 K to room temperature.

The pump-probe impulsive scattering experiments in this work utilized a colliding-pulse mode-locked (CPM) dye laser operating at a wavelength of 630 nm (1.98 eV). This source provided two pulse trains of ~100 fs pulses at a 100 MHz repetition rate. The pump-pulse train was used to impulsively excite the lattice, modulating the refractive index, and the resulting transmissivity change was monitored by passing the probe beam through the semitransparent thin film onto a photodiode. By varying the relative delay between the pump and probe pulse trains, the transmissivity change versus time was recorded. The pump and probe beam fluences were kept below ~10 $\mu J/cm^2$ to minimize bulk heating in the film. At the same time, it was necessary to maintain a large enough signal-to-noise ratio to clearly resolve the oscillations which produced fractional transmissivity changes ($\Delta T/T$) as small as 10^{-5}. This was accomplished by using a mixing technique which allowed modulation of the CPM laser in the radio frequency range where the noise is low while still utilizing the superior noise characteristics of an audio frequency lock-in amplifier.[4] A continuous flow cryostat with optical access allowed temperature-dependent measurements to be made.

The Y-Ba-Cu-O thin films used for this study were deposited on a MgO substrate using a standard laser-ablation technique. The epitaxial thin films were *c*-axis oriented and showed onsets to diamagnetism via ac susceptibility measurements below 87 K. The sharp transitions showed only weak field dependence. The films were rendered nonsuperconducting as determined by ac susceptibility measurements by heating them at 420 °C in flowing argon for 80 min.

Shown in Fig. 1 is the normalized transmissivity change for a nonsuperconducting YBCO film (~0.22 μm thick) at several sample temperatures. The initial rapid transient and subsequent decay is governed by the heating dynamics as discussed in Ref. 3. The focus of this report is the pronounced oscillations on the tails of the waveforms which start soon after the maximum transmissivity change is reached. These oscillations dampen with time as well as with increasing temperature. From the inset to Fig. 1 (sample temperature ~7 K) a period of ~232 fs can be obtained as well as a dephasing time (i.e., the time it takes for the amplitude of the oscillations to decay to $1/e$ of their original value) of roughly 2 ps. The oscillations were also seen in data obtained in a transient reflectivity mode, albeit weaker. We believe these oscillations are the result of the impulsive stimulation of coherent optical phonons in the material. These oscillations were not observed in the orthorhombic, superconducting material either above T_c (possibly due to an increase in scattering of the phonons with the much larger carrier concentrations) or below T_c (due to the observed dramatic increased in carrier relaxation time).[3]

To ensure that the observed phenomenon is an intrinsic property of the material and not an experimental artifact such as that resulting from light interference effects or multiple reflections of sound waves, a number of experiments were carried out on two independently produced

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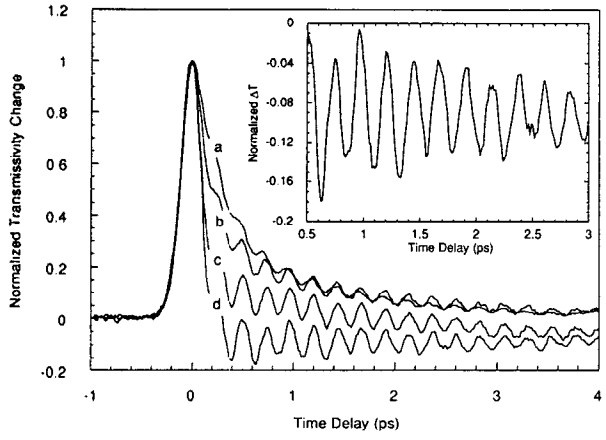

FIG. 1. Normalized transmissivity change for the nonsuperconducting YBCO sample is shown at several sample temperatures (*a*: 296 K, *b*: 152 K, *c*: 60 K, *d*: 7 K). The inset shows the oscillations (period = 232 fs) present in the tail of the data taken at a sample temperature of 7 K.

samples. The first sample was described in the preceding paragraph. The second sample was purposely produced with a thickness gradient ranging from roughly 0.05 to 0.15 μm. This film was then annealed under the same conditions as the first sample. Measurements were carried out to look for frequency changes due to variations in the film thickness. The only differences found were in the signal strength. This is to be expected since the amount of absorption and hence the modulation will change with film thickness.

To check that the oscillations correspond to a Raman active mode, the time-domain data were numerically transformed to the frequency domain by using a standard fast Fourier transform (FFT) routine. A FFT can be applied directly to the time-domain data since the modulation of the transmission intensity depends linearly on the refractive index change and hence on the phonon amplitude.[2]

An example of a spectrum shown for the lowest temperature data (sample temperature $\sim$7 K) is presented in Fig. 2. A sharp peak is seen at a wave number of $\sim$143 cm^{-1} ($\nu \sim$4.3 THz) corresponding to the oscillation period of 232 fs. Also obtained is the full width at half maximum (FWHM) linewidth $\sim$10 cm^{-1} ($\Delta\nu \sim$300 GHz), giving a $Q = (\nu/\Delta\nu)$ of 14. This frequency does correspond to a Raman active mode which has a frequency and intensity that is dependent upon the oxygen concentration.[5–7]

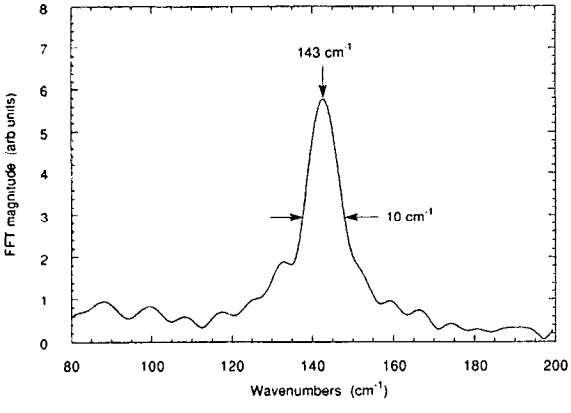

FIG. 2. Spectrum obtained from the time domain data at 7 K. Note the strong phonon peak at $\sim$143 cm^{-1} (4.3 THz) which has a FWHM linewidth of $\sim$10 cm^{-1} (300 GHz).

The orthorhombic structure of $YBa_2Cu_3O_7$ supports 15 active Raman modes, 5 of A_g symmetry, 5 of B_{2g} symmetry, and 5 of B_{3g} symmetry, (Ref. 8) all of which have been documented in twin-free single-crystal samples where the necessary orientations of the crystal were accessible.[9] Because of symmetry considerations only the five A_g modes are seen in *c*-axis oriented thin films.[10] These five modes are reported to have frequencies at approximately 114, 150, 336, 440, and 504 cm^{-1}, and they all involve atomic motion along the *c* axis. In the transition to the semiconducting tetragonal phase, a number of changes occur in the spectra, including the A_g modes becoming A_{1g} vibrations (except for the mode at 336 cm^{-1} which transforms to B_{1g} symmetry). There are also frequency and intensity changes which accompany the symmetry changes. The lowest frequency mode at 114 cm^{-1}, already the weakest, nearly disappears.[11] In contrast, the mode at 150 cm^{-1} *increases* in intensity as the oxygen content is *lowered*. This mode softens, shifting in frequency monotonically from 150 cm^{-1} in the $YBa_2Cu_3O_7$ material to $\sim$141 cm^{-1} in the $YBa_2Cu_3O_6$ material. Since this mode is believed to involve optic modes of the Cu(2) atoms moving along the *c* axis, the softening is consistent with the expansion of the unit cell along *c* upon transformation from the orthorhombic to tetragonal structure.[11]

With the above considerations, it can be seen that the only accessible phonon lines because of symmetry constraints and pulse duration limitations are the two lowest frequency modes at 114 and 150 cm^{-1}. Of these modes the one at 150 cm^{-1} is the dominant one becoming more intense as the oxygen content is lowered. It is this mode that we are then able to clearly resolve. Based on the frequency we observed (142 cm^{-1}) the oxygen content for the $YBa_2Cu_3O_{6+x}$ sample would be placed at $x \sim 0.3$ (from Ref. 6), a value that is in close agreement with the estimate based on an x-ray diffraction analysis.

To check the accuracy of the phonon line frequency as measured by ISRS, conventional Raman spectroscopy was performed on superconducting and nonsuperconducting YBCO thin films. Both films were obtained from the second sample, and the superconducting one was taken from a section of the sample which was not annealed. The results were in close agreement with those presented in Ref. 11. The same general trend is observed with respect to phonon line strength for the modes at 114 and 150 cm^{-1} with oxygen content. In the nonsuperconducting sample the mode at 114 cm^{-1} is barely resolvable while the line at 150 cm^{-1} increases in intensity and shifts to 143 cm^{-1}. This agrees to within 1% of the results obtained with ISRS.

Figure 3 shows the results of the spectral temperature dependent studies. In this figure, the peak amplitude of the phonon line is shown as a function of sample temperature.

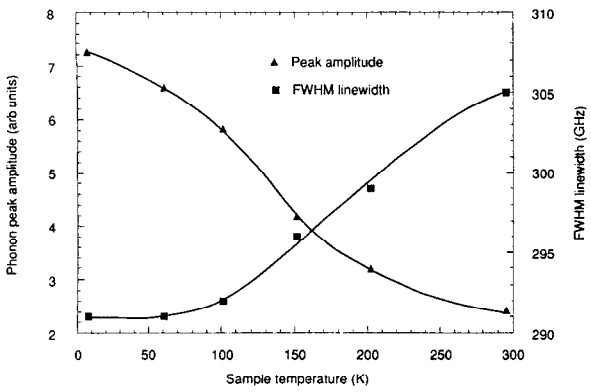

FIG. 3. Peak amplitude of the phonon line (▲) and the FWHM linewidth (■) as functions of sample temperature. The lines through the data points are meant *only* as a guide to the eye.

A near-linear decrease was seen as the sample temperature was raised indicative of thermal dephasing of the coherent process. Accompanying this amplitude decrease was a slight thermal broadening ($\sim 5\%$) of the phonon linewidth (see Fig. 3). Not shown was a small but measurable softening ($\sim 1\%$ decrease) of the frequency with increasing temperature. The softening of this line with increasing temperature has been reported in Raman experiments on thin films, although the shift was somewhat greater ($\sim 3\%$).[10]

In conclusion, we have directly time resolved through transmissivity modulation the impulsive generation of optical phonons in thin-film semiconducting YBCO. Unlike conventional Raman spectroscopy, the detection process in this technique is a coherent one allowing the persistence of the mode to be observed and hence the dephasing time to be directly measured. The stimulated mode was the dominant one given the symmetry of the sample and minimum time resolution (~ 120 fs) of the experiment. The phonon line was centered at ~ 142 cm^{-1} and had a FWHM linewidth of ~ 10 cm^{-1}. The intensity of this line was found to decrease as the sample temperature increased along with thermal broadening of the linewidth. A slight frequency softening was also noted as the sample temperature increased. Despite the presence of accessible Raman active modes in the superconducting sample no oscillations were observed. This suggests that the selection rules may differ from conventional ISRS as was noted in experiments involving the impulsive excitation of coherent phonons in Bi and Sb.[2] Future studies will involve the use of shorter pulses (< 50 fs) which could make the next higher frequency line at 342 cm^{-1} accessible.

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