Temperature dependence of doping-induced modes in Cu-O planes

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(Received 28 December 1992)

Measurements of the frequency-dependent conductivity confirm that unusual lattice vibrational modes are induced by doping of several materials containing Cu-O planes. We find that the modes broaden rapidly with increasing temperature, consistent with the presence of a large linear component. This broadening of these vibrational modes is similar to that of electronic modes found previously in these same materials and analyzed in attempts to understand high-temperature superconductivity.

There are two recent suggestions that interesting anomalies occur in the vibrational modes in Cu-O planes due to the coupling to dopants. The first is the prediction of electronic interactions in the dynamic tilting of the Cu-O planar bond.[1] The second is the prediction of a highly nonlinear feedback mechanism that enhances the effect of the electron-lattice coupling on local distortions in the Cu-O planar lattice.[2]

These theories follow a substantial body of studies of the electron-lattice interactions in semiconducting, antiferromagnetic precursors to the high-temperature superconductors.[3-9] Of particular importance is the series of photodoping measurements on the differential absorption which have indicated modifications of the vibrational spectrum by the added carriers.[4-7] Our experiments are an extension of this work in that we also measure the spectral change due to doping, but in addition we determine the absolute, frequency-dependent conductivity at thermodynamic equilibrium by using static doping. We confirm the previous indications of a reduced absorption near the phonons of the pure material and an enhanced absorption at doping-induced modes. In addition we can measure the spectral weight, the energy, and the linewidth of both phonons and new modes, and in particular, we can follow their changes as a function of temperature. Of particular interest is a measurement of the linewidth of a doping-induced mode as a function of temperature.

To study the temperature dependence we have focused on a particular doping-induced mode in a material with a simple crystal structure (containing no chains). This mode occurs at an energy just below the phonon that arises[10] from the opposing vibration (stretching and probably tilting) of Cu and O in the planes. The proximity in energy of these two modes suggests that they may involve similar atomic motions and may therefore be particularly sensitive to the charge density which is added to the planes. We find that the temperature dependence of the linewidth of this doping-induced mode is much larger than that of the phonons and is consistent with the presence of a substantial linear term. We find that this linear component is not present in the linewidth of the nearby phonon, and as a result the temperature change in the linewidth of the doping-induced mode turns out to be nearly 20 times larger below 100 K. The linewidth of the doping-induced mode can be modeled as an effective de-

cay rate due to interactions with the surrounding environment.

In previous work, decay rates have been found to follow a linear temperature dependence for the electrons in the normal state of many high-temperature superconductors.[8,9,11,12] A similar relaxation rate of the dopant charges[13] has been found in the insulating phase of this same class of planar Cu oxides. In contrast, phonon decay rates are usually dominated[14] by a faster variation. However, the phonon decay is known to be enhanced by the addition of carriers.[15]

We have measured both the phonons and doping-induced modes with optical reflectivity on crystals of cuprate hosts which, at higher doping levels, can produce high-temperature superconductivity.[16] We have studied these materials at dopant concentrations which are small compared to those that are required for superconductivity, because at these low levels we can measure the vibrational modes accurately without having to separate them from large electronic contributions. The charges at different concentrations are added by removing or adding O atoms during crystal growth or by annealing in a controlled O environment.

We have measured doping-induced modes in five different crystals of three host materials: $Ba_2YCu_3O_{6+x}$, La_2CuO_{4+x}, and Nd_2CuO_{4+x}. Our observed changes in the absolute spectra with doping confirm measurements of the differential absorption spectra with photoexcitation in similar materials.[4-7] Some of our measured spectra for these materials are shown in Fig. 1. In all cases we have measured the reflectivity, R, an example of which is shown in the left part of the figure. For $Ba_2YCu_3O_{6+x}$, the solid line is measured and the dashed line is a fit with a set of Lorentzian oscillators of the usual form,[8-10] neglecting the Fano corrections[17] due to the interaction between the phonons and the electronic band induced by doping.[9,13] The parameters of this fit show phonons, characteristic of the $x=0$ materials consistent with previous measurements.[3,4] These data were taken at room temperature where the doping-induced modes are not resolved as at lower temperatures. We did not measure *this crystal* further, because we wanted to focus on materials where x could be controlled in the range near zero.

We found that we could make crystals with apparently high dopant homogeneity at the desired lower values of x in the Nd and La compounds. The spectra for these ma-
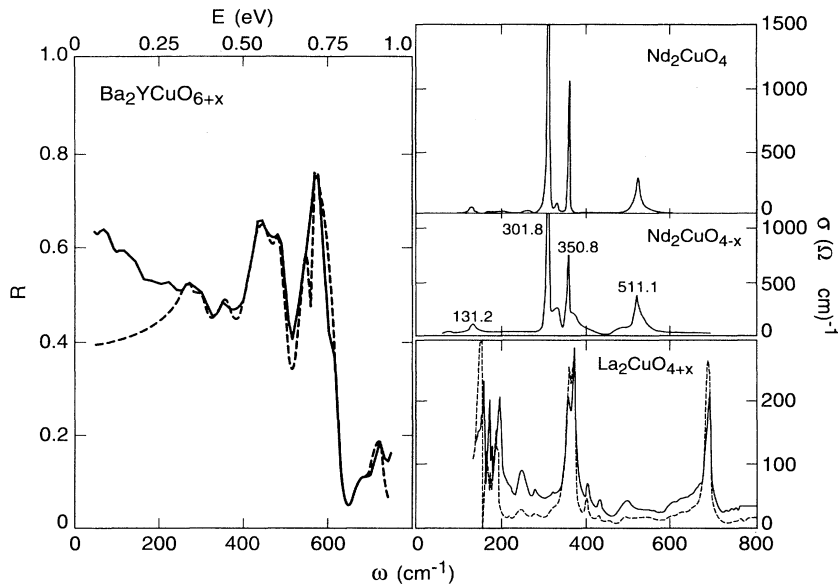
FIG. 1. Phonon spectral region of five crystals of insulating cuprates as labeled. The left part shows the measured reflectivity (solid line) and a fit (dashed line), as an example of the data as recorded. The right part of the figure shows the conductivity (at $T = 10$ K) for very low doping ($x < 0.005$), low doping ($x = 0.03$) (separate, solid curves) with O vacancies, and for very low doping ($x < 0.005$, dashed curve), and low doping ($x \sim 0.02$, solid curve) with added O.

terials are shown in the right part of Fig. 1. Here, our measured reflectivities have been transformed into the real part of the conductivity, σ, using the conventional Kramers-Krönig method.[8,9,12] We have also fit R directly, and find the same results as discussed below, but prefer to plot σ for a discussion of the results. In all cases the reflectivities in the limit of frequency approaching zero were interpolated to the dc resistivity. All the crystals shown in Fig. 1 were semiconducting and had σ near or below 10^{-4} $(\Omega$ cm$)^{-1}$ at low temperatures. The σ data in Fig. 1 are all for $T = 10$ K. The values of x for the four crystals on the right are estimated from the Néel temperature and from the spectral weight in the mid-IR to be (from top) $\lesssim 0.005$, ~ 0.035, ~ 0.015, $\lesssim 0.005$. Here, also, the doping-induced modes can be seen in addition to the phonons. We singled out the Nd compound for further study based on previous characterization of these materials.[9,13] We further decided to concentrate on the modes near 500 cm^{-1} because these involve the Cu-O stretch in the planes,[10] and are thus a vibration that might be expected to interact directly with the dopant charges that reside in the planes.

Figure 2 shows the optical conductivity in the frequency region near the Cu-O stretch vibrations for two crystals, the upper curves for a sample that is relatively pure and the lower for a sample with 3% vacancies. The phonon allowed by symmetry in the perfect crystal peaks at a frequency, $\omega = 511.1$ cm^{-1} in the limit as T approaches 0 K as shown in the upper figure. The effects of the doping can be seen in the lower part of the figure by the appearance of a doping-induced mode at a lower frequency.

In both parts of Fig. 2, curves are shown for $T = 10$, 180, and 300 K. With increasing T all the modes can be seen to broaden, and the doping-induced mode becomes unresolved at room temperature. We have fit all of these curves with a set of Lorentzians, and shall focus on the linewidths of the principal components, because these appear to be the most reliable and the simplest to interpret.

Figure 3 shows two examples of these fits. Here the

data are plotted as solid lines, the sum of the fitting curves as solid points, and the individual fitting components as light or dotted lines. These fits determine the intensity (plasma frequency squared, ω_p^2), center frequency, and linewidth (whose T-dependent part we interpret as the T dependence of the lifetime, $1/\tau$). Qualitatively, these fits indicate that the phonon is asymmetric but
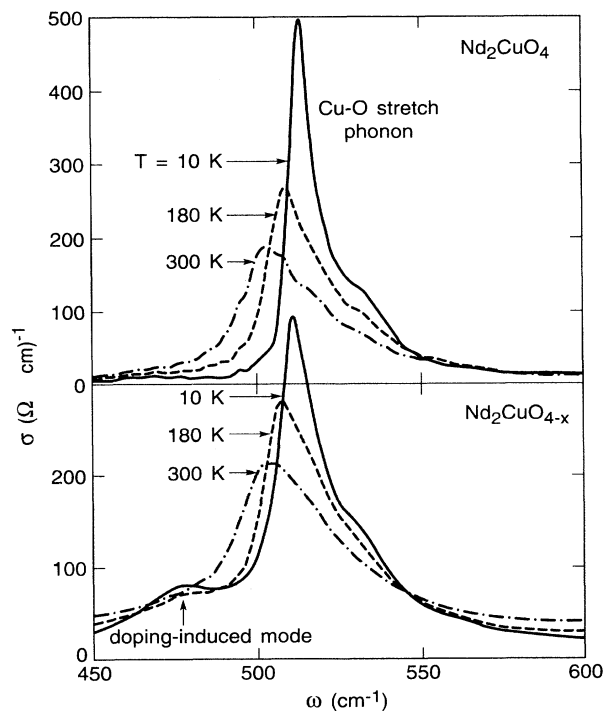

FIG. 2. The temperature dependence of the vibrational modes near 500 cm^{-1}, showing the broadening with T and also the broadening with doping and the appearance of a doping-induced mode.

dominated by a strong component. The buckling that occurs in similar materials suggests that the asymmetry arises from a tilting of the Cu-O unit, with lower frequency absorption where the tilting is greater. Furthermore, the intensity of the doping-induced mode is seen to increase dramatically over this doping range.

We find from the fits as a function of T that the spectral weights are essentially constant with T. Furthermore, the ratio of weight of the induced mode to that of the optical phonon is an indication of the dopant concentration. For a dopant concentration of 3%, the induced mode as analyzed in Fig. 3 has a spectral weight, which we characterize by ω_P^2, that is about 20% of the phonon. In the nearly pure crystal we do not have an accurate measure of the dopant concentration, but the corresponding ω_P^2 ratio is about 5%, which we interpret as confirming the low-dopant density. The T dependence of the center frequency ω_0, is clearly observable as shown in Fig. 2 and confirms the expected redshifts on heating.

The linewidths are plotted in Fig. 4, and illustrate the principal result of this paper. The solid points are the data and the solid lines are fits. We begin with the phonon in the nearly undoped crystal, shown in the bottom part of the figure, where we have plotted the width of the principal component of the line. (Analysis of this component has the smallest uncertainty because its lower en-
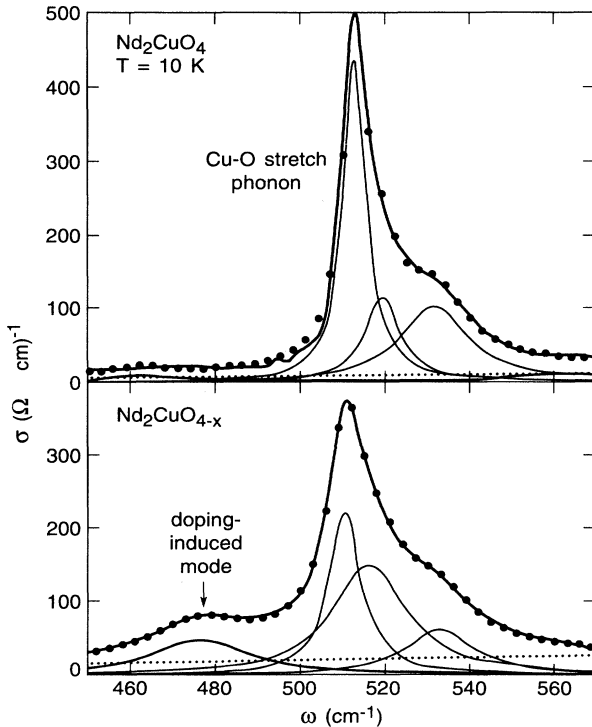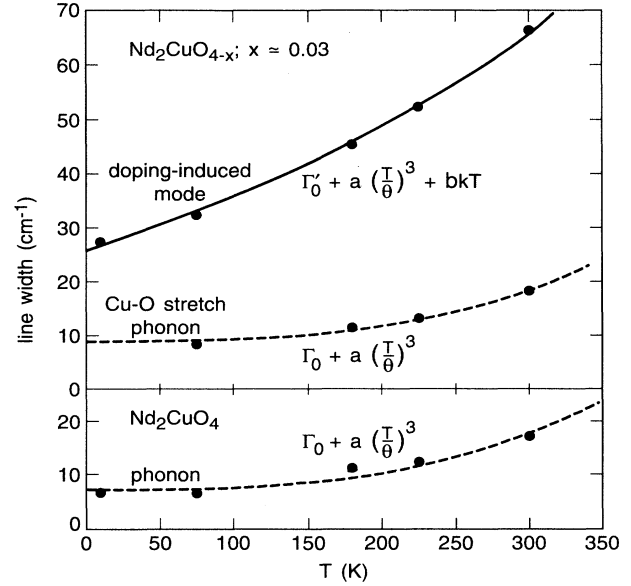

FIG. 4. Summary of the linewidths derived from the fitting as illustrated in Figs. 2 and 3. Solid circles are fitted values, with uncertainties ~ 2–5 cm^{-1}, lines are curves fitted to these points for the principal phonon component (dashed) and for the doping induced mode (solid).

FIG. 3. Fitting of the modes near 500 cm^{-1} at $T = 10$ K, as an example of the procedure used at each T, showing the data as the heavy curve, and the Lorentzians (light solid curves) summed to produce the fit (solid circles). The asymmetry of the phonon (both curves), the broadening with doping (lower curve), and the appearance of the doping-induced mode are all notable.

ergy edge dominates the lower edge of the phonon line.) We fit these linewidths, Γ, to the form

$$\Gamma = \Gamma_0 + a\,(T/\Theta)^3 \,, \tag{1}$$

where Γ_0 is the constant width at $T = 0$ K, a is a constant (presumably related to the conventional phonon broadening), and Θ is a characteristic energy (also presumably arising from the phonons). The fit determines Γ_0 of order 7 ± 1 cm^{-1}, which partly arises from our spectral resolution of 1 cm^{-1}. The fit also determines the product a/Θ^3, and, if we assume that Θ is of order this phonon energy, $\omega_0 = 511.1 \pm 0.5$ cm^{-1}, a is 67 ± 5. Although the T^3 fit is satisfactory we find that other similar functional forms can be used to fit the data, but that there is no significant term that is linear in T.

We analyze the phonon linewidth of the doped crystal in the same way, using Eq. (1) and find a good fit with the same value of the prefactor of the T^3 contribution, as shown in the lower curve in the upper part of Fig. 4. The zero-T width is larger by about 2 cm^{-1} due to the increased disorder arising from the doping.

The most interesting linewidth variation is that of the induced mode which requires a different functional form. (The T^3 form does not give a satisfactory fit, as can be seen by inspection of the upper set of points in Fig. 4.) We assume a form equal to that of the phonons plus a linear term:

$$\Gamma = \Gamma_0' + a\,(T/\Theta)^3 + bk_B T \,, \tag{2}$$

where b is a constant. We find that this form provides a satisfactory fit, as shown in the figure, when we assume the same magnitude of the T^3 term as in the phonon fit, and vary only Γ_0' and b. We find that Γ_0' is almost 3 times

larger than for the phonon, indicating a larger sensitivity of this mode to the environment around the dopants. The fit determines the constant b to be 0.09 ± 0.02. One possible interpretation of this constant is that it is analogous to the prefactor of the linear term due to electron-boson coupling that enters the change in linewidth of the electronic peaks near zero frequency and in the mid-infrared.[8,9,13] If we equate these terms we can define an effective coupling constant, λ, between the induced mode and its environment according to $b \equiv 2\pi\lambda x$. We include the concentration of the dopants, x, since the mode is induced by doping.[14,15] Given that a fraction, x, of the unit cells contains a dopant, the relaxation rate from this process is reduced by x from the full coupling, λ. Assuming this parametrization, the fit gives $\lambda=0.5\pm0.2$.

This coupling constant is comparable to that found[13] for another mode induced by doping at a higher energy. This higher mode peaks at 0.162 eV, near the antiferromagnetic exchange energy and about 2.5 times the upper phonon energy. The decay mechanism of this mode is unknown, but its large spectral weight indicates that it is an electronic excitation. The decay of this electronic mode was found[13] to be linear in T, with a prefactor $2\pi\lambda k_B T$ and a fitted λ of about 0.5.

The linear linewidth variation of the doping-induced mode shown in Fig. 4 also resembles the scattering of the conduction electrons in the normal metallic state of a number of related cuprate materials. Both the dc resistivity and the Drude-like component of the frequency-dependent conductivity have been analyzed[8,9,12] in terms of a scattering rate with a coupling constant of order 0.4. The similarity of the linear contribution to the linewidth of these three modes in planar cuprate crystals may be an indication that a similar interaction plays an important role in each case.

Recent theoretical work[2] has presented an approximate model of how lattice modes can be induced by doping, in qualitative agreement with our results. However, other effects undoubtedly play a role both in explaining the presence of the induced modes and in their broadening with temperature. At this time, we know of no satisfactory theoretical explanation for the mode broadening reported here, although we suggest that it may be related to the important electronic decay rates in this class of planar cuprates.

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