# Displacive excitation of coherent phonons in $YBa_2Cu_3O_7$

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(Received 14 June 1993; revised manuscript received 4 November 1993)

We suggest a microscopic model that provides a consistent explanation of the recent femtosecond pump-probe experiments on $YBa_2Cu_3O_7$, including the fact that the reflectivity change in the superconducting state is much larger than that in the normal state. In this model, not only the oscillatory part of the reflectivity, but also the total reflectivity change, is due to displacive excitation of coherent phonons. The microscopic reason for this excitation is that superconductivity induces small displacements in the equilibrium positions of the ions, since the pairing energy depends on the density of states at the Fermi level, which changes with the ionic positions. When superconductivity is destroyed by the femtosecond laser pulse, the ions are pulled back to their normal equilibrium positions, thus exciting coherent phonons. The relative size of the oscillatory contribution to the reflectivity depends upon the ratio of the phonon period to the time scale of the pair breaking, and when this ratio is small, the oscillations are suppressed, as observed in the experiment. *Ab initio* calculations confirm this model. The model also provides an explanation for why the magnitude of the 150 $cm^{-1}$ mode below $T_c$ may be much smaller than that of the 120 $cm^{-1}$ mode.

In the last decade, femtosecond pump-probe techniques have been widely used to study metallic and semiconducting materials. One of the newest developments is the so-called displacive excitation of coherent phonons (DECP). This refers to the process whereby pumping with a femtosecond laser results in reflectivity changes which oscillate with time, due to the impulsive excitation of the Raman-active phonons with $A_1$ symmetry. Zeiger *et al*.[1] have shown that this process can be described by a simple classical theory of a harmonic oscillator in an external field. They derived a formula for the $t$ dependence of the reflectivity change $\Delta R(t)/R_0$, and successfully applied it to several semiconducting materials. Very recently, oscillations in $\Delta R(t)/R_0$ have been observed in $YBa_2Cu_3O_x$ having semi-[2] or superconducting compositions.[3] The main characteristics of the observed $\Delta R(t)/R_0$ are (i) both in semiconducting $YBa_2Cu_3O_{6.3}$ (Ref. 2) and in $YBa_2Cu_3O_7$ (Ref. 3) above $T_c$, $\Delta R/R_0$ is small ($\sim 10^{-4}$), the width of the main maximum in $\Delta R(t)/R_0$ is a few tenths of a picosecond, and it is followed by weakly decaying (time constant $\tau \sim 1$ ps) DECP oscillations; (ii) below $T_c$ the reflectivity change has the opposite sign, is 1 order of magnitude larger, and the relaxation is 1 order of magnitude slower, and is superimposed by DECP oscillations; (iii) of the two observed phonons, the intensity of the 150 $cm^{-1}$ mode changes relatively little between 20 and 100 K, while the intensity of the 120 $cm^{-1}$ mode changes by a factor of $\approx 15$. The spectra obtained for the semiconducting $YBa_2Cu_3O_{6.3}$ (Ref. 2) and the metallic $YBa_2Cu_3O_7$ (Ref. 3) above $T_c$ are rather similar to those in the semiconductors studied in Ref. 1. However, the striking changes that occur below $T_c$ have so far not been explained. In this paper we shall argue that the theory of Zeiger *et al.* provides a consistent explanation of these changes, and that the difference from the semiconducting case considered by Zeiger *et al.*, is that the parameters in the DECP equation in superconducting $YBa_2Cu_3O_7$ are qualitatively different. We shall present a microscopic model for the DECP in this case, and calculate $\Delta R(t)/R_0$ using parameters obtained from our previous local density calculations.[4] The main idea in our model is that not only the oscillatory part of $\Delta R(t)/R_0$ in $YBa_2Cu_3O_{7-x}$, which we agree with previous suggestions[1,3] is due to DECP, but also the nonoscillatory part in the superconducting state, which previously was ascribed to the change in the *electronic* dielectric function (Refs. 3 and 5), is due mainly to the DECP.

In Ref. 1 the following model was adopted: The time-dependent laser intensity [$P(t) = \text{const} \cdot g(t)$, where $g(t)$ is normalized to 1] excites the electronic subsystem. The excited state represents a force acting on the ions. This time-dependent forcing function can be written as $p(t) = p_0 \int_0^\infty g(t-x)\exp(-\beta x)dx$ [in Ref. 1 $p(t)$ was suggested to be the electronic temperature or the concentration of the excited electrons]. For each $A_1$ phonon with frequency $\omega_0$, the equilibrium phonon coordinate $Q_0$ is then proportional to $p$, *via* the coupling constant $\kappa$. The time dependence of the phonon coordinate can be written as

$$Q(t) = \frac{\kappa p_0 \omega_0^2}{\Omega^2 + (\beta-\gamma)^2} \int_0^\infty g(t-x) \times \left[ e^{-\beta x} - \mathrm{Re}\left( \frac{\Omega + i(\beta-\gamma)}{\Omega} e^{-(\gamma+i\Omega)x} \right) \right] dx. \quad (1)$$

Above, $\beta$ and $\gamma$ are relaxation constants for the electrons and for the phonon, and $\Omega^2 = \omega_0^2 - \gamma^2$. The measured reflectivity change can then be calculated as

$$\frac{\Delta R(t)}{R_0} = A p_0 \int_0^\infty G(t-x) e^{-\beta x} dx + B \frac{\kappa p_0 \omega_0^2}{\Omega^2 + (\beta-\gamma)^2} \times \int_0^\infty G(t-x) \left[ e^{-\beta x} - \mathrm{Re}\left( \frac{\Omega + i(\beta-\gamma)}{\Omega} \times e^{-(\gamma+i\Omega)x} \right) \right] dx, \quad (2)$$

 

where $A$ and $B$ are defined so that $\Delta R(t)/R_0 = Ap(t) + BQ(t)$, and $G$ is the convolution of $g$ with the shape function of the probe pulse $g_0$, $G(t) = \int_{-\infty}^{\infty} g(t-x)g_0(x)dx$. Furthermore, since $g_0(t)$ has a width which is less than 0.1 ps, a good approximation is $g_0(t) = \delta(t)$, $G(t) = g(t)$. In the case of a semiconductor, considered in Ref. 1, and relevant for the semiconducting and the normal-state metallic $YBa_2Cu_3O_x$ as well, $p$ is the concentration of excited electrons, and $g(t)$ is basically the shape of the pump pulse, i.e., $g(t) = g_0(t) \approx \delta(t)$. [Note that Eq. (2) differs from Eq. (21) of Ref. 1 only in that we have allowed $g(t)$ to be different from $g_0(t)$.]

In Fig. 1 we compare the reflectivity change calculated in a DECP model for the normal state of $YBa_2Cu_3O_7$ with the measurements of Albrecht *et al.*[3,6] It may be seen that the model is remarkably accurate for the normal state of $YBa_2Cu_3O_7$. The relaxation rate for electrons excited into higher-energy bands was taken as $\beta \approx 13$ ps $^{-1}$ and for the lattice as $\gamma \approx 10$ ps$^{-1}$. For the pulse widths we used 0.08 ps, according to Ref. 3. Apparently, the assumption that the driving force for DECP in the normal state are interband electronic excitations is correct. It is also clear that this mechanism can neither explain the order-of-magnitude increase in $(\Delta R/R_0)_{\max}$ nor the increase in the amplitude of the coherent 120 cm$^{-1}$ phonon in the superconducting state. Both effects must be related to breaking of the superconducting pairs.[3]

However, it is easy to show that, contrary to a previous suggestion,[5] the changes in the *electronic* dielectric function at the relevant frequency ($\hbar\omega \gtrsim 2$ eV) due to the onset of the superconductivity are much too small to explain the observed change of $(\Delta R/R_0)_{\max}$. The relative change of the intraband dielectric function at $\hbar\omega = 2$ eV is of the order of $10^{-5}$ (calculated according to Genzel *et al.*[7] with $\omega_{\rm pl} = 1$ eV and $1/\tau = 200$ cm$^{-1}$), which is much too small to account for the observed change in the reflectivity, which is of the order of $10^{-3}$. The change in the interband dielectric function can, in principle, be substantial, but only in narrow frequency regions near critical points.[8] Therefore, we neglect parameter $A$ in Eq. (2) in the superconducting state.

An important hint about the anomalous behavior below $T_c$ can be drawn from comparing the curves above and below $T_c$ (Fig. 1 of Ref. 3). We observe that the maximum change of the reflectivity *below* $T_c$ occurs at about $t = 0.35$ ps, i.e., when the interband excitations have just relaxed for $T > T_c$. This implies that the pair-breaking agents are neither photons nor interband excitations (as suggested in the original experimental paper[3]), but rather the phonons emitted during the decay of these excitations. Thus, if DECP in the superconducting state is driven by pair breaking, the function $g(t)$ in Eq. (1) does not have the shape of the pump laser pulse, but follows the $t$ dependence of the number of excited electrons (which determines the phonon emission rate). In this case the periods of the relevant phonons (the five $A_1$ modes at 120, 150, 330, 440, and 500 cm$^{-1}$) become comparable to, or even smaller than the duration of the forcing function $g(t)$, and this would lead[9] to a suppression of the oscillatory term in Eq. (2), as mentioned in Ref. 1. It is relatively easy to reproduce the experimental curve by summing the five phonon contributions [Eq. (2)] with appropriately chosen parameters. However, in order to be convinced that the suggested model is relevant, one must check that the parameters are reasonable, and physically meaningful. To do that, we shall now make the link between the general arguments above and specific characteristics of $YBa_2Cu_3O_7$.

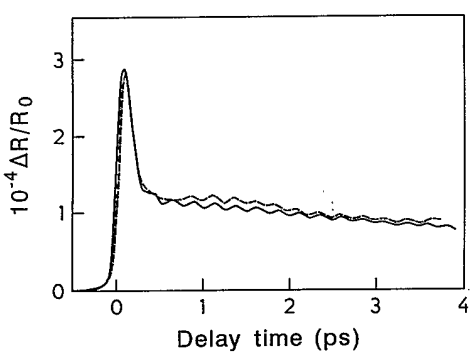


FIG. 1. Reflectivity change of $YBa_2Cu_3O_7$ above $T_c$. Dashed curve, experiment from Ref. 3; solid curve, DECP model calculations

We shall first estimate the fraction of pairs broken after a laser pulse. The number of broken pairs per unit volume is $n_b \approx I/2\Delta l$, where $l \approx 1000$ Å is the optical skin depth. The total number of superconducting pairs per unit volume is given, in BCS theory, by $n_0 \approx N\Delta/2$, where $N$ is the volume density of states at the Fermi level. Using the LDA (local density approximation) value $N = 2.5$ states/eV/cell/spin,[4] and 330 cm$^{-1}$ for $2\Delta$ (it is generally believed that the 330 cm$^{-1}$ phonon is close to $2\Delta$), we get $n_b/n_0 \sim 1$. Here we have assumed that all the pump energy is spent on breaking pairs, so the actual ratio may be somewhat smaller. Second we shall estimate the relative change in the reflectivity induced by a phonon, first assuming its amplitude $Q = 1$. [Here and below we use the normal phonon coordinates, so that the displacement of the $n$th atom is $Q\mathbf{e}_n(\hbar/2M_n\omega_{\rm ph})^{1/2}$, where $\mathbf{e}_n$ and $\omega_{\rm ph}$ are the phonon eigenvector and frequency, and $M$ is the ion mass.] For this purpose we shall use the experimental data for the Raman intensity[10] and make use of the fact that in the *calculation* of the Raman tensor[10] we found that the contributions from the real and the imaginary parts of the dielectric constant are of similar size for both the 120 and 150 cm$^{-1}$ modes (the situation for the other modes is more complicated). We find that $(\Delta R/R_0)_{120,150} \approx (0.04\text{–}0.05)Q_{120,150}$.

We shall now argue that breaking superconductivity induces ionic displacements of the order of $Q \sim 10^{-3}$, which gives $(\Delta R/R_0)$ values of the same order of magnitude as those observed. The physical reason for that is quite simple: In the normal state, the ions arrange themselves so as to minimize the elastic energy. However, if they can be displaced from their equilibrium positions so that the density of states at the Fermi level would increase, such a distortion would result in a larger pairing energy. Therefore, the equilibrium positions in the superconducting state will be different from those in the normal state, and the ionic displacements at a

given temperature result from the balance between the elastic energy and the pairing energy. The elastic energy is simply given by $\delta E_{\rm el} = \hbar\omega_{\rm ph}\delta Q^2/4$, and the pairing energy can be estimated using the BCS formula $E_{\rm pair} = \Delta^2 N/2$ where $\Delta \propto \exp(-1/\lambda)$ and $\lambda \propto N$. From this $\delta E_{\rm pair} = a\Delta^2\delta Q(dN/dQ)$ where $a = 1/2 + 1/\lambda$ (for strong coupling $a$ is even larger). We take $a \sim 2$ and find an estimate for the displacement $\delta Q$ induced by the superconducting transition: $\delta Q \sim 4\Delta^2(dN/dQ)/\hbar\omega_{\rm ph}$.[11] Finally, $dN/dQ$ is obtained from our frozen-phonon calculations described in Ref. 4. For the *pure* Ba and *pure* Cu modes we find, respectively, 0.11 and 0.10 states/eV/cell/spin. Substituting these in the above formula, we obtain $\delta Q_{\rm Ba} \approx 12\times10^{-3}$, $\delta Q_{\rm Cu} \approx 9\times10^{-3}$. For the higher frequency modes, we find $\delta Q_{330} \approx 3.3\times10^{-3}$, $\delta Q_{440} \approx 3.6\times10^{-3}$, $\delta Q_{500} \approx 9\times10^{-3}$. Note that $\delta Q$ corresponds to the $\kappa p_0$ coefficient in Eq. (2). Now, we can estimate $B' \equiv B\kappa p_0$ in Eq. 2, using the Raman efficiencies of the corresponding modes:[10] $B'_{\rm Ba} \approx 5.5\times10^{-4}$, $B'_{\rm Cu} \approx 3.6\times10^{-4}$, $B'_{330} \approx 3.3\times10^{-4}$, $B'_{440} \approx 1.0\times10^{-4}$, $B'_{500} \approx 9.0\times10^{-4}$. We assumed for simplicity that for all modes the contribution from the real and the imaginary parts of the dielectric function are about the same.

The $B'$ values above are of the right order of magnitude compared to the experiment. However, in the experiment $B'_{\rm Cu}$ is much smaller than $B'_{\rm Ba}$. This discrepancy may be due to an overestimate of either $B_{\rm Cu}$ or, less likely, of $\delta Q_{\rm Cu}$. It could also, at least partially, be due to the neglected mixing of the Ba and Cu movements in the two lowest modes. This we shall now discuss in detail. It is generally believed that the 120 $\rm cm^{-1}$ mode consists solely of Ba movement, while the 150 $\rm cm^{-1}$ is a pure Cu mode. This assignment for the two lowest-energy modes is based on the Raman spectra of $Cu^{63}$ and $Cu^{65}$ substituted samples,[12] where only the 150 $\rm cm^{-1}$ was found to shift upon isotope substitution. In the first-principles LDA calculations[4,13] the two lowest modes are mixed in such a way that they become $\approx$ 50 : 50 in-phase (120 $\rm cm^{-1}$) and antiphase (150 $\rm cm^{-1}$) combinations of the Ba and Cu displacements. The reason for this is that the two modes are so close in energy that even a small non-diagonal term in the dynamical matrix causes a substantial mixing. The experiment[12] sets an upper limit on the mixing to about 25%, which means that even the moderate LDA value of this term is in fact too large. On the other hand, it is hard to believe that this term is so anomalously small that the mixing between the two modes becomes negligible. We shall therefore discuss how a nonzero mixing, $\alpha$, influences the $B'$ coefficients. One has to appropriately mix the partial $dN(E_F)/dQ$'s and $B$'s, so that the effective

$$B'_{150} \approx [\alpha\delta Q_{\rm Ba} - (1-\alpha)\delta Q_{\rm Cu}][\alpha B_{\rm Ba} - (1-\alpha)B_{\rm Cu}]$$
$$B'_{120} \approx [(1-\alpha)\delta Q_{\rm Ba} + \alpha\delta Q_{\rm Cu}][(1-\alpha)B_{\rm Ba} + \alpha B_{\rm Cu}], \quad (3)$$

where the subscripts Ba and Cu refer to the traditional assignment. Using the LDA eigenvectors of Ref. 4 ($\alpha \approx 0.5$), we obtain $B'_{120} \approx 4.5\times10^{-4}$ and $B'_{150} \approx 0.3\times10^{-4}$, which gives very reasonable agreement with the experimental fact that $|\Delta R/R_0|_{150} \ll |\Delta R/R_0|_{120}$. If the mixing is reduced as indicated by the isotope experiments then cancellation in Eq. (3) for $B'_{150}$ can still be obtained when either $B_{\rm Ba}/B_{\rm Cu} \approx (1-\alpha)/\alpha$ or $\delta Q_{\rm Ba}/\delta Q_{\rm Cu} \approx (1-\alpha)/\alpha$. The LDA parameters correspond to the case when $B_{\rm Ba} \approx B_{\rm Cu}$, $\delta Q_{\rm Ba} \approx \delta Q_{\rm Cu}$, and $\alpha \approx 0.5$. If we take the experimental upper limit for $\alpha$, then a complete cancellation of $B'_{150}$ would require that our estimates of either of these ratios to be a factor of 3 too small, which is certainly within the limits of our accuracy. On the other hand, in reality one need not have a complete cancellation.[11]

The result of the calculations with the LDA values of $B'$ is shown in Fig. 2. We have taken the experimentally determined damping constant for the 120 $\rm cm^{-1}$ mode, $\gamma = 0.4$ $\rm ps^{-1}$, and used it for all five phonons. For the pair recombination rate we used $\beta = 0.74$ $\rm ps^{-1}$. As discussed above, the forcing function $g$ is proportional to the number of the initially excited electrons, whose relaxation rate we assume to be the same as in the normal state, i.e., 13 $\rm ps^{-1}$. The agreement with the experiment is very good, the only discrepancy being that the relative magnitude of the oscillatory part is overestimated. There may be several reasons for this overestimation, of which we think two are most likely: First, our calculations may underestimate the contribution from the highest frequency modes (where the oscillatory part is completely suppressed) relative to the 120 $\rm cm^{-1}$ mode. Second, the contribution from the high-energy modes can be actually higher than that calculated if the probe pulse has a polarization component parallel to $c$ polarization, since the 500 $\rm cm^{-1}$ mode is anomalously Raman active in this polarization.[10] Finally, as discussed above, the magnitude of the 150 $\rm cm^{-1}$ mode depends strongly on the delicate balance between its Ba and Cu components. A small temperature dependence of mixing $\alpha$ may be the reason for the increase of this magnitude below 40 K [the temperature dependence of $(\Delta R/R_0)_{120}$, $(\Delta R/R_0)_{\rm max}$ below $T_c$, and of $(\Delta R/R_0)_{150}$ from 40 K to $T_c$ agree completely with our model, cf. Ref. 11]. One should keep in mind, however, that the model itself is simplified, and the excellent agreement of the total magnitudes in Fig. 2 is likely to be accidental. The main sources of uncertainty (which can hardly be improved without knowing the mechanism of the high-temperature superconductivity) are (i) using the BCS formula for the pairing energy,

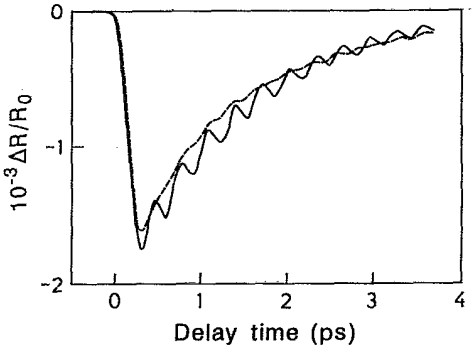


FIG. 2. Reflectivity change of $YBa_2Cu_3O_7$ below $T_c$. Dashed curve, experiment from Ref. 3; solid curve: our model calculations with the LDA parameters.

and (ii) the superconducting gap, and (iii) neglecting possible anisotropy of the gap, in particular the possibility of having substantially different gaps on the different sheets of the Fermi surface (see, e.g., Ref. 14).

In summary, we have shown that the pump-probe femtosecond laser pulse time response of $YBa_2Cu_3O_7$ both in the normal and superconducting states can be quantitatively described within the model of displacive excitation of the coherent phonons. This was suggested previously for the normal state.[1,3] The unique features of the superconducting state, which have not been understood before, are that (i) the nonphonon contribution to the total reflectivity change is small, and (ii) the role of the pump pulse in conventional DECP theory is played by pair breaking due to phonon emission during the relaxation of the optically excited electrons. This process is relatively slow and thus brings the DECP in a new regime, where the oscillatory part is strongly suppressed. The striking difference in the observed reflectivity changes for the two lowest $A_1$ modes can be explained if the two modes are mixed with the phases suggested by the LDA calculations, i.e., that the 120 $cm^{-1}$ and 150 $cm^{-1}$ modes are the in-phase and out-of-phase combinations of the Cu and Ba vibrations, respectively. The isotope experiments, however, set an upper limit for the strength of this mixing. Finally, our model sheds some light on the intensively discussed problem of the sign change of $\Delta R$ below $T_c$ : since the mechanisms of the reflectivity changes in the normal and the superconducting state are completely different they need not result in reflectivity changes of the same sign.

We are grateful to S. Brorson for many valuable discussions and careful reading of the manuscript.

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