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Anomalous behavior of phonons in superconducting $Tl_2Ba_2Ca_2Cu_3O_{10}$ detected by far-infrared spectroscopy

T. Zetterer, M. Franz, J. Schützmann, W. Ose, H. H. Otto, and K. F. Renk
Fakultät für Physik, Universität Regensburg, D-8400 Regensburg, West Germany

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We report anomalous behavior of phonons in superconducting $Tl_2Ba_2Ca_2Cu_3O_{10}$ at T_c (~ 112 K) detected by a far-infrared reflectivity study of a ceramic sample. Our results indicate strong and abrupt softening of an infrared-active phonon and a decrease of oscillator strength of this and of another phonon. We associate the effects with anomalous vibrations of the bridging oxygen in the BaO layers and the off-center oxygen in the TlO layers, respectively. Our results give experimental evidence for strong electron-phonon interaction.

At present, $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Ref. 1) has the highest superconducting transition temperature ($T_c \sim 120$ K) of all high-T_c superconductors. In this paper we will present experimental results of a far-infrared reflectivity study of a ceramic $Tl_2Ba_2Ca_2Cu_3O_{10}$ sample indicating at T_c strong and sudden softening of an infrared-active phonon and a decrease of oscillator strength; we attribute both effects to anomalous vibrational behavior of oxygen in the BaO and TlO layers.

Softening of a phonon at T_c is known for $YBa_2Cu_3O_{7-\delta}$ from Raman scattering studies;[2] sample-dependent softening by 1–2% of the phonon frequency (~ 330 cm^{-1}) has been found. Far-infrared reflectivity measurements[3] also show softening ($\sim 1\%$) of a phonon (near 300 cm^{-1}) in $YBa_2Cu_3O_{7-\delta}$ at T_c, and an increase of oscillator strength.[3]

We have prepared $Tl_2Ba_2Ca_2Cu_3O_{10}$ ceramic pellets from highly pure powders of Tl_2O_3, $Ba(NO_3)_2$, CaO, and CuO. Single-phase samples with high far-infrared reflectivity have been obtained by a multistep sintering and regrinding procedure. The homogeneously mixed and pressed material (nominal composition 2:2:2.2:3.2) was sintered in a gold foil at 920 °C for 2 h, then reground and the procedure repeated. In a final step the reground material was pressed at high pressure (10 tons/cm^2) and the pellets sintered in a closed gold bag together with a small amount of additional Tl_2O_3 (few mg) at 900 °C for 10 min in flowing oxygen resulting in single-phase $Tl_2Ba_2Ca_2Cu_3O_{10}$ with smooth and highly reflecting pellet surfaces and zero resistivity at $T_c \simeq 112$ K, with a superconducting range (measured resistively) beginning at 118 K. The resistivity (150 $\mu\Omega$ cm at 300 K) was almost proportional to temperature between 120 and 300 K. Single phase was concluded from an x-ray powder-diffraction analysis. We note that high far-infrared reflectivity is critically dependent on the preparation method; i.e., one has to avoid evaporation of thalliumite oxide from the sample surface during the sintering procedure. Conservation of the surface quality has been achieved by the gold bag and the high pressure for pressing of the pellet. Note that for the far-infrared reflectivity measurements the surface has been kept untreated. Polished $Tl_2Ba_2Ca_2Cu_3O_{10}$ ceramic samples showed much lower reflectivity.[4]

In our far-infrared reflectivity measurement we used a Fourier-infrared spectrometer and determined the reflectivity by comparing the reflection of the sample with that of a gold mirror. In addition to specular reflection we also studied diffuse reflection; experimental details have been described earlier.[5]

The reflectivity (Fig. 1) shows a pronounced phonon structure that is similar between room temperature (300-K curve) and a temperature just above T_c (115-K curve); however, it changes strongly below T_c (25-K curve). The main changes are a shift of frequency of a phonon near 300 cm^{-1} and a strong change of the shape of the reflectivity at higher frequencies. The reflectivity drops above 1000 cm^{-1} (inset); diffuse reflection sets in above 650 cm^{-1}.

By a Kramers-Kronig analysis we find the conductivity curves of Fig. 2(a). Superimposed on the electronic conductivity is a structure due to phonons with vibrational motion perpendicular to the *a-b* plane; we suggest that, because of high electronic conductivity in the *a-b* plane, phonons with vibrational motion in the plane did not contribute to the structure of the reflectivity curves. The phonon structure consists of eight infrared-active phonons — in accordance with a lattice-dynamical study.[6] One of the phonons (near 300 cm^{-1}) softens at T_c and shows a

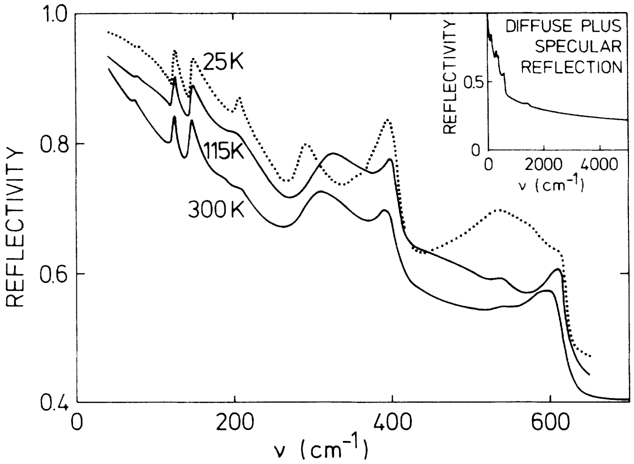

FIG. 1. Far-infrared reflectivity of a $Tl_2Ba_2Ca_2Cu_3O_{10}$ ceramic sample; inset, infrared reflectivity.

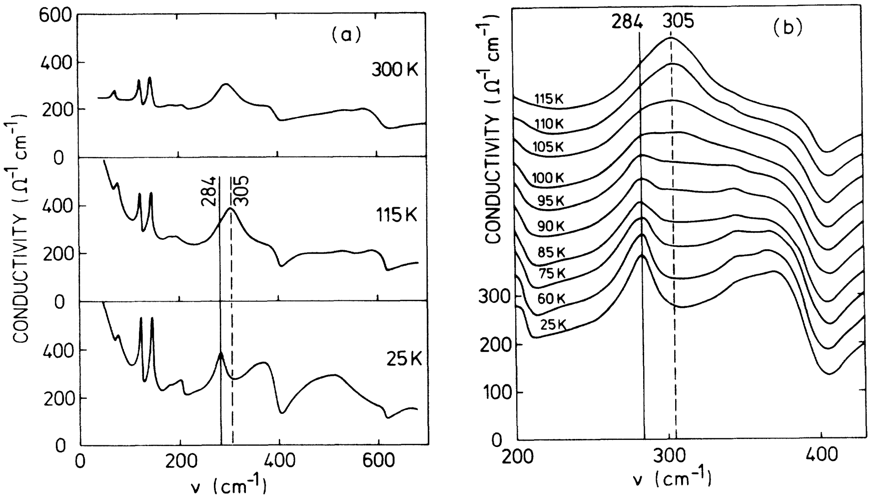

FIG. 2. Dynamical conductivity of $Tl_2Ba_2Ca_2Cu_3O_{10}$; (a) survey and (b) phonon-softening effect.

very large change of frequency [~7%; see vertical lines of Fig. 2(a)]. The frequency shift is much larger than observed for $YBa_2Cu_3O_{7-\delta}$.[2,3] The softening of the phonon does not occur as a continuous frequency shift, but an unshifted and a softened phonon are observed simultaneously [Fig. 2(b)], with a separation independent of temperature.

A further analysis, describing the phonon resonances by Lorentzian shapes, shows (Fig. 3) that the frequency of the anomalous phonon increases slightly (2%) between room temperature and T_c and decreases abruptly at T_c. The analysis also delivers the oscillator strength. As a measure of strength we take the change of dielectric function caused by the phonon. We find that the strength (upper part of Fig. 3) is transferred in a narrow temperature range from the unsoftened to the softened phonon. We attribute incomplete softening at T_c to spatial inhomogeneity of the material of our sample causing a distribution of T_c values (with a half-width of 10% relative to the resistivity measured $T_{c,\rho}$ value, and a tail down to 60 K).

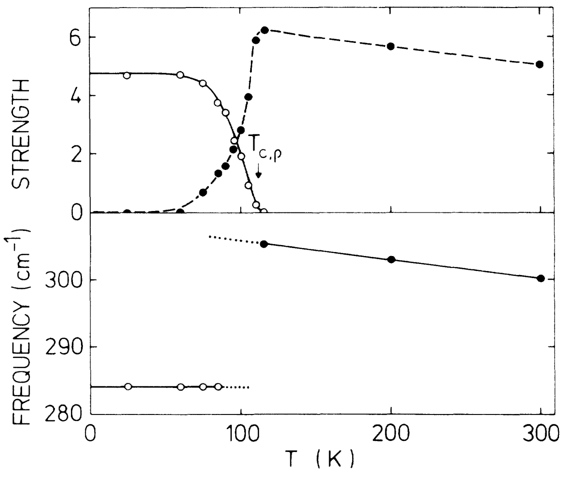

FIG. 3. Phonon softening.

We found that the anomalous phonon (Fig. 3) is the only infrared-active phonon showing a frequency shift between room temperature and low temperature (25 K). All phonons, however, change their strength (Fig. 4). The strength of each of the phonons increases slightly between room temperature and T_c and changes strongly at T_c. While for most of the phonons the strength increases further at low temperatures, there are two exceptions. The phonon near 300 cm^{-1}, with the anomalous frequency jump at T_c, shows a decrease of strength at T_c, as does the highest-frequency phonon (at 580 cm^{-1}).

Four low-frequency phonons, with vibrations of the heavy atoms (Tl,Ba,Cu), and two high-frequency phonons with vibrations of the light atoms (Ca,O),[6] show an increase of oscillator strength below T_c, while the phonon that softens shows a decrease of strength at T_c, as does the highest-frequency phonon (Fig. 4). These two phonons

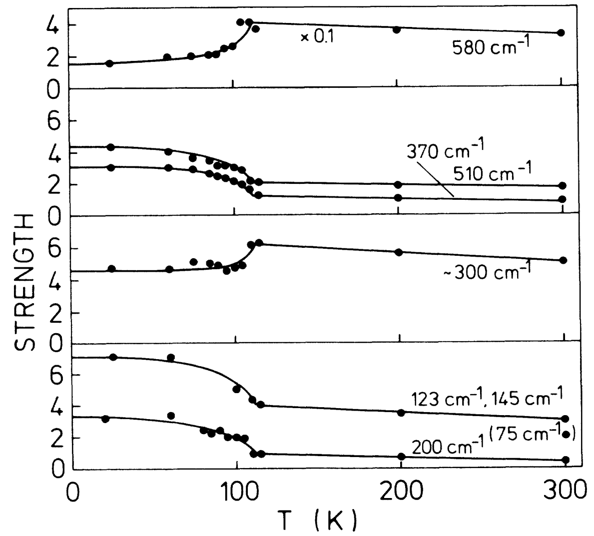

FIG. 4. Strengths of the infrared-active phonons in $Tl_2Ba_2Ca_2Cu_3O_{10}$.

correspond mainly to the vibrations of the "bridging oxygen" (oxygen in the BaO layer), i.e., the oxygen on the composition plane between the pervoskite and the rocksaltlike structural building units, and to the vibration of oxygen in the TlO double layers, respectively.[6]

In a neutron-scattering study[7] no structural phase transition at T_c was found; this is consistent with temperature-independent phonon modes we observed for most of the infrared-active phonons. X-ray-diffraction studies[8,9] give evidence that the bridging oxygen has not a well-defined position along the direction perpendicular to the *a-b* plane—a situation conducive to anharmonic vibration, and possible phonon softening at T_c. Furthermore, it was found[9] that oxygen in the TlO layers possesses off-center positions, with four equivalent positions in the *a-b* plane around the regular lattice site, and that a large concentration of Tl vacancies[9] occurs, delivering more space for oxygen; off-center positions and vacancies have also been found for $Tl_2Ba_2CaCu_2O_8$.[10] We suggest that the structural peculiarities of the bridging and the off-center oxygen atoms may be responsible for both anomalies: the observed softening of an infrared-active transverse-optic phonon and the change of oscillator strength for all phonons at T_c. Our results give evidence for strong interaction of these phonons with free charge carriers. Changes of oscillator strengths at T_c of infrared-active transverse phonons indicate that macroscopic polarization fields are influenced by the transition to superconductivity; we suggest that longitudinal phonons belonging to the corresponding transverse phonons change their frequencies strongly—while the transverse phonons (with the exception of the phonon with the strong shift) are almost uninfluenced by these fields.

Phonon softening suggested from a recent electron-scattering experiment[11] may be related to the anomalous behavior of phonons described in this paper.

Our results indicate that strong electron-phonon interactions occurs giving evidence that a strong-coupling theory[12] is adequate for a description of the electron-phonon system; whether the extremely large influence of superconductivity on the phonons has to do with the opening of a gap as discussed as a possibility[13] remains an open question. Our results give support for the idea of phonon-mediated high-T_c superconductivity via anharmonic vibrations[14] of the bridging oxygen or of the off-center oxygen.

In conclusion, we have reported on anomalous behavior of phonons in $Tl_2Ba_2Ca_2Cu_3O_{10}$ at T_c (~ 112 K). Our results indicate strong and abrupt softening of an infrared-active phonon and a decrease of oscillator strength for this and another phonon at T_c. We associate these effects with anomalous vibrations of the bridging oxygen in the BaO layers and the off-center oxygen in the TlO layers. Our results give evidence for strong electron-phonon interaction.

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