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Temperature effects on the phonon spectrum in $YBa_2Cu_3O_7$ single crystals and thin films

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We have performed detailed investigations on the temperature dependence of the $335\,cm^{-1}$ phonon in single crystals and thin films of the $YBa_2Cu_3O_7$ superconductor. The frequency of this phonon exhibits a downshift of about $5\,cm^{-1}$ on passing the superconducting transition from above. The shift of the phonon in thin epitaxial films on MgO or $SrTiO_3$ substrates is only about $2.5\,cm^{-1}$. The width of the asymmetric phonon line displays a slight increase below T_c due to the electron-phonon interaction in these systems.

I. Introduction

Several lattice vibrations of the high T_c superconductor have been observed in Raman scattering experiments by many groups [1-4]. The phonon at about $335\,cm^{-1}$ at room temperature exhibits some softening below T_c [5-8]. This is attributed to an electron-phonon coupling [7-9] which may be responsible for the occurrence of superconductivity in these oxide superconductors within strong coupling theory [9]. The fact that this $335\,cm^{-1}$ phonon is confined to the CuO_2-planes [3, 10, 20] supports this assumption. Other theories, however, completely do without any electron phonon coupling [11, 12] or use a Jahn-Teller/bipolaron picture [13, 14].

Neutron scattering experiments on phonons [15] and crystal electric field (CEF) excitations [16] in superconducting materials have given insight in the electron-phonon interaction and the coupling of $4f$-electrons to conduction electrons. Our intention was to perform similar investigations on the lattice vibrations of the high T_c materials by means of Raman scattering.

II. Experimental procedures

We have investigated three samples: A single crystal, and two thin films. The single crystal was grown in a BaO−CuO flux [17] and had the dimension $0.5 \times 0.5 \times 0.7\,mm^3$. The as-grown crystal was not superconducting and was additionally annealed in oxygen atmosphere. After this procedure it exhibited diamagnetism in susceptibility measurements below 89 K. Additional 4-terminal resistive measurements with a dc-current along the c-axis confirmed this, but the sharp decrease of the resistance at 89 K was followed by a slow approach of zero resistance at about 40 K (see insert in Fig. 1). We believe that this indicates some inhomogeneity in the single crystal possibly due to oxygen deficiency in the bulk material because the oxygen diffusion is less in the ideal crystal than in sintered material. At least the surface region, however, which we investigate in the Raman experiment to a depth of about 1000 nm, should consist of the superconducting phase responsible for the sharp drop in the resistivity at 89 K.

At the $a-b$ face of the crystal different twin domains (about 6–7) could be observed with a polarizing microscope. The twin boundaries [(110)-planes] intersected each other at almost 90 deg and were oriented under 45 deg with respect to the crystal boundaries. After several thermal cycles during the course of the experiments the number of twin boundaries (and also the number of twins) increased. Therefore our Raman experiments averaged over the two twin domain orientations.

The YBa$_2$Cu$_3$O$_7$ films were grown on two different substrates: MgO and SrTiO$_3$. The preparation conditions (details are presented in Ref. 18) were adjusted to give epitaxial films about 700 nm thick. Additional annealing in oxygen led to very sharp superconducting transition temperatures at around 85 K, as shown in the inserts of Fig. 1.

The samples were mounted in a closed cycle refrigerator which could span the range from 10 to 300 K. To warrant good thermal contact the single crystal was pressed into indium fixed to the sample holder. The substrates with the superconducting films were glued to the sample holder with vacuum grease. Local heating in the laser beam was reduced using low laser power of about 20–30 mW and by focusing the laser beam with a cylindrical lens in one dimension only.

The temperature of the sample in the laser spot, especially at low temperatures, may differ from the bulk sample. Usually the temperature can be determined by observation of the Raman spectrum on both sides of the laser line (Stokes and Antistokes). This failed in the present case because the observable excitations in the superconducting material are too high in energy and have too small scattering cross-sections to give a signal with good statistics on the Antistokes side of the spectrum at low temperature. To overcome this uncertainty we used a thin layer of sulfur on top of the superconducting film in a separate test run of the experiment. The use of only a thin sulfur film ensured that the reflectivity on the (black) superconducting film is only slightly increased. Heating the superconductor in the laser beam also heats the sulfur film. As sulfur exhibits strong Raman lines at low frequency shifts it is possible to use the Stokes/Antistokes ratio of these lines for a temperature calibration. Thus we ensured that the temperature reading of the resistive thermometer attached to the sample holder and the local temperature did not differ more than 5 K at temperatures above 60 K for 30 mW laser power. At the lowest temperatures laser heating produced a temperature rise of about 14 K, which is taken into account in the temperature scales of Figs. 1–4.

The Raman spectra were excited using the 514 nm line of an argon ion laser. The scattered light was collected by a $f/1.2$ aspheric photographic objective and focused to the entrance slit of a Jobin-Yvon U 1000 double monochromator. The Raman spectra were partly registered with an optical multichannel detector. When low elastic background scattering was necessary, as for the measurements shown here, a single channel detection with a cooled photomultiplier was used. A further elastic background reduction was achieved collecting the Raman spectra with crossed incident and scattered polarization. Then, because of

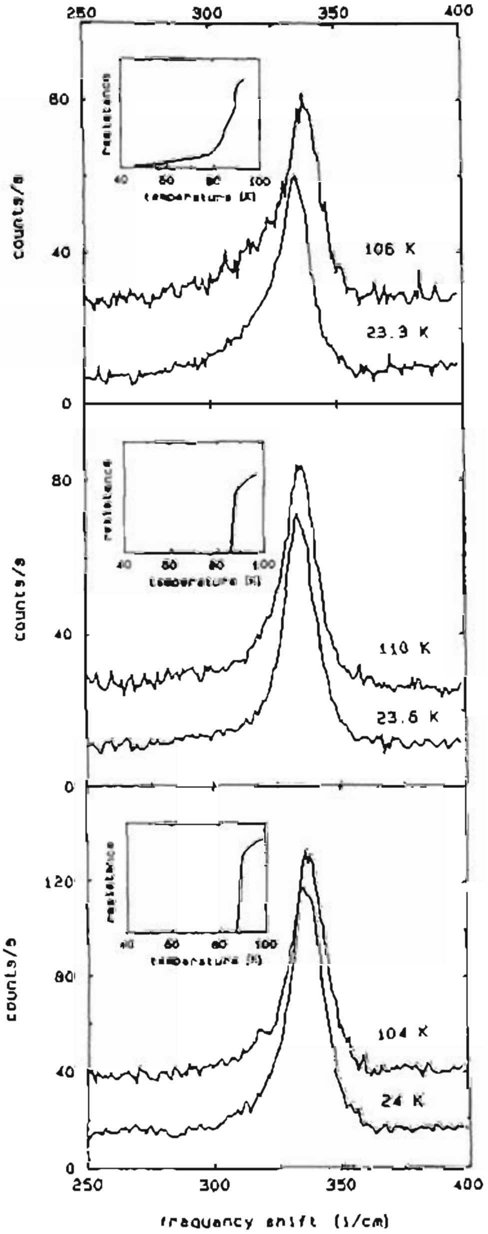

Fig. 1. Raman spectra from the 335 cm^{-1} phonon line in different YBa$_2$Cu$_3$O$_7$ samples for several temperatures. The top pair of spectra is obtained from a single crystal, the middle and bottom pair from epitaxial films on MgO and SrTiO$_3$ substrates, respectively. The inserts give the superconducting transitions measured resistively

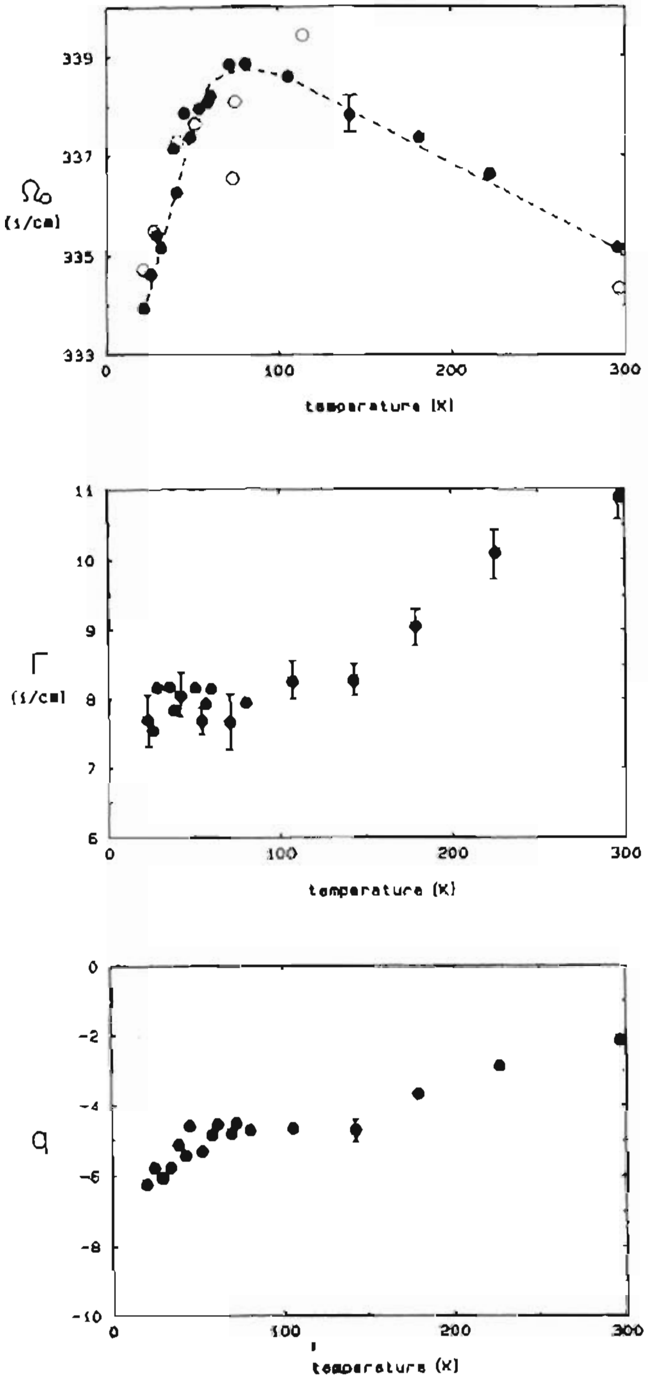

Fig. 2. Temperature dependence of the center frequency (Ω_0) linewidth (Γ), and asymmetry (q) of the 335 cm^{-1} phonon line in a $YBa_2Cu_3O_7$ single crystal. For details of the Fano lineshape see text. The open circles are the results for the center frequency obtained from a polycrystalline film [6]

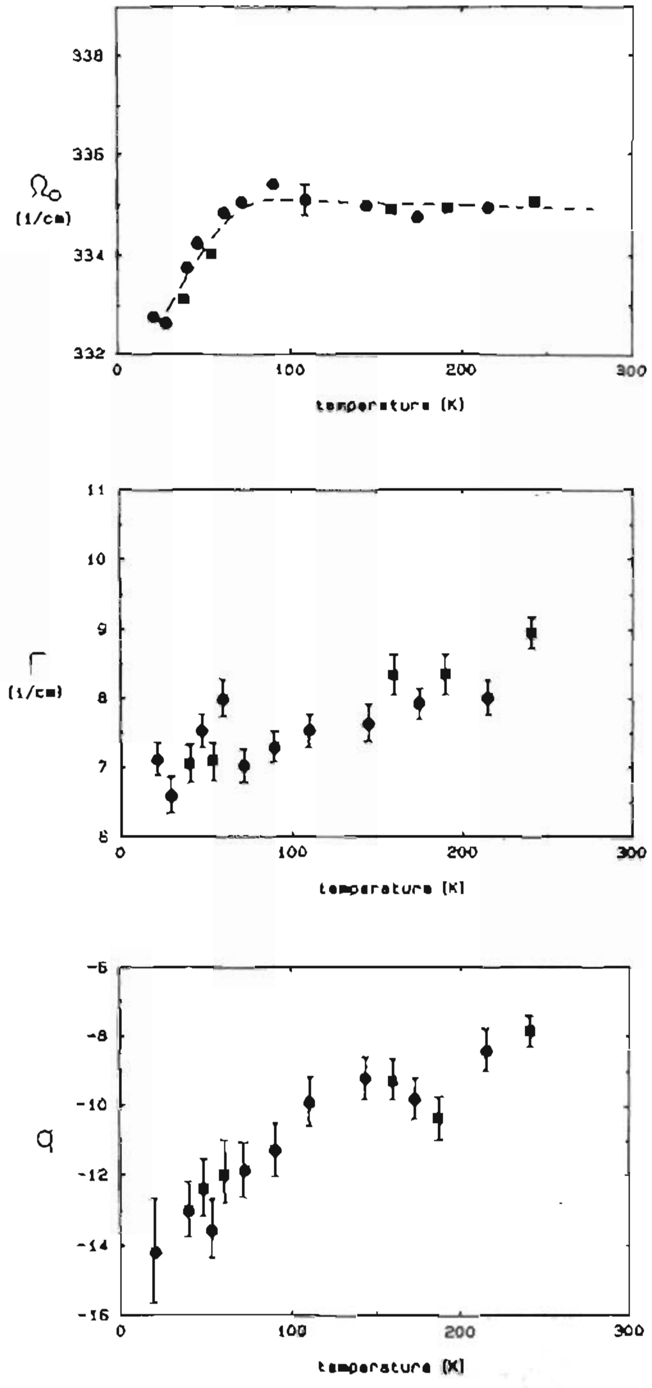

Fig. 3. Temperature dependence of the center frequency (Ω_0), linewidth (Γ), and asymmetry (q) of the 335 cm^{-1} phonon line in an epitaxial film of $YBa_2Cu_3O_7$ on $SrTiO_3$. For details of the Fano lineshape see text. Squares and circles give the results for two different thermal cycles

the selection rules [3, 8], the samples had to be aligned with the direction of the polarization bisecting the *a* and *b* axes of the single crystal in order to observe the 335 cm^{-1} phonon of the superconductor. For the thin films with MgO and $SrTiO_3$ as substrates the same symmetry arguments hold for the superconducting films [6] because of the epitaxy. This was confirmed by Raman experiments with fixed scattering geometry and rotating the substrates around an axis perpendicular to the surface. They yielded the

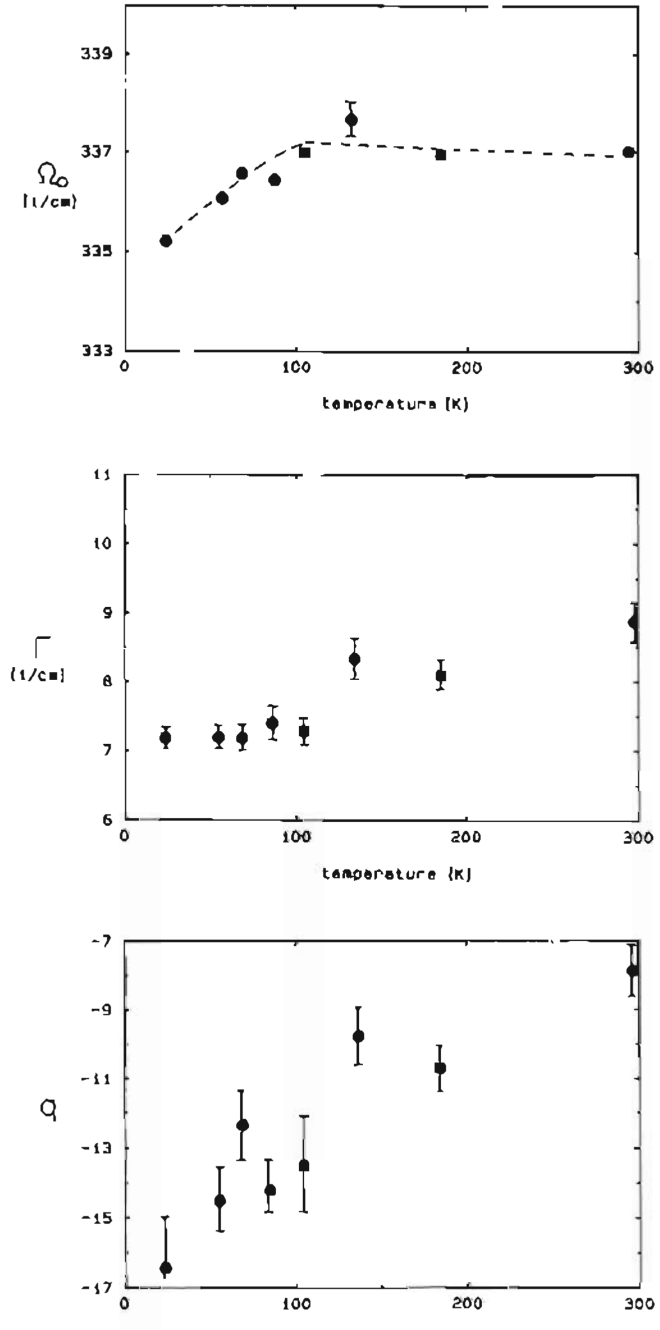

Fig. 4. Temperature dependence of the center frequency (Ω_0), linewidth (Γ), and asymmetry (q) of the 335 cm^{-1} phonon line in an epitaxial film of $YBa_2Cu_3O_7$ on MgO. For details of the Fano lineshape see text. Squares and circles give the results for two different thermal cycles

same angular dependence of the Raman intensity as for the single crystal, proofing epitaxy of the films with an orientation of the crystalline a and b axes of the film parallel to the axes of the substrate.

Figure 1 displays the Raman spectra from the single crystal and the films on the two substrates for two temperatures. The spectra clearly exhibit the asymmetric Breit-Wigner-Fano lineshape [7, 8] represented by formula (1) [19]

$$I(\Omega)=I_0\left[1+\left(\frac{\Omega-\Omega_0}{q\Gamma}\right)\right]^2\left[1+\left(\frac{\Omega-\Omega_0}{\Gamma}\right)^2\right]^{-1}. \qquad (1)$$

Here Ω and Ω_0 are the Raman shift and the center frequency, respectively, I_0 the intensity, Γ the linewidth, and q the inverse Wigner-Breit-Fano coupling coefficient which in the limit $q \to \infty$ gives a symmetric Lorentzian lineshape. The results of the fits of the parameters for different temperatures are shown in Figs. 2–4 for the three samples, respectively.

III. Discussion

The Raman line at 335 cm^{-1} has similar lineshape in the three samples. The obvious asymmetry is more pronounced in the spectra from the single crystal than in the spectra of the films. At lower temperature no dramatic changes in the lineshape appear on the shown frequency scale except that the single crystalline line becomes a little more symmetric. More details of the influence of decreasing temperature can be seen from the values for the different parameters obtained from fitting the lineshape (1) to the experimental data given in Figs 2–4.

As already shown in earlier papers on single crystals [5, 7, 8] and polycrystalline thin films [6] the Raman shift first becomes larger for that phonon when the temperature is lowered from room temperature, and then decreases below the superconducting transition temperature of the material. The overall reduction of the phonon frequency in the single crystal measured from the maximum value at T_c is 5 cm^{-1}. The same value is obtained in the other experiments [5–8]. The softening extends down to the lowest temperature achievable in the experiment, similar to the other reference [5–7], but it differs from the results of Thomsen et al. [8] who found that the softening takes place within 10 K below T_c. These differences may possibly result from different superconducting properties of the various samples. The details of the temperature variation of the phonon softening are sensitive to the relation between gap and phonon energy [9].

The softening of about 2.5 cm^{-1} observed in the thin epitaxial films (Figs. 3, 4) is only half of the value for the shift seen in experiments on polycrystalline material or single crystals. Also the increase of the phonon frequency between room temperature and T_c is almost zero in both films. This raises the question if the observed softening is an effect of the superconducting transition only, or if additional lattice instabilities influence the frequency shift. A few experimental results support this latter possibility. Datta et al. observed reentrant softening in the $YBa_2Cu_3O_7$ superconductor below T_c which may resemble the lattice instabilities in the A15 superconductors [21]. Structural transformations also are observed in neutron diffraction experiments on this high T_c material [22]. In our thin films the epitaxy to the substrate leads to additional stress in the film when the temperature is changed, which may suppress the lattice transformation. This assumption is supported by the fact that the phonon softening in thin polycrystalline films, where the individual crystallites are not clamped by the epitaxy to the substrate, is the same as in the single crystal as seen from the experimental data from ref. 6, which are included in Fig. 2 as open circles.

If the suppression of a lattice instability by the substrate is real, two explanations are possible. Either the smaller softening in the film reveals the pure (weaker) electron phonon-coupling, or the influence of the (stronger) electron phonon interaction in the single crystal is reduced in the films by mechanical stress.

Further information about the electron-phonon interaction may be received from the phonon lineshape: The linewidth of the excitations should reveal the interaction with the electronic continuum in the superconductor as demonstrated for phonons [15] and CEF transitions [16] in systems containing 4*f*-electrons. One expects different behavior of the temperature dependence of the linewidth if the excitation (phonon in this case) lies above or below the superconducting gap. In the first case the linewidth will increase below T_c if the phonon couples to transitions between the increased quasiparticle density of states near the gap, provided the energy of the phonon is not too large compared to the gap. If the phonon lies below the gap $2\Delta(0)$ at $T=0$ the linewidth first should first increase if the gap $2\Delta(T)$ crosses the phonon energy and then decrease exponentially to lower temperatures. The linewidth of the 335 cm^{-1} phonon in the films displays only a slight linear decrease with temperature with no indication of the superconducting transition. This is different from the data from the single crystal where the changes with temperature are larger. In addition, if one extrapolates the high temperature behavior linearly to low temperatures, an increased linewidth may be observed below T_c as expected for a phonon above the gap.

Also the absolute values for the asymmetry parameter q, as shown in Figs. 2–4, reflect weaker coupling of that phonon to the electronic continuum in the films than in the single crystal. The parameter q for the two film samples have almost the same linear temperature shift when the temperature is lowered, but no influence of the superconducting transition can be seen.

IV. Summary

Our results on the temperature dependence of the 335 cm^{-1} phonon in a single crystalline superconductor display the same softening as found by other authors. A less pronounced softening is observed in epitaxial films for this phonon, ascribed here to stress due to the epitaxy to the substrate, which may reduce the influence of the electron-phonon coupling. The overall electron-phonon interaction itself, possibly leading to the superconductivity in this material, is not changed because the superconducting transition temperatures are only slightly reduced and the transitions are very sharp. The coupling is also displayed in the increased linewidth below T_c in the single crystal spectra. From this one can deduce an energy gap $2\Delta(0)$ of the same order as the phonon energy. The influence of a structural transition on the different behavior of films and single crystals cannot be analysed before structural information on the films are available, which could be used for a detailed lattice dynamics calculation.

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