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TEMPERATURE EFFECTS ON THE PHONON SPECTRUM IN $YBa_2Cu_3O_7$ SINGLE CRYSTALS AND THIN FILMS*

R. FEILE and P. LEIDERER

Institut für Physik, Universität Mainz, D-6500 Mainz (F.R.G.)

J. KOWALEWSKI and W. ASSMUS

Physikalisches Institut, Universität Frankfurt, D-6000 Frankfurt (F.R.G.)

J. SCHUBERT and U. POPPE

Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich (F.R.G.)

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Summary

We have performed a detailed investigation of the temperature dependence of the 335 cm^{-1} phonon in single crystals and thin films of the $YBa_2Cu_3O_7$ superconductor by means of Raman spectroscopy. In the single crystal the frequency of this phonon shows a downshift of about 5 cm^{-1} on passing the superconducting transition from above, which is referred to a strong electron–phonon interaction in the superconductor. The shift of the phonon in thin epitaxial films on MgO or $SrTiO_3$ substrates is only about 2.5 cm^{-1}. This difference may be a result of a structural transition in the single crystal which is possibly suppressed in the films because of the epitaxy. The electron–phonon interaction is also indicated by the asymmetry of the phonon line and a slight increase of the linewidth below T_c.

The central question about the high-T_c superconductors is: what is the coupling mechanism for the Cooper pairs to give the high transition temperatures — is it the classical electron–phonon interaction [1] or are other mechanisms [2 - 5] responsible? Raman experiments on the $YBa_2Cu_3O_7$ superconductors [6 - 15] revealed a softening of the 335 cm^{-1} phonon in this material, which differs from the temperature dependence of the other observable phonons. A detailed analysis of the experiments [8, 14, 15] showed that this phonon is confined to the CuO_2 planes. These results support theories which favour phonon-mediated coupling. Our intention was to perform a detailed investigation of the temperature dependence of the 335 cm^{-1} phonon

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and its lineshape, similar to the neutron experiments on phonons [16] and crystal electric field excitations [17] which gave insight into the interactions in which the conduction electrons are involved.

We have investigated three samples by Raman spectroscopy: a single crystal and two sputtered thin films (one on $SrTiO_3$ substrate, the other on MgO). Both films grew epitaxially on their substrates. We have given a detailed description of the samples and the experimental conditions in ref. 18, where we also discussed the problems of exact temperature measurement in the Raman experiment on these highly absorbing materials.

Figure 1 shows the Raman spectra from the single crystal and the films on the two substrates for two temperatures. The line at 335 cm^{-1} has a similar asymmetric lineshape in the three samples. At lower temperature no dramatic changes in the lineshape appear on the frequency scale shown except that the line in the single crystal becomes a little more symmetrical. Further details of the influence of decreasing temperature can be obtained from the values for the different parameters (Figs. 2 - 4) obtained from fitting the Breit–Wigner–Fano lineshape [12, 13], represented by eqn. (1) [19], to the experimental data:

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

Here Ω and Ω_0 are the Raman shift and the centre frequency, respectively, I_0 the intensity, Γ the linewidth, and q the inverse Wigner–Breit–Fano coupling coefficient which in the limit $|q| \rightarrow \infty$ gives a symmetrical lorentzian lineshape.

As already shown in earlier papers on single crystals [10, 12, 13] and polycrystalline thin films [11], the Raman shift first becomes larger for the 335 cm^{-1} phonon when the temperature is lowered from room temperature, and then decreases below the superconducting transition temperature of the material. The softening extends down to the lowest temperature achievable in the experiment, with an overall reduction of the phonon frequency of 5 cm^{-1} in the single crystal, measured from the maximum value at T_c.

In the thin epitaxial films (Figs. 3 and 4), the observed softening of about 2.5 cm^{-1} is only half the value for the shifts in the single crystal. Also, the increase of the phonon frequency between room temperature and T_c is almost zero in both films.

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 behaviour linearly to low temperatures, an increased linewidth may be observed below T_c, as expected for a phonon above the gap.

The parameter q for the two film samples has almost the same linear temperature shift when the temperature is lowered, but no influence of the superconducting transition can be seen.

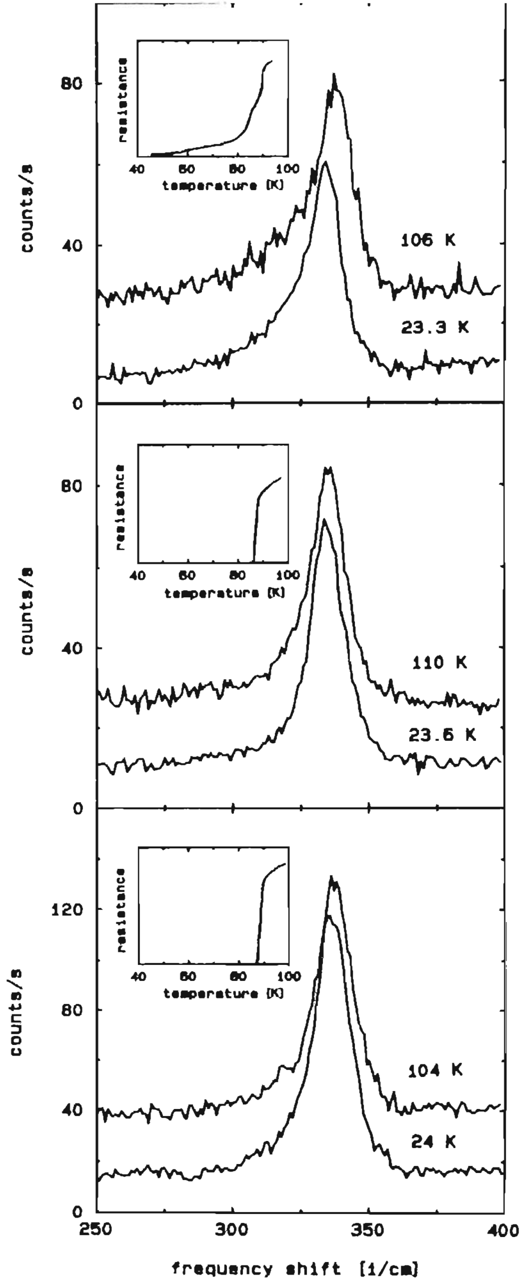

Fig. 1. Raman spectra from the 335 cm^{-1} phonon line in various $YBa_2Cu_3O_7$ samples for several temperatures. The top pair of spectra is obtained from a single crystal, and the middle and bottom pairs from epitaxial films on MgO and $SrTiO_3$ substrates respectively. The insets give the superconducting transitions measured resistively.

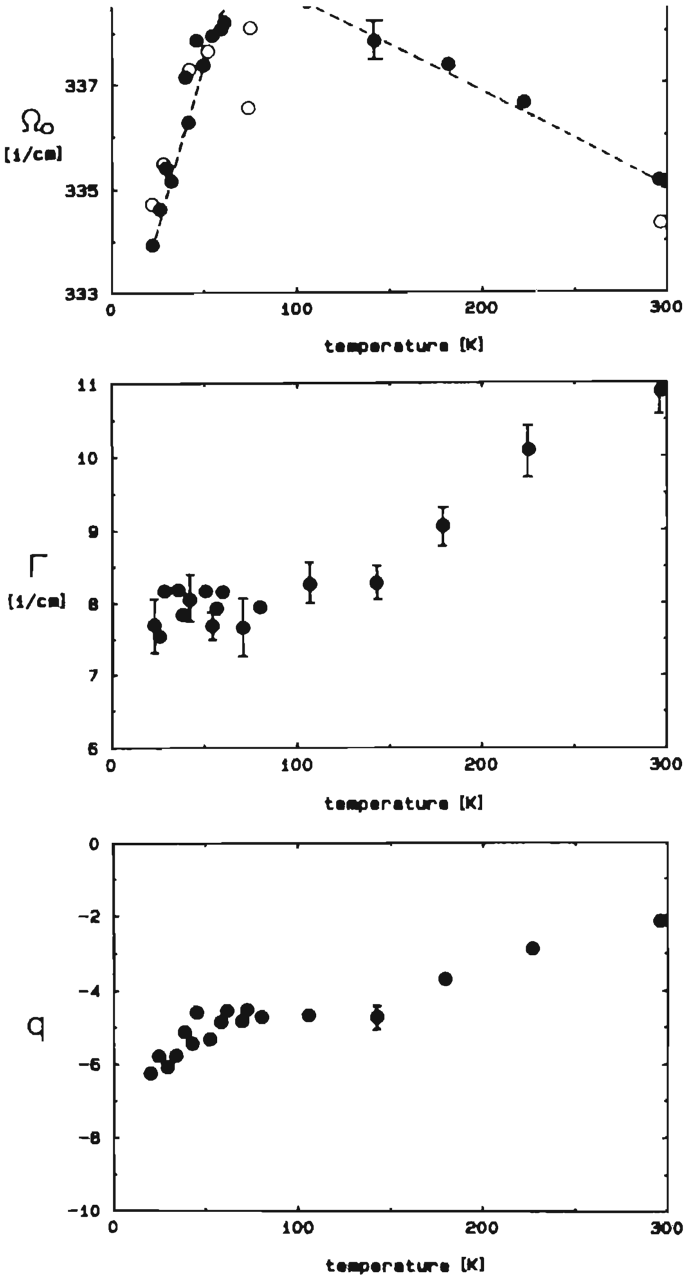

Fig. 2. Temperature dependence of the centre frequency (Ω_0), linewidth (Γ) and asymmetry (q) of the 335 cm^{-1} phonon line in a $YBa_2Cu_3O_7$ single crystal. For details of the Fano lineshape see text. The open circles are the results for the centre frequency obtained from a polycrystalline film [6].

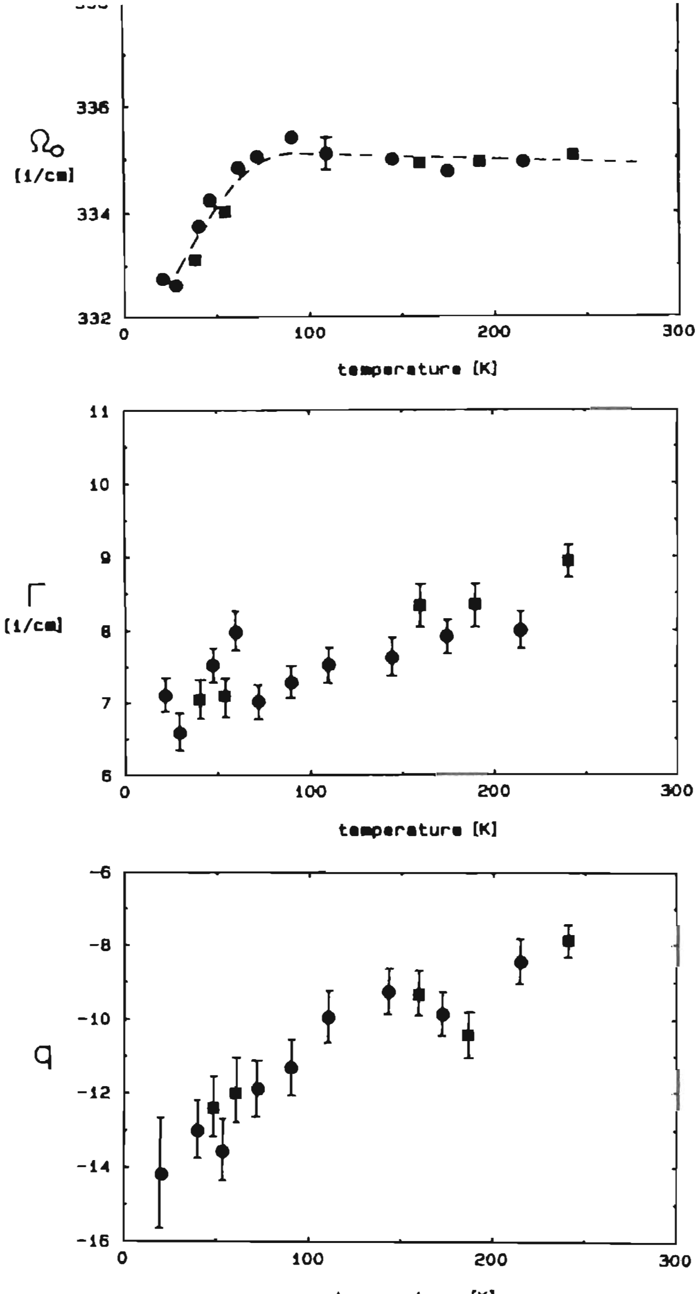

Fig. 3. Temperature dependence of the centre frequency (Ω_0), linewidth (Γ) and asymmetry (q) of the 335 cm^{-1} phonon line in an epitaxial film of $YBa_2Cu_3O_7$ or $SrTiO_3$. For details of the Fano lineshape see text. Squares and circles give the results for two different thermal cycles.

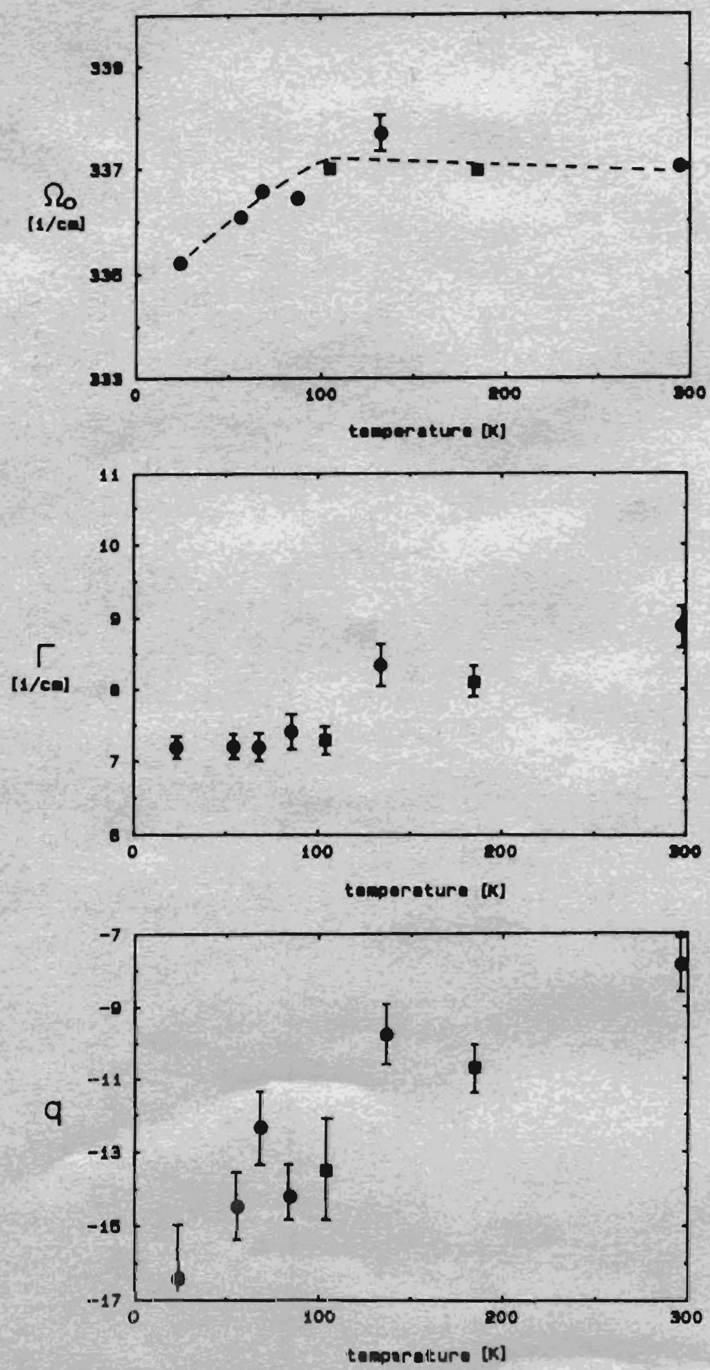

Fig. 4. Temperature dependence of the centre frequency (Ω_0), linewidth (Γ) and asymmetry (q) of the 335 cm^{-1} phonon line in an epitaxial film of $YBa_2Cu_3O_7$ on MgO. For details of the Fano lineshape see text. Squares and circles give the results for two different thermal cycles.

The results for the softening raise the question: is it an effect of the superconducting transition only, or is an additional lattice instability responsible for the frequency shift? A few experimental results support the latter possibility. Datta *et al.* [20] observed re-entrant softening in the $YBa_2Cu_3O_7$ superconductor below T_c, which may resemble the lattice instabilities in the A15 superconductors. Also, structural transformations are observed in neutron diffraction experiments on this high-T_c material [21]. In the thin films, the epitaxy to the substrate leads to additional stress in the film when the temperature is changed and 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 to the substrate by epitaxy, is the same as in the single crystal, as can be seen from the experimental data of ref. 6, which are included in Fig. 2 as open circles.

A further argument for the contribution of at least two effects to the phonon softening is that if only the electron–phonon interaction were reduced in the films then the transition temperature should also be reduced, but this is not the case.

The linewidth of the excitations should reveal the interaction with the electronic continuum in the superconductor, as demonstrated for phonons [16] and CEF transitions [17] in systems containing 4f electrons. One expects different behaviour 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 comapred with the gap. If the phonon lies below the gap $2\Delta(0)$ at $T = 0$, the linewidth should first increase if the gap $2\Delta(T)$ crosses the phonon energy and then decrease exponentially to lower temperatures. The trend of the linewidth below T_c may indicate a gap of the order of the phonon energy.

The increasing absolute value of the inverse coupling parameter q reflects the reduced coupling of the 335 cm^{-1} phonon to the conduction electron system at low temperatures.

To summarize, we found that different behaviour of the 335 cm^{-1} phonon in epitaxial films and single crystals may indicate two contributions to the softening: a structural transition and electron–phonon interaction. The latter also influences the temperature dependence of the phonon lifetime, which itself indicates an energy gap of the order of the phonon frequency.

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