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LETTER TO THE EDITOR

Critical behaviour of bulk phonons in $YBa_2Cu_3O_{7-\delta}$ as observed by infrared absorption spectroscopy

B Güttler†‡, E Salje†‡, P Freeman†, J Blunt†, M Harris†‡, T Duffield§, C D Ager§ and H P Hughes§

† Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, UK

‡ Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

§ Department of Physics, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, UK

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Abstract. The frequencies and the absorption cross sections of infrared active phonons show anomalies related to the transition between the normal and superconducting phase in $YBa_2Cu_3O_7$. The excess intensity of the absorption line and the frequency shift of the mode near 585 cm^{-1} are proportional to each other. Correlating these parameters with the thermodynamic order parameter using hard model spectroscopy leads to an order parameter of the superconducting phase which follows formally mean field theory of the BCS or Landau–Ginzburg type.

The physical role played by phonons in high temperature superconductors is far from being understood [1–5]. The non-existence of isotope effects [6, 7] or apparently temperature-independent bulk phonons [9–10] is controversial in the light of recent observations by Franck *et al* [11] of oxygen isotope effects in $YBa_2Cu_3O_7$. We shall argue in this letter that large (i.e. $\simeq 1\%$) changes of phonon frequencies and excess intensities also exist in the same material. In fact, we shall show that the impact of the superconducting phase transition on optical phonons is very similar to that commonly observed in structural phase transitions and that—in the well-established tradition of investigations of structural phase transitions—a thermodynamic order parameter can be extracted from experimental spectra [12]. This thermodynamic order parameter is closely related to the gap energy which we then find to follow a temperature dependence with BCS or Landau–type behaviour. We have chosen for this study infrared absorption spectroscopy for the following reasons. Firstly, it allows us to observe the frequency of bulk phonons with the highest possible accuracy. Secondly, all visible IR active phonons have polarization vectors perpendicular to the *a–b* plane of the $Cu–O_2$ layers [13]. The relevant gap energy is around 170 cm^{-1} [14] in this direction and around 500 cm^{-1} in the *a–b* plane. The most prominent IR active mode is at 585 cm^{-1} which is well above both gap energies. Phonon renormalization is, thus, direct and not largely influenced by intergap transitions [15].

Temperature-dependent phonon frequencies have already been reported by Genzel *et al* [16] and Obhi and Salje [17]. In this letter we report for the first time the quantitative analysis of such data with respect to intensity and frequency measurement.

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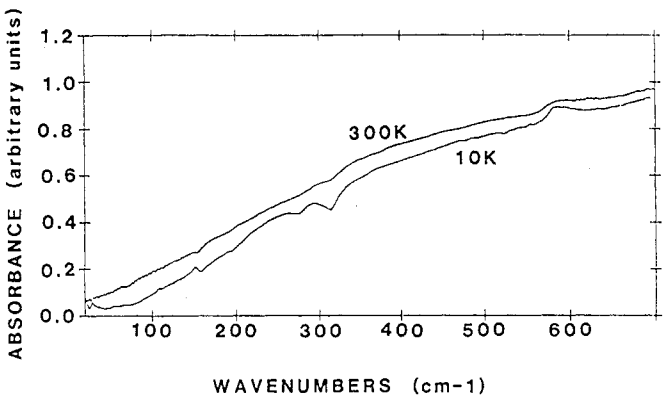

Figure 1. Absorption spectra of $YBa_2Cu_3O_{7-\delta}$ at 10 K and 300 K.

A Bruker IFS 113v spectrometer equipped with a deuterated triglycerine sulphate detector at energies above 400 cm^{-1} was used for data collection. Measurements at lower frequencies between 20 cm^{-2} and 650 cm^{-1} were conducted with a liquid-helium-cooled Si bolometer. The spectral resolution was set to 1.0 cm^{-1}. Sample temperatures between 10 K and 300 K were achieved using an Oxford Instruments constant flow cryostat equipped with KRS–5 and polyethylene windows.

Samples of $YBa_2Cu_3O_{7-\delta}$ were prepared from Y_2O_3, $BaCO_3$ and CuO by a multi-stage process resulting in a single-phase ceramic with $\delta \leq 0.1$. The details of this procedure and sample characterization are described elsewhere [18]. The magnetic properties of the superconducting ceramic were checked before and after the grinding procedure. Magnetic measurements showed the onset of the superconductivity transition around 92 K. The diamagnetic shielding of the ground powder (particle size around 0.1 μm) was found to be about 50% reduced compared with the unground crushed ceramics.

CsI and polyethylene pellets were used for the experiments. The ground starting material was mixed with the predried dilutant (CsI, polyethylene) such that each pellet (13 mm dia.) contained 2 mg of sample. These mixtures were then pressed into pellets (10 tons cm^{-2}) at room temperature. The pellets were held at room temperature under dry conditions (desiccator, silica gel) and were measured within a maximum of 24 h after preparation. Pellets of the pure dilutant were used as a reference. The first deterioration effects were found after about three weeks if the sample was kept under these conditions. Pellets kept in a drying oven (100 °C) showed deterioration effects within 24 h. The deterioration results in the appearance of additional peaks in the absorption spectrum between 400 cm^{-1} and 500 cm^{-1} and between 200 cm^{-1} and 300 cm^{-1}. Similar peaks were found in deteriorated powders of $YBa_2Cu_3O_{7-\delta}$ with vanishing diamagnetic shielding.

Absorption spectra of superconducting powder at 10 K and 300 K are shown in figure 1. The complete phonon frequency range of $YBa_2Cu_3O_{7-\delta}$ as measured by absorption spectroscopy is shown here for the first time. The spectra exhibit an electronic background increasing almost linearly towards higher energies at room temperature. This background is overlain by phonon bands at about 152 cm^{-1}, 193 cm^{-1} and 585 cm^{-1} and a complex double-peak structure around 300 cm^{-1}. These features are in good agreement with data from reflection spectroscopy concerning their number and position [16] but we cannot confirm the extreme intensity observed by Genzel *et al* [16] for the 152 cm^{-1}

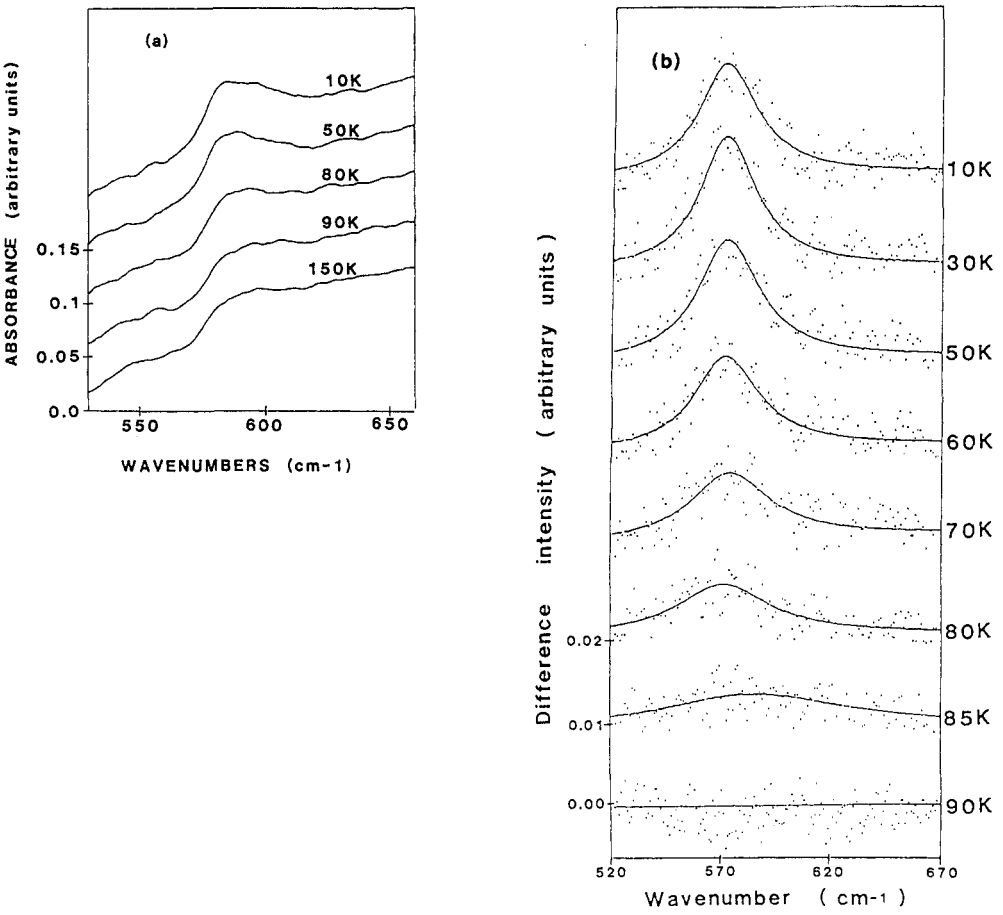

Figure 2. (a) Temperature effect of the mode near 585 cm^{-1} at various temperatures. (b) Difference absorption spectra of the mode near 585 cm^{-1} showing the absorption spectra at various temperatures substracted by the absorption spectra at 150 K. The line indicates the result of a least-square-fit procedure using a Lorentzian line profile.

mode; this discrepancy may well be related to surface grain size effects [19] in Genzel's reflection measurements. Our direct observation of the intensity changes in an absorption experiment is also in good agreement with the results of the Kramers–Kronig analysis of reflection spectra by Genzel *et al*. Recent experimental results by Obhi and Salje [17] on Co–doped $YBa_2Cu_3O_7$ are in full agreement with our findings. These authors also demonstrate that the change in T_c with the degree of Co content is also found in the temperature dependence of the phonon spectra.

All the phonon bands reveal a distinct temperature dependence at low temperatures. The temperature dependence of the 585 cm^{-1} mode is shown in figure 2. This mode is of particular interest because its energy is significantly larger than the highest estimates made for the superconducting gap energy ($\sim 8\,kT_c \sim 500\ cm^{-1}$) [6, 14]. This is important as it excludes electron–phonon interaction effects related to the excitation of charge carriers across the energy gap. Such effects have been observed in conventional superconductors and can cause sudden changes of phonon bands with energies $\omega < 2\Delta$ [15].

We used the temperature dependence of the 585 cm^{-1} mode in the vicinity of the phase transition around 92 K for an evaluation of the transition behaviour on a thermodynamic basis. The excess free energy related to any phase transition should lead to a phonon renormalization provided a physical coupling mechanism between the mode susceptibility and the order parameter exists. We do not wish to repeat the general results of coupling theory at this point and refer to [20–24] for further reference. Symmetry considerations show that a nonlinear coupling of the type $\xi Q_1^2 Q^2$ between the phonon normal coordinate Q_1 and the thermodynamic order parameter Q is always compatible with the symmetry requirements of the phonon [24]. The strength ξ obviously depends on the physical mechanism of the coupling and the polarization of the phonon mode (i.e. *c*-axis in this case). Here we argue that the strength is non-zero even for modes with phonon energies well above the superconducting gap energy. The coupling strength between the mode frequency and the thermodynamic order parameter has already been discussed by Obhi and Salje [17] and its consequences for other thermodynamic properties, such as the specific heat, were outlined by Salje [25]. Here we concentrate on the temperature evolution of the absorption cross section.

The excess intensity of the 585 cm^{-1} mode related to the low temperature phase is shown by the difference spectra shown in figure 2. The spectrum at 150 K is subtracted from the spectra at lower temperatures. Let us normalize $Q = 1$ at absolute zero temperature. We then find that the absorption intensity of the mode i at any temperature T in the low temperature phase is:

$$A_i(T) = A_i(150\ \mathrm{K})(1 + \alpha Q(T)^2)$$

with $\alpha = 0.9 \pm 0.1$ for the 585 cm^{-1} mode. The temperature dependence of the total intensity $A_{585\,cm^{-1}}$ and the frequency shift $\omega_{585\,cm^{-1}}$ are shown in figure 3. The intensity increases almost linearly for $T_c > T > \frac{1}{2}T_c$ on lowering the temperature while a mode softening of about 5 cm^{-1} is observed at the same time. The temperature effect flattens out at lower temperatures. The expected proportionality between the excess intensity ΔA_i and the excess frequency $\Delta\omega_i$ of the mode i in the low temperature phase is shown in figure 4. Figure 5(a) shows a comparison between the temperature dependence of $\Delta A_{585\,cm^{-1}}$ and the square of the gap energy as predicted by BCS theory. We find a reasonable agreement between our data and the BCS curve. This, of course, does not imply that BCS theory is directly relevant for $YBa_2Cu_3O_{7-\delta}$ but only shows that the temperature dependence of the order parameter is formally BCS-like [14, 26, 27]. In fact, Salje *et al* [28] have shown that Landau–Ginzburg energy in which saturation is properly taken into account leads to numerically the same results as BCS theory although starting from a totally different microscopic Hamiltonian. Although the largest frequency shift was found for the 585 cm^{-1} mode, most other phonons showed similar effects. The modes near 300 cm^{-1} possess rather large temperature dependencies of the absorption cross section (figure 5(b)). Our results are also in good agreement with recent observations by Kuztmary *et al* [29] who found temperature dependencies of the mode frequencies near 312 cm^{-1}, 190 cm^{-1}, 154 cm^{-1} and 90 cm^{-1}. Only the mode at 190 cm^{-1} shifts by 4 cm^{-1} whereas the other shifts are between 1 cm^{-1} and 2 cm^{-1} which are presumably too small for a quantitative analysis in the same manner as for the 585 cm^{-1} mode.

In conclusion, we have shown unambiguously that phonon renormalization of infrared active modes due to the superconducting phase takes place. The order of magnitude of the frequency shifts is as great as in structural phase transitions with typical stabilization excess Gibbs energies of the low symmetry phase of some 2–5 kJ mol^{-1}.

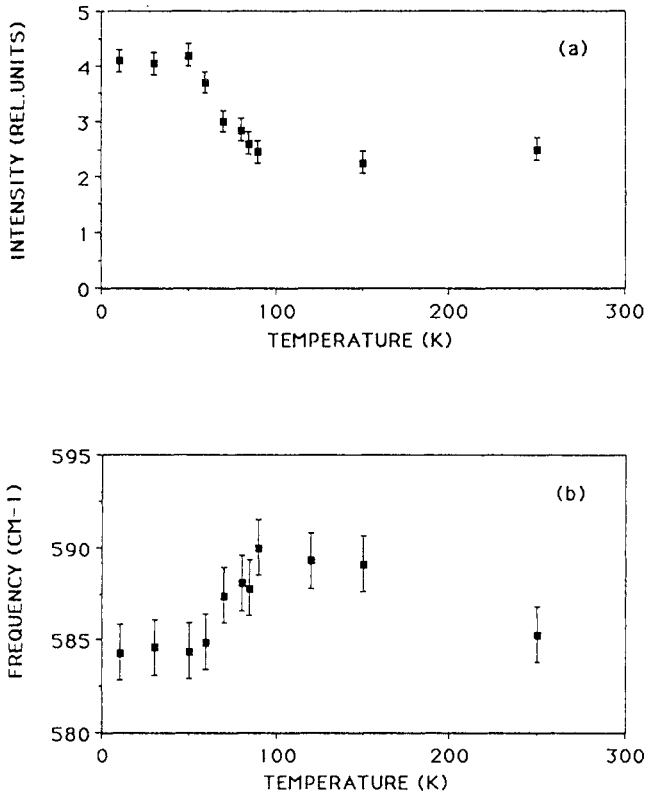

Figure 3. Temperature dependence of the mode intensity (a) and frequency (b) of the mode near 585 cm^{-1} between 10 K and 250 K.

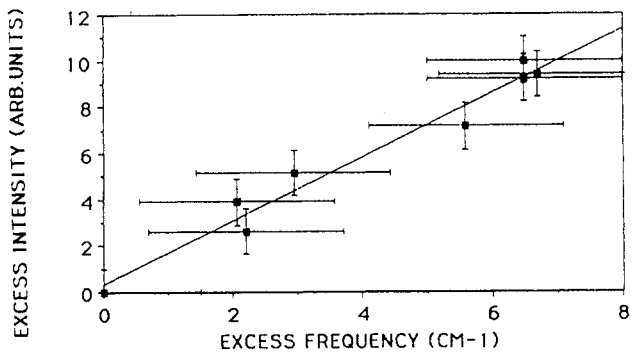

Figure 4. Excess intensity against excess frequency of the mode near 585 cm^{-1} in the low-temperature phase ($T \leqslant 92$ K). The line is a guide for the eye.

Phonons are, thus, relevant for the *thermodynamic* stability of the superconducting phase. Finally, although we wish to abstain from the discussion of our experimental results in terms of microscopic theories, it is relevant to note that large phonon effects of this kind due to purely magnetostrictive coupling, or its like, are exceedingly improbable. Also, due to the short correlation length of the superconducting carriers, the effect of

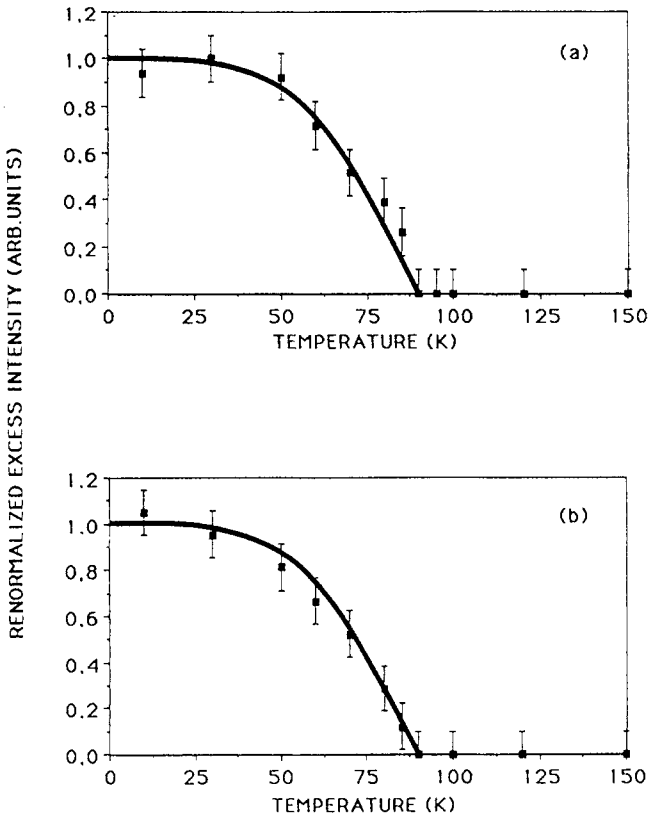

Figure 5. Temperature dependence of the modes near 585 cm^{-1} (a) and 300 cm^{-1} (b) at low temperatures. Squares indicate the normalized excess intensities in arbitrary units. The curves show the square of the temperature dependence of a BCS-like gap energy.

the phonon coupling is not sharply restricted in k-space leading to changes of around 1% in the frequency spectrum of the phonon density of states. This, in turn, leads to phononic specific heat anomalies as discussed by Salje [25]. Our results clearly support his arguments.

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