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# Far-infrared reflectivity study of vibrational structure in superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

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**Abstract.** We report the anomalous temperature behaviour of phonons in the superconducting  $a$ -axis-oriented  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  texture detected by far-infrared reflectivity spectroscopy.

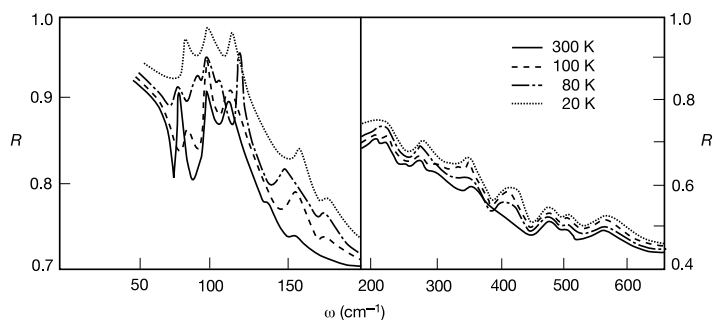
## 1. Introduction

Since the discovery of YBCO superconductors, many Raman and infrared studies have been devoted to the analysis of the phonon properties of this compound below and above the superconducting transition [1–5]. Two types of anomalous temperature dependence of vibrational modes have been found around  $T_c$ . One is a softening of some modes which has been explained by a strong-coupling model [1, 2]. The other is caused by the Fano effect [5].

There are a few reports on phonon anomalies in the bismuth superconductors [6–8]. Infrared measurements are insufficient. In this paper we present the spectra of reflectivity and loss function of a  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  texture in a frequency range 50–700  $\text{cm}^{-1}$  at temperatures of 20, 80, 100 and 300 K. The new results show firstly a softening of the 153  $\text{cm}^{-1}$   $A_{2u}$  mode near  $T_c$ , secondly the splitting of the phonon structure below 120  $\text{cm}^{-1}$  at a temperature in the vicinity of the superconducting transition and thirdly increases in the strength and the linewidth of the 280  $\text{cm}^{-1}$  in-plane oxygen phonon ( $B_{2u}$ ) at  $T < T_c$  without detecting a frequency shift and the appearance of minima or an antiresonance feature in the loss-energy function near 280  $\text{cm}^{-1}$  instead of maxima, indicating a strong Fano-type electron–phonon interaction.

## 2. Experiment and results

The measured sample of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  (2212) were obtained using the ‘out-of-the-crucible’ zone-melting technique [9]. The samples are characterized by a highly oriented grain structure which consists of bond-like and rod-like single crystals of dimensions 0.1 mm  $\times$  (0.5–5) mm  $\times$  20 mm aligned parallel to the growth direction of the  $a$  axis. The 2212 material has the centrosymmetric space group  $D_{4h}^{17}$  with unit-cell parameters  $a = b = 5.413(2)$  Å and  $c = 30.75(2)$  Å. Textured samples have a marked anisotropic electrical resistivity at the value of  $\rho(\rho_{\perp}/\rho_{\parallel} = 300 \text{ K})$  [10]. The  $\rho_{\parallel}(T)$  dependence shows a superconducting transition at  $T_c = 83 \text{ K}$  with a width of 4 K.



**Figure 1.** Infrared reflectivity spectra of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$  at 20, 80, 100 and 300 K.

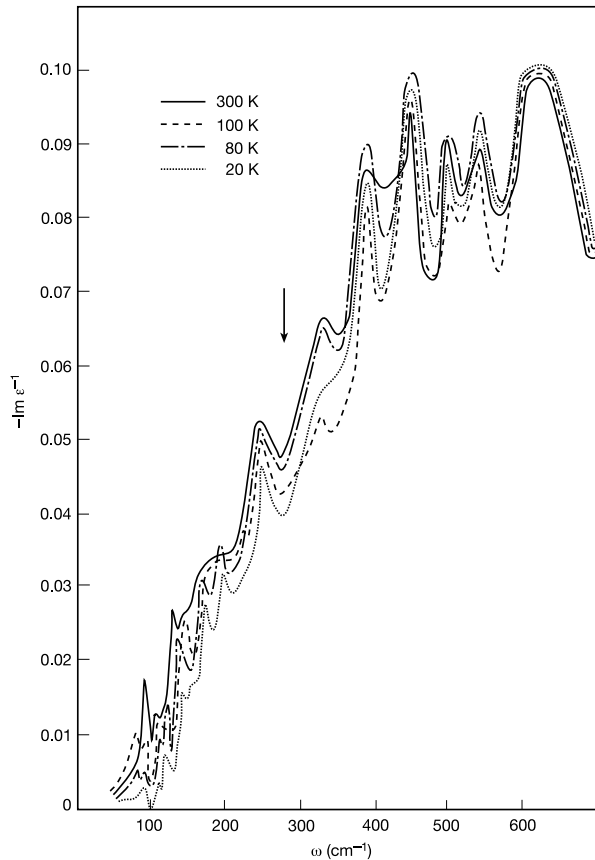
**Table 1.** The changes in the peak positions with temperature.

| Frequency ( $\text{cm}^{-1}$ ) |       |      |      |
|--------------------------------|-------|------|------|
| 300 K                          | 100 K | 80 K | 20 K |
| 225                            | 225   | 220  | 220  |
| 210                            | 210   |      |      |
| 153                            | 158   | 150  | 155  |
| 120                            | 120   | 110  | 120  |
|                                |       | 125  |      |
| 100                            | 100   | 100  | 100  |
| 80                             | 85    | 80   | 85   |
|                                |       | 90   |      |

**Table 2.** Frequencies  $\omega$ , linewidths  $\gamma$  and oscillator strengths  $f$  of the phonons in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$  superconductor at  $20 \text{ K} \leq T \leq 100 \text{ K}$ .

| 300 K                            |                                  |      | 100 K                            |                                  |      | 80 K                             |                                  |       | 20 K                             |                                  |      |
|----------------------------------|----------------------------------|------|----------------------------------|----------------------------------|------|----------------------------------|----------------------------------|-------|----------------------------------|----------------------------------|------|
| $\omega$<br>( $\text{cm}^{-1}$ ) | $\gamma$<br>( $\text{cm}^{-1}$ ) | $f$  | $\omega$<br>( $\text{cm}^{-1}$ ) | $\gamma$<br>( $\text{cm}^{-1}$ ) | $f$  | $\omega$<br>( $\text{cm}^{-1}$ ) | $\gamma$<br>( $\text{cm}^{-1}$ ) | $f$   | $\omega$<br>( $\text{cm}^{-1}$ ) | $\gamma$<br>( $\text{cm}^{-1}$ ) | $f$  |
| 280                              | 22                               | 0.33 | 280                              | 24                               | 0.36 | 280                              | 32                               | 0.48  | 280                              | 32                               | 0.48 |
| 153                              | —                                | —    | 158                              | 12                               | 0.67 | 150                              | 12                               | 0.637 | 155                              | 10                               | 0.53 |

Reflectivity spectra in the frequency region  $50\text{--}5000 \text{ cm}^{-1}$  were obtained with a Bruker FTS 113v spectrometer in the temperature range  $20\text{--}300 \text{ K}$ . A SF-8 spectrophotometer was used in frequency region  $5000\text{--}10000 \text{ cm}^{-1}$  at  $300 \text{ K}$ . Reflectivity spectra of the  $2212$   $a$ -axis-oriented plate at  $20, 80, 100$  and  $300 \text{ K}$  are presented in figure 1. The phonon peaks visible at  $300 \text{ K}$  are  $80, 100, 120, 153, 210, 225, 280, 350, 415, 475, 505$  and  $565 \text{ cm}^{-1}$ . These frequencies are close to the data of previously published reports [11–13]. The main temperature changes are observed at low frequencies below  $300 \text{ cm}^{-1}$ . The phonon structure caused by Bi vibration at  $85, 100$  and  $120 \text{ cm}^{-1}$  in the  $100 \text{ K}$  spectrum appears to split into the  $80, 90, 100, 110$  and  $125 \text{ cm}^{-1}$  peaks at  $80 \text{ K}$ . The splitting vanishes at  $20 \text{ K}$  and its origin is still unclear. In contrast the doublet at  $210$  and  $225 \text{ cm}^{-1}$  in the  $300 \text{ K}$  spectrum is transformed into the singlet at  $220 \text{ cm}^{-1}$  upon cooling to  $20 \text{ K}$ . Perhaps these effects indicate local changes in the crystal composition of the oxygen-deficient  $2212$  superconductors near  $T_c$ . The frequency of phonons as a function of temperature is shown in table 1. Between  $300 \text{ K}$  and  $100 \text{ K}$  the  $153 \text{ cm}^{-1}$  mode displays the normal shift to higher



**Figure 2.** The imaginary part of the inverse dielectric function,  $-\text{Im}(-1/\epsilon)$ , of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$  at 20, 80, 100 and 300 K.

frequencies ( $\Delta\omega = 5 \text{ cm}^{-1}$ ); the phonon softens, its frequency falling  $8 \text{ cm}^{-1}$  by 80 K (see figure 1). Simultaneously, the  $153 \text{ cm}^{-1}$  phonon exhibits slight decreases in linewidth and oscillator strength below  $T_c$ . The phonon near  $150 \text{ cm}^{-1}$  has been assigned to the  $\text{Sr}(z) A_g$  mode or the  $\text{Cu}(2)$  vibration analogous to YBCO [8]. Phonon parameters were obtained by Kramers–Kronig transformation of the reflectivity, fitting the  $\text{Im}[\epsilon(\omega)]$  spectra to Lorentzian lineshapes, and are summarized in table 2. The temperature behaviour of the  $B_{2u}$  mode at  $280 \text{ cm}^{-1}$  (see figure 1) is also illustrated in table 2. In the superconducting state both the linewidth and the strength of the  $280 \text{ cm}^{-1}$  phonon show anomalous increases upon cooling to 20 K, while no frequency anomaly is detected. Such anomalous broadening of the  $B_{1g}$ -like phonon is known for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  below  $T_c$  [7]. The phonon at  $280 \text{ cm}^{-1}$  has been identified as the out-of-phase  $c$ -axis vibration of the O atoms in the  $\text{CuO}_2$  planes, analogous to the  $340 \text{ cm}^{-1}$  mode in YBCO [1, 3]. In contrast, the linewidth of the corresponding  $B_{1g}$  mode at  $285 \text{ cm}^{-1}$  decreases in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  crystal and is observed by Raman scattering below  $T_c$  [6]. The broadening and narrowing effects depend on the position of the phonon relative to the energy gap and are described by the theory of Zeyer and Zwicknagl [1]. The effect of gap formation on the frequency, linewidth and oscillator strength of the  $153$  and  $280 \text{ cm}^{-1}$  phonons is seen in table 2. The results of Drude–Lorentz fits to the reflectivity support these data. The low-frequency phonon at  $153 \text{ cm}^{-1}$  and in-plane oxygen

mode at  $280\text{ cm}^{-1}$  show controversial temperature behaviours. Anomalous broadening of the  $280\text{ cm}^{-1}$  phonon is related to the Fano-type interaction. Figure 2 displays a loss function,  $-\text{Im}(-1/\epsilon)$ , calculated by a Kramers–Kronig analysis at selected temperatures. The feature of this temperature dependence is the ‘suppression’ of the peak at  $320\text{ cm}^{-1}$  and the appearance of minima near  $280\text{ cm}^{-1}$  below  $T_c$ . This result indicates a strong Fano-type electron–phonon interaction and supports the fact that the  $a$ – $b$  plane response affects the phonon structure in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  [5, 10].

### 3. Conclusions

In summary, we have presented anomalous temperature changes of some phonons below  $300\text{ cm}^{-1}$  in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  superconductor at temperatures between 300 K and 20 K. We have observed softening of the  $153\text{ cm}^{-1}$   $A_{2u}$  mode with a decrease in its linewidth below  $T_c$  and broadening of the  $B_{2u}$   $280\text{ cm}^{-1}$  phonon without detecting a frequency change upon cooling to 20 K. In principle the linewidth of phonons with an energy below the superconducting gap decreases in the superconducting state because the superconductivity reduces the number of possible electronic decay channels, while phonons above the gap broaden in the superconducting phase [1, 6]. Assuming the existence of a superconducting gap or pseudo-gap, we can estimate an energy gap value  $2\Delta$  as follows:  $150\text{ cm}^{-1} < 2\Delta < 280\text{ cm}^{-1}$ .

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