Journal of Alloys and Compounds, 195 (1993) 355–358
JALCOM 7484

Comparison of IR - active phonons In YBCO ceramics with different carrier concentrations

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Abstract

We report on a study of temperature dependent far infrared reflectivity measurements of partly substituted YBCO ceramics with different carrier concentrations. Reflectivity spectra show, depending on the carrier concentration, high metallic reflectivity and strong phonon structures. A comparison of the data of these measurements shows that the temperature dependent phonon response clearly scales with T_C. A theoretical fit based on the two fluid model can be used to describe the phonon behavior. The assumption of a superconducting gap derived from these measurements will be discussed. Below the critical temperatures a correlation between phonons and superconducting carriers was found. From these data an energy gap in the superconducting states can be estimated. The assumption of a superconducting BCS-like gap in the range of 3.2 k_BT to 4.6 k_BT is consistent with our data.

1. Introduction

Since the discovery of the HT_C structures worldwide activities started to find an energy gap or at least some spectral features giving evidence for a superconducting pairing by infrared spectroscopy. By using single crystals or crystalline thin films, oriented reflectivity can be measured. Due to the high normal state reflectivity a superconducting gap cannot be extracted by a Kramers Kronig transformation [1]. Various groups claim the existence of a large gap [2,3], some authors argue for an anisotropic gap distribution [4], while others believe that a gap cannot be seen [5]. In addition the interpretation of reflectivity spectra is complicated due to a mid-infrared absorption, the origin of which is still unknown.

Evidence for strong phonon interaction was given by Raman scattering[6] and infrared measurements [7]. We use IR-active phonons to probe changes in the underlying electronic continuum. From the changes in the phonon response at the transition temperature we want to investigate the existence of superconducting carriers at a certain phonon frequency.

2. Samples

The critical temperature of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples decreases with increasing substitution of copper by zinc atoms, while the carrier concentration remains constant. Substituting yttrium by praseodymium leads to a reduction of the carrier concentration and decreasing T_C with increasing praseodymium concentration. Additional substitution of yttrium by calcium compensates the reduction of the carrier concentration and the superconducting properties remain. To get a set of samples with different T_C's and different carrier concentrations, we substituted Y by Pr and Ca. This substitution leads to a hole filling and pair breaking as described elsewhere [8,9].
$YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ and $Y_{1-X-Y}Pr_XCa_YBa_2Cu_3O_7$ samples were prepared by solid-state reaction of appropriate mixtures of high purity CuO, Y_2O_3, ZnO, Pr_6O_{11}, $CaCO_3$ and $BaCO_3$. Oxygen stoichiometry was kept constant as described in Ref. 8. The set of samples used for FIR measurements is listed in Table 1.

Composition	Sample	T_C
$YBa_2Cu_3O_{7-\delta}$	Zn1	92K
$YBa_2(Cu_{0.99}Zn_{0.01})_3O_{7-\delta}$	Zn2	78K
$YBa_2(Cu_{0.975}Zn_{0.025})_3O_{7-\delta}$	Zn3	61K
$YBa_2(Cu_{0.95}Zn_{0.05})_3O_{7-\delta}$	Zn4	46K
$YBa_2Cu_3O_7$	Pr1	92K
$Y_{0.72}Ca_{0.08}Pr_{0.2}Ba_2Cu_3O_7$	Pr2	76K
$Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$	Pr3	75K
$Y_{0.6}Pr_{0.4}Ba_2Cu_3O_7$	Pr4	48K
$PrBa_2Cu_3O_7$	Pr5	-

Table 1: Zn, Pr and Ca substituted "123" ceramics and their T_C's

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3. Experimental

FIR reflectivity measurements are performed with a Fast Fourier Transform spectrometer in the range from 20 cm^{-1} to 650 cm^{-1}. Absolute reflectivities of the samples were obtained using a diffuse reflection unit, as a reference a gold mirror was used. The resolution of the system was set to 0.5 cm^{-1}. Temperature dependent measurements between 6K and 300K are performed with a continuous flow cryostat.

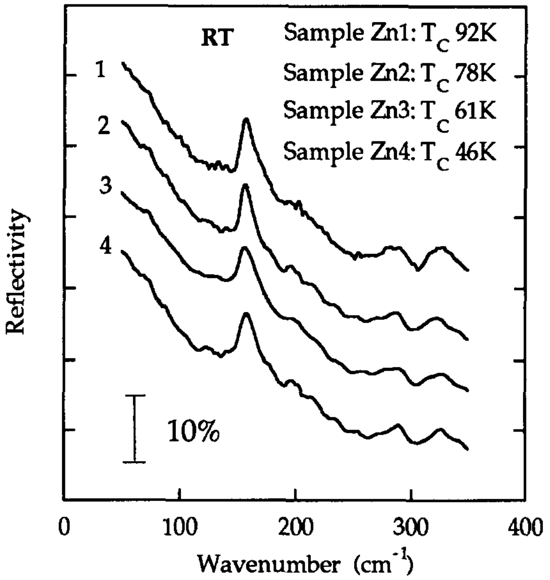

Fig. 1: FIR reflection of Zn samples at room temperature. Different curves are shifted by 0.1 respectively.

Fig. 1 shows the measured FIR reflection spectra of our set of Zn substituted samples. For better clarity each spectrum is shifted by 0.1. It can be seen that there are only minor differences in the reflectivity behavior and no changes in the phonon frequencies. Thus, above T_C, we believe to have a set of samples with different T_C's (Table 1), but the same phonons and a comparable electronic continuum. Changes in the spectra below the critical temperature belong to differences in the superconducting states.

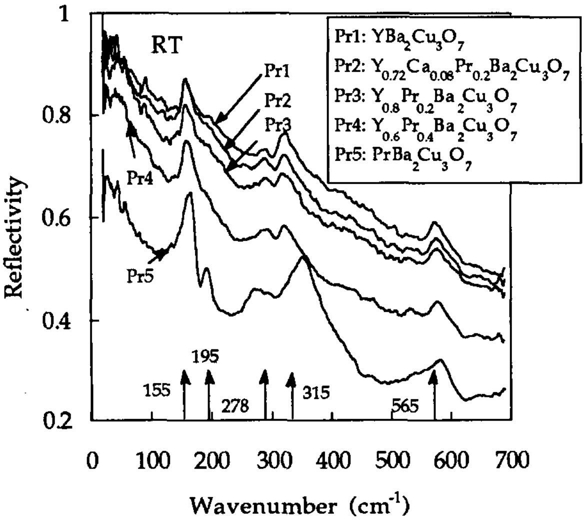

Fig. 2: FIR reflection data of samples Pr1 to Pr4 at room temperature.

Fig. 2 shows the measured FIR reflection spectra of our set of Pr substituted samples at room temperature. It can be seen that except for the pure Pr sample there are only minor differences in the reflectivity behavior and no changes in the phonon frequencies. The reduction of the reflectivity is caused by the lower carrier concentration.

From the reflection behavior of sample Pr5 (PrBaCuO) a shift in the phonon positions can clearly be seen. The size of this shift can be explained by the displacement of the IR active phonons, taking the Y/Pr position into account.

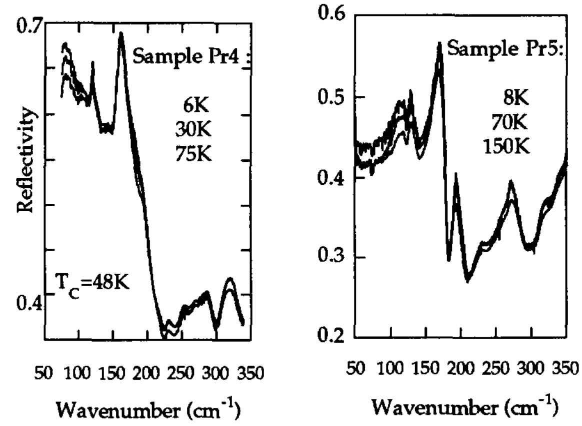

Fig. 3: Temperature dependent measurements of sample Pr4 and Pr5.

Fig. 3 shows the temperature dependent FIR reflectivity of sample 4 and 5. Beside the different phonon positions and a reduced absolute reflectivity of sample 5 the behavior of these two samples is compatible . There is no indication for a pronounced

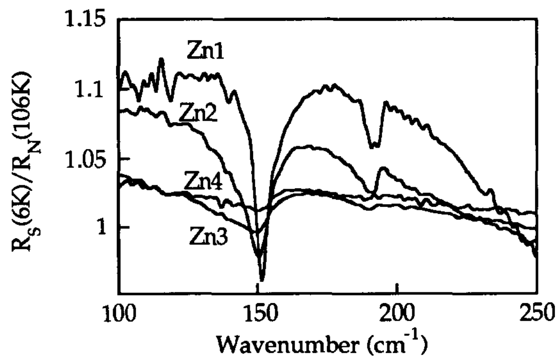

Fig. 4: Reflectivity ratio of the superconducting to the normal conducting reflectivity Rs/Rn of the Zn samples.

temperature dependence of the phonons. The only deviation is an increase of the reflectivity at lower temperatures for sample 4 below the lowest phonon energy (120 cm^{-1}). In Fig. 4 the ratio of the superconducting to the normal conducting reflectivity Rs/Rn of the Zn substituted samples are shown. An increase of the reflectivity below T_C can clearly be seen, indicating an increase due to the superconducting carriers. The response of the phonons below 200 cm^{-1} narrows and changes from dispersive in the normal state to absorptive in the superconducting state. This qualitative change in the phonon response can be assumed as evidence for the existence of superconducting carriers at this energy, which is consistent with a gap energy larger than the phonon energy.

This phonon behavior is not existing in Fig. 3, an indication that for sample Pr4 and Pr5 there are no superconducting carriers. above 120 cm^{-1} .

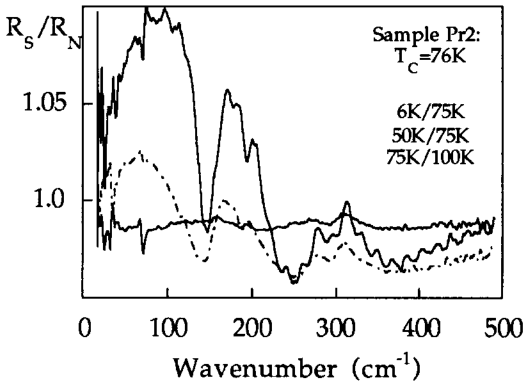

Fig. 5: Reflectivity ratio of the superconducting to the normal conducting reflectivity Rs/Rn of sample Pr2 at different temperatures.

In Fig. 5 sharp minima at the phonon positions and a reflection enhancement proof that there is a drastic change in the underlying electronic continuum at the transition temperature.

4 Dielectric Function and FIR Reflectivity

Different theoretical approaches were used to describe the reflection behavior of HT_C ceramics: fits with one, a set or without any energy gap have been used to describe the reflectivity data of one particular set of samples. As shown before [10] we are able to fit our YBaCuO reflectivity data with a fit including a BCS-like gap as well as with a mid infrared oscillator model. In this paper we want to show, that a set of samples with different grades of substitutions can be described with a BCS like gap and a two fluid model.

A model dielectric function according to the Mattis-Bardeen model[11] can be used to obtain the frequency and temperature dependent reflectivity[12].

Thus, the total model dielectric function used here is

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \hat{\varepsilon}_{Ph}(\omega) + (1 - f_s)\hat{\varepsilon}_D(\omega) + f_s\hat{\varepsilon}_{SC}(\omega) \quad (1)$$

where e. is a real constant and

$$\hat{\varepsilon}_{Ph}(\omega) = \sum_j \frac{\omega_{TOj}^2 \Delta\chi_j}{(\omega_{TOj}^2 - \omega^2 - i\Gamma_j\omega)} \quad (2)$$

is the harmonic oscillator model dielectric function for phonons. w_{TOj} stands for the phonon frequency, $\Delta^c{}_j$ is the oscillator strength, and G_j is the damping frequency of the corresponding phonon j (typical values for our samples are given in Table 4).

The Drude dielectric function

$$\hat{\varepsilon}_D(\omega) = -\frac{\omega_p^2}{(\omega\ (\omega\ -i\omega_\tau)} \quad (3)$$

contains a plasma frequency w_p and a frequency dependent damping w_t.

The contribution of the superconducting carriers to the dielectric function is

$\hat{\varepsilon}_{SC}(\omega) = \frac{4\pi}{i\omega}\hat{\sigma}_{SC}(\omega)$, where $s_{SC}(w)$ is given in[11]. The real and the imaginary part of the dielectric function for the superconducting carriers can be written as

$$\varepsilon_{1SC} = -\frac{\varepsilon_{2D}}{2}\left[(1+\beta)E\left(\frac{2\sqrt{\beta}}{1+\beta}\right) - (1-\beta)K\left(\frac{2\sqrt{\beta}}{1+\beta}\right)\right] \quad (4)$$

$$\varepsilon_{2SC} = \varepsilon_{2D}\left[(1+\beta)E\left(\left|\frac{1-\beta}{1+\beta}\right|\right) - 2\beta K\left(\left|\frac{1-\beta}{1+\beta}\right|\right)\right]\Theta(1-\beta)$$

where β is the ratio $\frac{E_g}{hw}$ and E(m) and K(m) are elliptic integrals of the first and second kind. Θ is a step function, representing the imaginary part of e_{2SC} which vanishes below the superconducting gap E_g.

The factor f_S (the ratio of superconducting to not superconducting carriers) in equation (1) takes into account that not all carriers are superconducting. This two fluid model includes the temperature dependent ratio of the free carriers and a non temperature dependent portion of carriers at T=0K. This normalconducting carriers can be located in nonsuperconducting surface regions as well as between different grains. Within this model we calculate the FIR reflectivity

$$R(\omega) = \left(\frac{\sqrt{\hat{\varepsilon}(\omega)} - 1}{\sqrt{\hat{\varepsilon}(\omega)} + 1}\right)^2 \quad (5)$$

5. Results

A theoretical fit based on a modified two fluid model[13] can be used to describe the temperature dependent phonon behavior. As long as there is a reasonable number of carriers in the superconducting state, we are able to distinguish from the shape of the phonon response, whether there is a gap well above, well below or in the vicinity of the phonon energy. Thus, phonons in superconductors are a good tool to proof the existence and even the size of an energy gap.

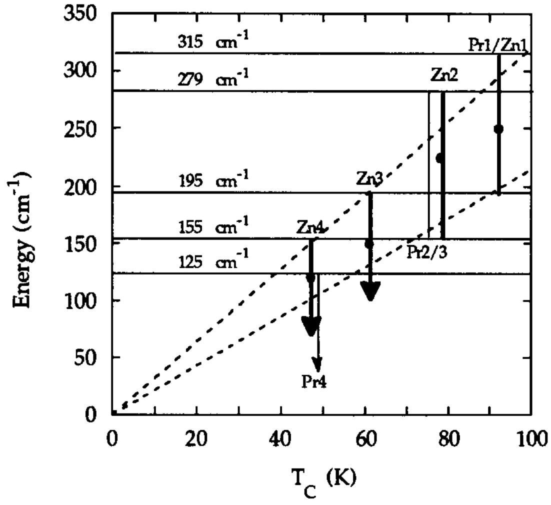

Fig. 6: Energy gap over T_C: Vertical bars indicate the possible range of E_G for the different samples, horizontal lines show phonon positions. Dashed lines indicate the lower and upper limits for an energy gap, assuming linear E_G over T_C dependence. Solid dots indicate where a reflectivity increase due to superconducting carriers takes place.

From the above discussion we are able to give an estimation for an energy gap in the different samples shown in Fig. 6. The range where an energy gap is located is indicated by a vertical bar at T_C for the different samples. Horizontal lines are positioned at the phonon energies. Looking at the phonon response in the above described way, a gap for sample Zn1 and Pr1 is located between the two phonons at 195 cm^{-1} and 315 cm^{-1}. For sample Zn2, Pr2 and Pr3 a gap is expected between 155 cm^{-1} and 279 cm^{-1}. A decision, whether a gap for these samples is above or below 195 cm^{-1} cannot be made, because this phonon shows a mixture of absorptive and dispersive behavior. This is an indication for an energy gap close to 200 cm^{-1}. The gap region for sample Zn3 lays below 195 cm^{-1}, for sample Zn4, Pr4 and Pr5 it is below 155 cm^{-1}. If we assume a linear gap over T_C dependence, this estimate leads to a lower and an upper limit for an energy gap as shown in Fig. 6 by the two dashed lines.

Thus an energy gap range between 3.2 k_BT_C and 4.6 k_BT_C can be given.

6. Summary

We have performed temperature dependent FIR reflectivity measurements on Zn, Pr and Ca substituted $YBa_2Cu_3O_{7-\delta}$ ceramics. A theoretical fit based on a modified two fluid model can be used to describe the temperature dependent phonon behavior. From the phonon and the overall reflectivity behavior these data show strong evidence of a energy gap in the superconducting states. If we assume a linear gap over T_C dependence, this leads to a lower and an upper limit for an energy gap between 3.2 k_BT_C and 4.6 k_BT_C.

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