Fine structure of IR reflection spectra of $YBa_2Cu_3O_{6+x}$ single crystals

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The far-IR reflection spectra of $YBa_2Cu_3O_{6+x}$ single crystals with different oxygen content were investigated in the polarizations **E**⊥**C** and **E**‖**C**. It is shown that in the superconducting state the fine structure of the **E**⊥**C** spectra, which includes irregularities at 150–250 cm^{-1} and 480 cm^{-1}, can be explained by the scattering of normal free carriers in the chains by optical phonons and by the direct excitation of optical phonons. Investigation of the temperature dependence of the optical phonon frequencies showed that two superconducting gaps are present in the crystal with $T_c = 80$ K: the gap $5.0 \leqslant 2\Delta_1/kT_c \leqslant 5.6$ in the spectrum of carriers in the CuO_2 planes, and $2\Delta_2/kT_c \approx 2$ possibly connected with carriers in the chains. The experimental results can be interpreted by assuming that the superconductor $YBa_2Cu_3O_{6+x}$ has an *SNS* structure.

1. INTRODUCTION

The investigation of the properties of high-T_c superconductors in the far-IR region of the spectrum is of great interest primarily in connection with measurement of the superconducting gap.[1–5] The two main singularities in the **E**⊥**C** reflection spectra at 150–250 and ≈ 450 cm^{-1} were interpreted as superconducting gaps or as the edge of an absorption band lying in the middle-IR range[1–3] or as polaron absorption.[4] In spite of the large number of publications, the nature of the irregularities in the optical spectra of high-T_c superconductors in the far-IR range has still not been finally determined.

In the present work we investigated the reflection spectra in the polarizations **E**⊥**C** and **E**‖**C** in homogeneous single crystals $YBa_2Cu_3O_{6+x}$ (123) with different oxygen contents giving a phase composition ranging from an insulator to a high-T_c superconductor. Steplike changes in the reflection, whose spectral positions are correlated with the energy of some optical phonons, were observed in the superconducting crystals in the polarization **E**⊥**C**. These phonons are distinguished by the fact that the atomic bonds O1–Cu1–O4, where O1 and O4 are chain and bridge oxygens, respectively, make a significant contribution to their energy. This correlation suggests that in the wave number range $\nu > 100$ cm^{-1} the scattering of free carriers in the chains by optical phonons is responsible for the main irregularities of the 123 reflection spectra in **E**⊥**C** polarization at temperatures $T < T_c$, which were previously observed near 150–250 and 400–500 cm^{-1}. This electron-phonon interaction makes it difficult to observe directly the superconducting gap in the spectrum of the carriers in the CuO_2 planes which determine the superconductivity of 123 single crystals. In addition, it was found that in crystals with a high superconducting transition temperature T_c the optical phonons are not completely "screened" by free carriers in the spectra with **E**⊥**C**. The temperature dependences of the frequency of one such mode near ≈ 345 cm^{-1} as well as the frequencies of modes with B_{1u} symmetry (**E**‖**C**) indicate the presence of two irregularities in the density of states which are similar to the manifestation of two superconducting gaps in single crystals with $T_c = 80$ K: a gap $2\Delta_1$ in the spectrum of carriers in CuO_2 planes ($5.0 \leqslant 2\Delta_1/kT_c \leqslant 5.6$) and a gap $2\Delta_2$ ($2\Delta_2/kT_c \approx 1.8$), possibly associated with carriers in O1–Cu1–O4 chains.

2. EXPERIMENT

The bulk of the measurements were performed on 123 single crystals with characteristic dimensions of $2 \times 2 \times 0.4$ mm^3. The crystals were grown by the solution-in-a-melt method in alundum crucibles. For this reason, the composition of the crystals, determined by the method of x-ray microprobe analysis, corresponded to the formula $YBa_2Cu_{3-y}Al_yO_{7-x}$, where $y = 0.1$. For this value of y approximately 10% of the chain copper atoms are replaced with aluminum.[6] To determine the possible effect of aluminum on the optical properties, we also investigated several thin 123 single crystals, grown by the method of spontaneous crystallization in platinum crucibles. The initial crystals were superconductors with a wide transition near 40 K (measured by the screening method). The wide transition indicates that the oxygen distribution in the samples is nonuniform. This nonuniformity can be easily visualized with the help of a polarization microscope in the visible range and it also can be recorded with the help of an IR microscope of a Fourier spectrometer.[7,8] In order to obtain uniform single crystals the samples were annealed at low temperatures (400–450 °C) in an oxygen atmosphere at different pressures. The crystals had to be annealed for substantially longer times than ceramics in order to obtain comparable degrees of uniformity. In our case the annealing time was two weeks.

Figure 1 shows the $T_c(x)$ dependence and the width of the superconducting transition $\Delta T(x)$ in the annealed single crystals. The quantity ΔT was evaluated as the temperature interval between the values 0.1 and 0.9 of the screening curve. The oxygen content x was determined by the x-ray structural method from the value of the crystal lattice parameter C with the help of a calibration curve.[9] Here x is the content of electrically active oxygen, and it is approximately 0.2 less than the total oxygen content.[10]

The study of annealed single crystals by the methods of visible and IR microscopy showed that the oxygen distribution is highly uniform. This means that the scale of the possible nonuniformity is less than several microns. Additional

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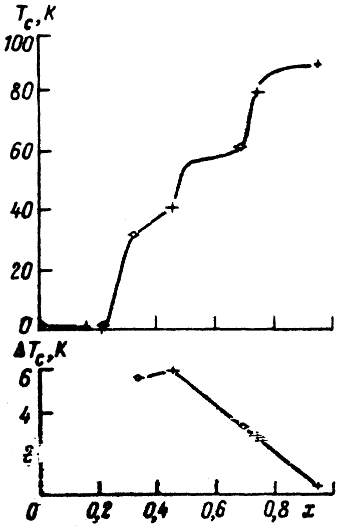

FIG. 1. Transition temperature T_c and width ΔT of the superconducting transition versus the oxygen content x in $YBa_2Cu_3O_{6+x}$ single crystals. The width ΔT was measured as the temperature interval between the values 0.1 and 0.9 of the screening curve. The crosses correspond to the samples investigated in the present work.

information about the oxygen distribution was obtained by the method of x-ray diffraction. As an example, Fig. 2 shows the x-ray spectrum of a 123 single crystal with $T_c = 30$ K. The small width of the main lines (CuK_α doublet of the x-ray source) and the absence of additional irregularities at the level of 10^{-3} of the intensity of the main lines confirm that the investigated single crystals are single-phase and uniform at the microscopic level. This is also indicated by the comparatively small width of the superconducting transition (from 0.5 K in crystals with high T_c up to 8 K in the case of low T_c, Fig. 1). The increase in the transition width for low values of T_c is most likely connected not with the multiphase nature of the samples but rather with defects in the ordering of oxygen atoms in the chains.

We were mainly interested in studying the reflection spectra in E⊥C and E‖C polarizations in the spectral range 50–650 cm^{-1}. The IR spectra were nonetheless measured in the range from 50 to 9000 cm^{-1}. The wide spectral range is necessary in order to calculate correctly the dielectric function in the range 50–650 cm^{-1} by the Kramers–Kronig method. The spectra were measured in a geometry close to normal incidence of light (deviation $\approx 10°$), with the help of a Fourier spectrometer. To investigate the temperature dependence of the spectra, the samples were secured to the cold finger in the vacuum cavity of a continuous-flow helium cryostat. After the spectra of the sample were measured at different temperatures from 300 to 10 K, the spectra of a comparison mirror (Al or Au film sputtered on a glass substrate) were measured at the same temperatures. The necessity of comparing the spectra of the sample and the mirrors is the main reason for the approximately 2% accuracy of the measurement of the absolute value of the reflection coefficient. The quite low accuracy is caused by the temperature drift of the spectrometer and the difficulty of precise optical alignment of the system when the sample is replaced with the mirror. At the same time, the relative accuracy of the measurements of the reflection spectrum was not worse than 0.3%.

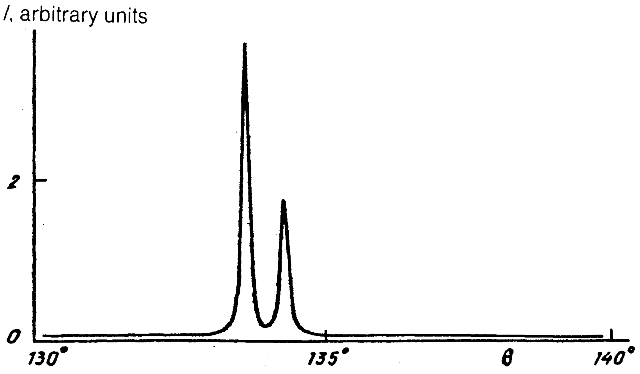

FIG. 2. X-ray diffraction spectrum of the single crystal with $T_c = 30$ K: reflection from the (001) surface, the order of reflection is 14. The two lines correspond to the CuK_α doublet of the x-ray source and θ is the diffraction angle.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Careful measurements of the reflection spectra of 123 single crystals in E⊥C polarization were performed, for example, in Ref. 1. It should be noted that in Ref. 1 smoothing of the reflection spectra was used in the analysis of the experimental data and comparatively weak irregularities, indicating the presence of appreciable absorption of light by phonons, were also excluded from the analysis. In our investigations we pay attention to the fine structure of the reflection spectra. Figure 3 shows the reflection spectra from the basal plane of 123 single crystals (E⊥C) with $T_c = 80$ K. Attention is focused on the spectra of crystals with this transition temperature T_c because such crystals were investigated in greatest detail in Ref. 1. This makes it possible to compare our results with the data in Ref. 1. At low temperature ($T \leqslant 150$ K) two types of features can be seen clearly in the reflection spectrum. The irregularities of the first type are minima at 180, 240, ≈ 300, 350, 480, and 590 cm^{-1}. Irregularities of the second type consist of stepped decreases of the reflection coefficient with increasing wave number ν at 110, 152, and 225 cm^{-1} and an inflection at $\nu \approx 480$ cm^{-1}, similar to those observed in Ref. 1 (Fig. 15 in Ref. 1). Irregularities of both types are discussed below in Secs. 3.1 and 3.2, respectively. It should be noted that they are insensitive to aluminum impurity: The spectra of the single crystal with $T_c = 80$ K, grown by the method of spontaneous crystallization in a platinum crucible, were found to be identical to those presented in Fig. 3.

3.1. Minima in the reflection spectrum, E⊥C

It is often stated in different publications that there are no phonon irregularities in the reflection spectra of superconducting single crystals in E⊥C polarization. This is explained by the effective "screening" of phonons by free carriers. The results of high-resolution investigations of the reflection spectra, presented in Figs. 3 and 4, show that at low temperatures this assertion is, strictly speaking, wrong. Indeed, distinct phonon maxima are observed only in the spectrum of the semiconductor phase of 123 single crystals (Fig. 4c). With high reflection coefficients, owing to free carriers, the phonons and electronic transitions excited directly by the electromagnetic field are manifested in the form

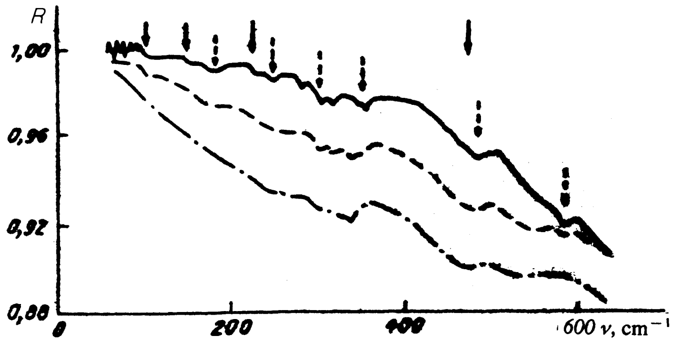

FIG. 3. Reflection spectra of the (001) basal plane of the $YBa_2Cu_3O_{6+x}$ single crystal with $T_c = 80$ K at $T = 10$, 150, and 300 K (solid, dashed, and dot-dashed curves, respectively). Polarization: E⊥C. The dashed arrows mark the minima and the continuous arrows mark the step changes in the reflection spectrum.

of comparatively weak minima in the reflection spectra of uniform single crystals with $T_c \geqslant 40$ K (Figs. 3 and 4a, b). These minima transform into maxima of the spectra of the imaginary part of the permittivity ε_2 (see below, Fig. 7) and high-frequency conductivity.

In crystals with $T_c \leqslant 80$ K, a 189 cm^{-1} "yttrium" mode and a 248 cm^{-1} "deformation vibration of the O4 bridge oxygen" can be seen at low temperatures. These phonons are effectively "screened" only in crystals with $T_c = 90$–93 K.

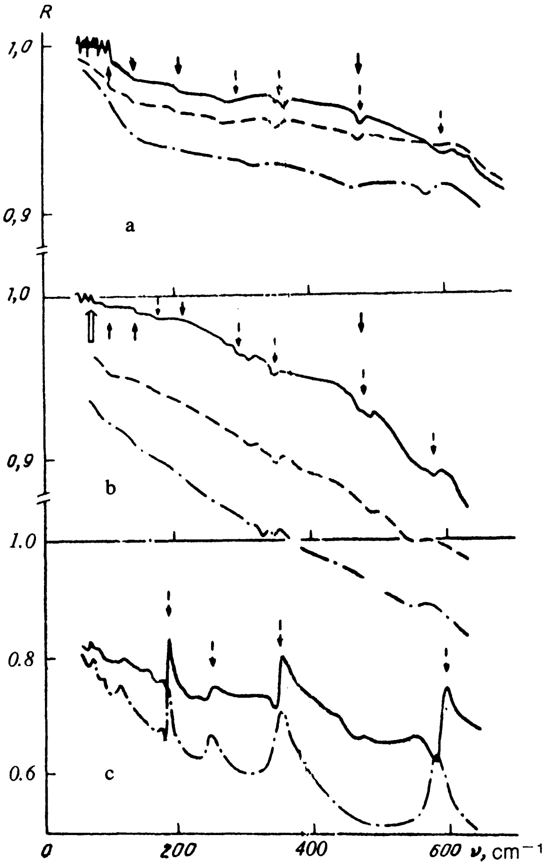

FIG. 4. Reflection spectra of the (001) basal surface (E⊥C polarization) of $YBa_2Cu_3O_{6+x}$ single crystals with $T_c = 90$ (a), 40 (b), and ≈ 0 K (c). The oxygen content $x = 0.9$, 0.45, and 0.2, respectively. $T = 10$ K for the solid curves, 150 K (100 K for the crystal with $T_c = 40$ K) for the dashed curves, and 300 K for the dot-dashed curves. The arrow designations are similar to Fig. 3; the double arrow marks the superconducting gap in the crystal with $T_c = 40$ K.

Here the frequencies of the transverse optical modes (TO) in the semiconductor phase of a 123 crystal are indicated.[7] As the oxygen content x increases from 0 to 0.8 the phonon frequencies decrease somewhat. The minimum at 347 cm^{-1} ($T = 300$ K) differs from the low-energy minima in that its intensity in the spectra of crystals with $T_c = 93$ K is comparatively high. In the dielectric phase it corresponds to the 355 cm^{-1} mode, identified as the "deformational vibration of oxygen atoms O2 and O3 of the cuprate plane."[7] The spectral position of the 590 cm^{-1} minimum correlates with the "stretching vibration of the O2, O3 oxygen atoms of the cuprate plane." An additional minimum was observed at 477 cm^{-1} in the spectrum of the crystal with $T_c = 90$ K. In crystals with $T_c = 80$ K it is strongly broadened, in the case $T_c = 40$ K it has the form of a comparatively narrow irregularity, and in the semiconductor phase of the 123 crystal it is absent altogether (Fig. 4).

To verify the phonon nature of the last three minima, we investigated single crystals in which ^{16}O was replaced with the isotope ^{18}O. The reflection spectra presented in Fig. 5 show unequivocally that all three minima correspond to the excitation of optical phonons, to whose energy the vibrations of oxygen atoms make the main contribution. At $T = 10$ K the relative displacements $\Delta\nu/\nu$ of the 353 and 590 cm^{-1} modes, which are determined primarily by the vibration of oxygen atoms of the cuprate plane, are equal to 4.6 and 5.6%, respectively. On the basis of theoretical calculations of Ref. 11, it can be concluded that in our case the

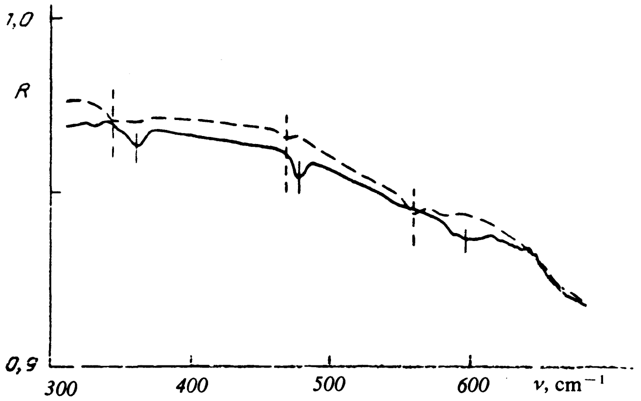

FIG. 5. Reflection spectra of $YBa_2Cu_3O_{6.9}$ single crystals containing ^{16}O (solid curve) and crystals in which ^{16}O is partially replaced with the isotope ^{18}O (dashed curve). $T = 10$ K, $T_c = 90$ K, and E⊥C.

oxygen of the cuprate plane was completely replaced with the isotope ^{18}O.

The relative displacement of the 477 cm^{-1} mode ($T = 10$ K) is equal to $\Delta\nu/\nu = 2\%$. On the basis of the identification of the known phonon modes and the fact that this line appears only in the orthorhombic phase of the 123 crystal, when fragments of CuO chains have formed, this mode must be assigned to the "stretching vibration of chain oxygen O1." The observed isotopic effect for this mode is appreciably weaker than the expected value 4.5%,[11] corresponding to complete replacement of oxygen. Therefore, chain oxygen is not completely replaced with the isotope in our case. This seems to contradict the fact that the binding energy of chain oxygen O1 in the 123 lattice is minimum. Incomplete isotopic substitution of chain oxygen, in contrast to plane oxygen, probably occurs for the following two reasons. First, in accordance with the experimental conditions, in our case chain oxygen entered the lattice at the final stage of isotopic substitution, when the gas medium in the annealing chamber contained an appreciable quantity of ^{16}O impurity as a result of both the release of oxygen from the samples and the natural inflow from the atmosphere. Second, in the samples investigated, approximately every tenth Cu1 atom is replaced with an Al atom. In accordance with our data the bond between the oxygen and aluminum in the O1–Al–O4 fragments is significantly stronger than in O1–Cu1–O4. Thus it is very likely that the oxygen bound with aluminum was not replaced with the isotope.

In conclusion we now consider the smearing of the 477 cm^{-1} line in crystals with $T_c = 80$ K (Fig. 3). Since this mode is determined by the vibration of chain oxygen O1, the mode must be sensitive to disordering of this oxygen. Indeed, this line is narrow in the crystal with oxygen content $x = 0.9$ ($T_c = 90$ K), which is close to the case of ordered chains of the ortho-I phase. The appearance of vacancies in chains with decreasing x ($T_c = 80$ K) leads to broadening of the line. As the oxygen content decreases further to $x = 0.45$ ($T_c = 40$ K) the line once again becomes narrower, remaining approximately two times wider than in the crystal with $T_c = 90$ K (see Fig. 4). The last case is close to the ordered structure of chains of the ortho-II phase ($T_c = 60$ K).

Among the minima of the reflection spectrum in **E**⊥**C** polarization, the 300 cm^{-1} line remained unstudied. Additional investigations showed that this irregularity corresponds to an interband electronic transition between states of bridge oxygen. Summarizing the experimental data presented above, it must be concluded that when interpreting **E**⊥**C** reflection spectra of high-T_c superconductors, both the contribution of free carriers and the direct excitation of optical phonons and electronic transitions by an electromagnetic field must be taken into account.

3.2. Step changes in the reflection

At low frequencies, $\nu < 100$ cm^{-1}, the noise in the reflection spectra in our case is strong compared with the rest of the spectrum. It can nonetheless be concluded that for $T < T_c$ the average reflection coefficient is close to the constant $R = 1.00$ (1 ± 0.02) for ν less than some value ν_0, and for $\nu > \nu_0$ the reflection coefficient decreases. This behavior of the spectrum is a characteristic of the manifestation of a superconducting gap $2\Delta = \nu_0$. Indeed, this behavior is not observed in nonsuperconducting single crystals (Fig. 4b), in which the oxygen content $x < 0.3$. In our case this quantity determines the semiconductor-superconductor phase boundary. In a crystal with low T_c, for example, $T_c = 40$ K, $\nu_0 \approx 3.5kT_c$ (Fig. 4b, double arrow), which agrees with the data of Ref. 1. In addition, stepped changes of the reflection coefficient are observed at $\nu_i \approx 100$ and 150 cm^{-1} and inflections are observed at $\nu_i \approx 220$ and 480 cm^{-1}, which are marked in Fig. 4 by the continuous arrows ($i = 1$–4), in the reflection spectrum of the crystal with $T_c = 40$ K at low temperatures. As T_c increases the gap irregularity at ν_0 reaches $\nu_1 = 110$ cm^{-1} and seemingly stops there. One can see from Figs. 3 and 4a and b that the spectral positions of the features ν_i are virtually independent of T_c. Moreover, they are observed at temperatures much higher than T_c, in particular, at $T = 150$ K (Figs. 3 and 4). Thus if the behavior of the threshold at ν_0 as a function of the temperature and the value of T_c in crystals with low T_c agrees satisfactorily with the interpretation of this phenomenon presented in Ref. 1 as a direct manifestation of the superconducting gap, then the irregularities at ν_i are determined by the properties of the normal state of the superconductor.

The character of the change in the reflection spectrum at ν_i and the presence of these irregularities at temperatures known to be higher than T_c indicate that they can be a manifestation of interband electronic transitions, whose properties do not change with a transition into the superconducting state. A different explanation of the nature of these singularities is also possible. It consists of the fact that at arbitrarily low temperature $T < T_c$ crystals with $T_c = 80$ and 93 K contain, together with Cooper pairs, normal free carriers at least at frequencies $\nu \geqslant 108$ cm^{-1}. In addition, the rate of scattering of these carriers increases stepwise at ν_i. Since at the present time band calculations do not give any grounds for the existence of such a system of interband transitions,[12] the observed irregularities are most likely caused by scattering of normal free carriers by optical phonons, i.e., intraband transitions. This proposition is also based on the fact that, for example, in a crystal with $T_c = 80$ K the optical conductivity at $\nu = 120$ cm^{-1} and $T = 10$ K is only three times smaller than the conductivity at 100 K. At the same time, according to the BCS theory, in this case the concentration of thermodynamically equilibrium normal carriers at $T = 10\,K$ should be approximately 10^6 times lower than the concentration at $T = 100$ K. Correspondingly, the optical conductivity in the frequency range $\nu < 2\Delta = 3.5kT_c \approx 200$ cm^{-1} ($T_c = 80$ K) should be many orders of magnitude lower than the optical conductivity in the normal state.

One can see from Fig. 4 and Table I that the spectral position of the features at $\nu_{1,2} = 110$ and 152 cm^{-1} is not correlated with the energy of optical phonons active in **E**⊥**C** polarization. However, the results of the investigation of the reflection spectrum of the single crystal with $T_c = 80$ K in **E**‖**C** polarization (Fig. 6) showed that the spectral position of these irregularities coincides, to a high degree of accuracy, with the frequencies of the optical phonons $\nu_{TO} = 113$ and 154 cm^{-1} with B_{1u} symmetry (ν_{TO} were determined as the positions of the maxima of the imaginary part of the permittivity ε_2). The inflection occurring in the reflection spectra at $\nu_4 \approx 480$ cm^{-1} also coincides with the optical mode $\nu_{TO} = 480$ cm^{-1}, active in **E**⊥**C** polarization. As mentioned above, the presence of oxygen defects in CuO chains leads to

TABLE I. Frequencies (cm^{-1}) of optical phonons and steplike irregularities in the reflection spectrum of the single crystal $YBa_2Cu_3O_{6.8}$ with $T_c = 80$ K at $T = 10$ K.

Atoms determining the mode	B_{1u} (E ∥ C)	$B_{2,3u}$ (E ⊥ C)	A_g (E ∥ C)	Steplike irregularities
O1–Cu1	113	–	–	110
Ba	–	–	115	–
Cu1	–	–	150	152
Ba	154	–	–	–
Y	191	181	–	–
O4–Cu1, 2	–	240	–	220
O2, 3–Cu2	281	–	–	–
	311	345	330–B_{1g}	–
	–	–	435	–
O1–Cu1	–	477	–	480
O4–Cu1. 2	–	–	498	–
O4–O1–Cu1	565	–	–	–
O4–Cu1	610	–	–	–
O2, 3–Cu2	–	590	–	–

Note. B_{iu}—IR active modes; A_g—known modes which are active in Raman scattering.[13]

long-wavelength broadening of the line of this vibration in the crystal with $T_c = 80$ K. Correspondingly, this gives rise to a long-wavelength shift and inflection to $\nu \approx 420\ \mathrm{cm}^{-1}$. Finally, the irregularity at $\nu_3 = 225\ \mathrm{cm}^{-1}$ is located near the $\nu_{TO} = 240\ \mathrm{cm}^{-1}$ phonon active in E⊥C polarization (Fig. 4). Table I gives, aside from the dipole-active phonons considered above, the frequencies of the known vibrational modes which have A_g symmetry and are active in Raman scattering (RS).[13] One can see that the A_g modes at 115, 150, and 498 cm^{-1} can also contribute to the formation of the irregularities at $\nu_{1,2,4}$ in the reflection spectrum as a result of the interaction with the normal carriers.

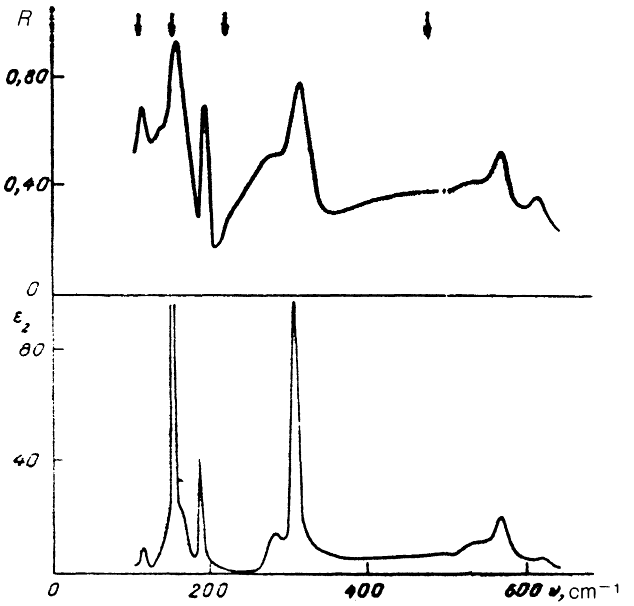

FIG. 6. Reflection coefficient R and imaginary part of the permittivity ε_2 as a function of the frequency in the crystal with $T_c = 80$ K, polarization E∥C, $T = 10$ K. The arrows show the spectral positions of step changes in the reflection spectrum in E⊥C polarization (Fig. 3).

In order to see if the fine structure of reflection spectra can be described on the basis of the proposed model, we analyzed the spectrum of the imaginary part of the permittivity ε_2 at $T = 10$ K in a crystal with $T_c = 80$ K. This was the largest (dimensions $4 \times 4 \times 0.4\ \mathrm{mm}^3$) of the samples investigated, and for this reason its spectrum was distinguished by minimum noise. This is important for converting the reflection spectrum $R(\nu)$ with the help of the Kramers–Kronig relations, since the weak noise in the reflection coefficient $R(\nu)$ results in strong noise in ε_2 at $R \approx 1.0$. Thus, suppose that normal carriers are present in 123 crystals at any temperature $T \geqslant 0$ K and $\nu > 0$. In this case Drude's approximation can be used to describe the reflection of light by free carriers at temperatures $T < T_c$ and frequencies $\nu < 2\Delta$. Figure 7 shows the frequency dependence $\varepsilon_2(\nu)$ and the approximation of asymmetric features at ν_1, ν_2, and ν_3 by Drude's formula

$$\varepsilon_2 = \nu_p^2 \Gamma / \nu (\nu^2 + \Gamma^2), \tag{1}$$

where ν_p is the plasma frequency and $\Gamma = \Gamma(\nu, T)$ is the rate of scattering of free carriers.

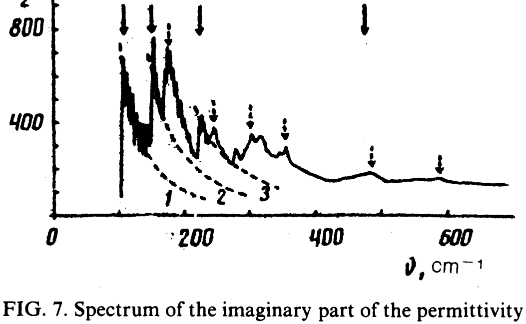

FIG. 7. Spectrum of the imaginary part of the permittivity $\varepsilon_2(\nu)$ in E⊥C polarization at $T = 10$ K in the single crystal with $T_c = 80$ K. The dashed curves are the Drude approximation of the features ν_i with different parameters: 1—$\nu_1 = 108\ \mathrm{cm}^{-1}$, $\nu_p = 7200\ \mathrm{cm}^{-1}$, $\Gamma = 17 \pm 3\ \mathrm{cm}^{-1}$; 2—$\nu_2 = 152\ \mathrm{cm}^{-1}$, $\nu_p = 8400\ \mathrm{cm}^{-1}$, $\Gamma = 30 \pm 5\ \mathrm{cm}^{-1}$, 3—$\nu_3 = 225\ \mathrm{cm}^{-1}$, $\nu_p = 8000\ \mathrm{cm}^{-1}$, $\Gamma = 100 \pm 15\ \mathrm{cm}^{-1}$. The arrow designations are the same as in Fig. 3.

In this analysis the dispersion of the phonons was neglected. The basis for this was that available results on inelastic neutron scattering show that the dispersion of the vibrational modes which were studied in small.[14] For $\nu \leqslant 100$ cm^{-1} the rate of scattering of the normal carriers is low, $\Gamma \approx 0$, which also can be interpreted as manifestation of a superconducting gap. For $\nu > 100\ \mathrm{cm}^{-1}$ the normal carriers excited by an electromagnetic wave with $\mathbf{E}\perp\mathbf{C}$ interact effectively with the longitudinal optical (LO) mode of the 113 cm^{-1} phonon with B_{1u} symmetry (Fig. 7) and (or) the A_g mode with wave number 115 cm^{-1}. This results in an increase in the scattering rate. The formula (1) satisfactorily describes the dependence $\varepsilon_2\ (\nu)$ in the spectral range 108–150 cm^{-1} with $\Gamma_1 = 17 \pm 3\ \mathrm{cm}^{-1}$ and plasma frequency of the carriers $\nu_{p1} \approx 7200\ \mathrm{cm}^{-1}$.

At low temperatures the scattering mechanism considered above presupposes excitation of a normal carrier by a light wave, followed by emission of an optical phonon. In the frequency range $\nu \geqslant 152\ \mathrm{cm}^{-1}$ additional scattering of normal carriers as a result of interaction with the LO mode of the 154 cm^{-1} phonon with B_{1u} symmetry and (or) 150 cm^{-1} A_g mode is switched on: The quantities $\Gamma = \Gamma_2 = 30 \pm 5\ \mathrm{cm}^{-1}$ with $\nu_{p2} \approx 8400\ \mathrm{cm}^{-1}$ determine the frequency dependences $R(\nu)$ and $\varepsilon_2(\nu)$ in the spectral range 150–225 cm^{-1}. The third increase in Γ occurs at $\nu_3 = 225$ cm^{-1} as a result of switching on an additional electron-phonon interaction with the 240 cm^{-1} TO mode with $B_{2,3u}$ symmetry (Fig. 4): $\Gamma = \Gamma_3 \approx 100\ \mathrm{cm}^{-1}$ and $\nu_{p3} \approx 8000$ cm^{-1}. This irregularity is manifested as a step in the reflection spectra for crystals with high T_c and as an inflection for the crystal with $T_c = 40$ K. The symmetric lines at 180 and 240 cm^{-1} in Fig. 7 correspond to minima of the reflection spectrum (Fig. 3), which represent direct excitation of optical phonons. The inflection at 480 cm^{-1} can be interpreted as additional scattering by 480 cm^{-1} optical phonons with B_{2u} symmetry and (or) by the 498 cm^{-1} A_g mode. The interpretation of this inflection as the red limit of absorption, lying in the middle-IR range, also has not been excluded.[1]

Stepped changes in the reflection spectra, whose spectral position was determined from the position of the thresholds in the spectrum of ε_2 (Fig. 7), are observed at frequencies somewhat lower than the frequencies of the corresponding TO modes, for which, in turn, the inequality $\nu_{TO} \leqslant \nu_{LO}$ is satisfied. This disagreement can be explained with the help of theoretical calculations.[4] In this work it was assumed that the IR absorption at 160 and 480 cm^{-1} in 123 crystals is due to the normal carriers present in the superconductor. Calculation of the optical absorption of polarons on the basis of Varma's phenomenological model[15] showed low-energy broadening of the optical conductivity of polarons with increasing polaron relaxation rate Γ. For example, the polaron absorption threshold should be observed at $\nu \approx 0.9\nu_{LO}$ for $\Gamma/\nu_{LO} = 0.10$. To make an approximate estimate, we employ the TO–LO splittings, measured for the dielectric phase of 123.[7,16] As the oxygen content increases the TO–LO splitting decreases somewhat as a result of the screening of the Coulomb interaction of the ions in the crystal by free carriers.[17] As a result, for the first threshold $\nu_1 = 110\ \mathrm{cm}^{-1}$ we obtain $\nu_1 \approx 0.96\nu_{LO}$ with $\Gamma_1/\nu_{LO} \approx 0.15$; for the second threshold $\nu_2 = 152\ \mathrm{cm}^{-1}$ we obtain $\nu_2 \approx 0.9\nu_{LO}$ with $\Gamma_2/\nu_{LO} \approx 0.1$; and for the third threshold $\nu_3 = 225\ \mathrm{cm}^{-1}$ we obtain $\nu_3 \approx 0.9\nu_{TO}$ with $\Gamma_3/\nu_{TO} \approx 0.3$, which agrees satisfactorily with the calculation in Ref. 4.

It was assumed above that normal carriers are present in a superconducting 123 crystal at any temperature $T \geqslant 0$ K and $\nu > 0$. Indeed, these carriers can be superconducting with comparatively small gap $2\Delta \approx 110\ \mathrm{cm}^{-1}$. In this case Drude's model can be used to describe normal excitations with $\nu \geqslant 4\Delta$,[2] and the analysis presented must be regarded in this case as an approximation. Nonetheless it seems reasonable to interpret the well-known irregularity of the optical conductivity spectrum of superconducting single crystals at 150–250 cm^{-1} (Ref. 1) as the result of scattering of free carriers, which are normal below T_c at frequencies $\nu > 110$ cm^{-1}, by optical phonons.

The fact that such carriers are very likely to exist is due to the complicated band structure of 123 crystal. Calculations in the local-density approximation[12,18] show that besides free carriers of the cuprate planes, which, as is well known, determine the superconducting properties of high-T_c superconductors, 123 crystals contain free carriers in chains, whose state is determined by the dominant contribution of the wave functions of O1 oxygen and Cu1 copper, as well as carriers whose band lies near the S point of the Brillouin zone. The results of high-resolution investigations of the reflection spectra of superconducting 123 single crystals in $\mathbf{E}\perp\mathbf{C}$ and $\mathbf{E}\|\mathbf{C}$ polarizations allow us to conclude that the steps in the reflection spectrum in $\mathbf{E}\perp\mathbf{C}$ polarization are determined by the interaction of precisely the carriers in O1–Cu1–O4 chains with optical phonons. Indeed, theoretical calculations of the dynamics of the crystal lattice[19–21] and the phonon-mode, assignments in Ref. 7 and Sec. 3.1 show that the optical phonons at 113, 154 cm^{-1} (B_{1u}) and 240, 480 cm^{-1} ($B_{2,3u}$) as well as the Raman-active A_g modes 115, 150, and 498 cm^{-1} are distinguished from the other modes by the fact that the vibrations of O1–Cu1–O4 atoms make the predominant contribution to their energy. The fact that only these phonons participate in the scattering of the normal carriers discussed above allows us to conclude that these carriers are located in O1–Cu1–O4 chains.

Thus, in the frequency range $\nu \geqslant 110\ \mathrm{cm}^{-1}$ the IR reflection spectrum of 123 superconducting single crystals in $\mathbf{E}\perp\mathbf{C}$ polarization cannot be interpreted on the basis of simple ideas about the reflection of light by free carriers. At low temperatures a number of irregularities appear in the spectrum and can be attributed to intraband excitation of normal carriers in O1–Cu1–O4 chains and to direct excitation of optical phonons and an electronic transition by the electromagnetic field. This makes it much more difficult to observe directly the superconducting gap 2Δ in 123 crystals with high T_c and can result in an incorrect interpretation of the irregularities of the spectrum as a manifestation of the gap 2Δ. Thus the singularity at 480 cm^{-1} is sometimes interpreted as a superconducting gap;[2] this was disputed, for example, in Ref. 1. Our experimental investigations confirm the result obtained in Ref. 1. Indeed, the spectral position of the singularity at 480 cm^{-1} does not depend on T_c (Fig. 4), and, more importantly, is manifested in the spectrum at a temperature significantly above T_c, for example, at 150 K in a crystal with $T_c = 80$ K (Fig. 3). The proposed interpretation of the fine structure of the reflection spectra also makes it possible to explain the incomprehensible saturation of the superconducting gap with increasing T_c, as observed in Ref. 1 (see Fig. 17 in Ref. 1). In crystals with $T_c \leqslant 50$ K the gap width 2Δ increases with increasing T_c in good agreement with the BCS theory; this is also confirmed by our investigations. However, at $T_c \approx 50$ K the gap width 2Δ is equal to the energy of the IR-active optical phonons 113 and 154 cm^{-1} and (or) the A_g modes 115 and 150 cm^{-1}. As T_c increases further, it is actually not the superconducting gap that is detected, but rather the scattering of normal carriers by these optical phonons. Because of the difficulty of direct detection of the gap 2Δ against the background of normal carriers, optical phonons, and the electronic transition, in the present work we made an attempt to measure 2Δ directly by the method of the temperature dependence of the frequencies of optical phonons.

3.3. Temperature dependence of optical-phonon frequencies

The method of the temperature dependence of optical-phonon frequencies for measuring the superconducting gap 2Δ is now under development.[21-27] The physical reason for the change in the phonon frequencies at the transition of the crystal into the superconducting state is the interaction of optical phonons with above-gap excitations, in whose density of states there appears an anomaly at $\nu = 2\Delta$, $T < T_c$. As a result of their energy repulsion, phonons with frequency $\nu < 2\Delta$ will become softer and phonons with $\nu > 2\Delta$ will become harder if the rate of scattering of normal free carriers is sufficiently low. The bulk of the experimental investigations[21-24] and the theory[25] of this method have been developed for Raman-active phonons. The experiments of Refs. 21 and 26 and the theory of Ref. 26 have shown that a similar result is also possible for the interaction of the IR modes with above-gap excitations.

Figure 8 shows the temperature dependence of the frequencies of *TO* modes with B_{1u} and $B_{2,3u}$ symmetry in $YBa_2Cu_3O_{6+x}$ single crystals with $T_c = 80$ K. Some of these results agree qualitatively with existing data obtained for 123 ceramics.[21] As in Ref. 21, softening of the 311 and 566 cm^{-1} modes with decreasing temperature below T_c is clearly observed. The difference lies in the magnitude of the softening of the 311 cm^{-1} phonon. It is 1.5 times higher in the single crystal: 4.5 ± 0.5 cm^{-1} versus 3.0 ± 0.5 cm^{-1} in the ceramic. This effect can be explained by the influence of grain boundaries on the rate of scattering of free carriers. The theory of Ref. 25 shows that the phonon shifts at the superconducting transition decrease strongly with increasing rate of scattering of free carriers primarily for phonons whose energy lies close to 2Δ.

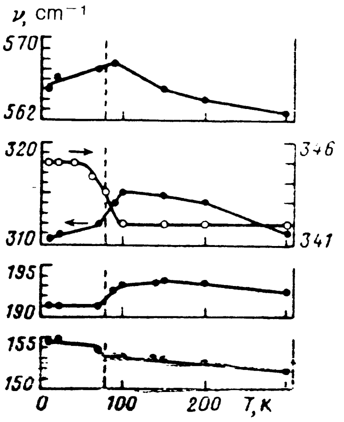

FIG. 8. Temperature dependence of the frequencies of IR active optical phonons (*TO* modes) with B_{1u} (black dots) and $B_{2,3u}$ (light-colored dots) symmetry in $YBa_2Cu_3O_{6.8}$ single crystals with $T_c = 80$ K. The vertical dashed line marks the critical temperature T_c. The solid lines were drawn freehand.

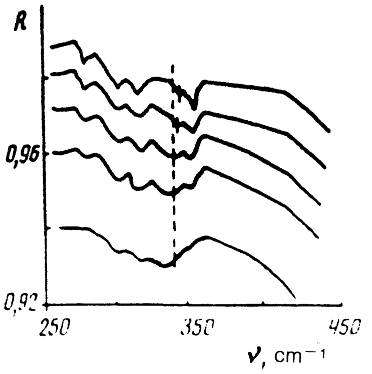

FIG. 9. Temperature dependence of the reflection spectrum in E⊥C polarization in the single crystal $YBa_2Cu_3O_{6.8}$ with $T_c = 80$ K with $T = 10$, 60, 100, 150, and 300 K (top to bottom). The vertical dashes show the spectral position of the *TO* mode of the 353 cm^{-1} optical phonon with $B_{2,3u}$ symmetry.

The new results refer to the behavior of the phonons 155 and 191 cm^{-1} with B_{1u} symmetry and the mode 353 cm^{-1} with $B_{2,3u}$ symmetry. The "yttrium" mode at 191 cm^{-1}, unlike other phonons, softens at temperatures $T \leqslant 140$ K significantly higher than T_c. All other modes become harder with decrease of temperature from 300 to 100 K as a result of the usual temperature compression of the crystal lattice. However, the main softening of the 191 cm^{-1} mode by approximately 2 cm^{-1} is observed below T_c. A more significant new result is the hardening of the 155 cm^{-1} "barium" mode (B_{1u} symmetry) and the 353 cm^{-1} mode ($B_{2,3u}$) below T_c. Up to now it has not been possible to follow the behavior of the $B_{2,3u}$ modes as a function of the temperature. For this reason, we present in Fig. 9 the temperature dependence of the reflection spectra of the basal plane (E⊥C) of the single crystal $YBa_2Cu_3O_{6.8}$ with $T_c = 80$ K in the region of the 353 cm^{-1} phonon.

The relative change in the phonon frequencies at the superconducting transition is important for analyzing the interaction of phonons with above-gap excitations. Figure 10 shows the corresponding experimental values and the

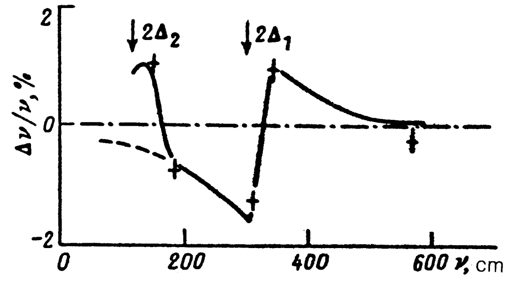

FIG. 10. Spectral dependence of the relative shifts in the phonon frequencies at the superconducting transition. Solid curve—the qualitative dependence taking into account the theoretical calculations of Refs. 25 and 26; $2\Delta_1$ and $2\Delta_2$ are the positions of the anomalies in the density of states of free carriers.

curve drawn through them is the qualitative dependence, based on the calculations in Refs. 25 and 26. The 311 cm^{-1} (B_{1u}) mode and the 353 cm^{-1} ($B_{2,3u}$) mode have different symmetry, and both modes are determined by flexural vibrations of oxygen atoms O2 and O3 in the CuO_2 planes. Also, since the relative changes in their frequencies at the superconducting transition are maximal (1.3 and 0.9%, respectively) and they shift in the opposite directions, it can be concluded that at the superconducting transition there arises an anomaly $2\Delta_1$ in the density of states of free carriers in the CuO_2 planes with energy $297 \leqslant 2\Delta_1 \leqslant 327$ cm^{-1}, i.e., $5.0 \leqslant 2\Delta_1/kT_c \leqslant 5.6$ ($T_c = 80$ K). We have taken here, into consideration the fact that the minimum in the spectral dependence of the real part of the polarizability lies approximately 1.06 times higher than 2Δ.[25,26]

The softening of the 191 cm^{-1} "yttrium" mode at $T < T_c$ by 1% qualitatively agrees with the appearance of the anomaly $2\Delta_1 \approx 310$ cm^{-1}. The weak softening of the 566 cm^{-1} phonon by $\approx 0.3\%$ is not fully understood. One would expect a weak hardening of this vibration as a result of the appearance of the anomaly $2\Delta_1 \approx 310$ cm^{-1}. It is possible that this behavior of the 566 cm^{-1} phonon is related with the increase in the rate of scattering of free carriers with increasing frequency, as discussed in Sec. 3.2. The significant (by 1%) hardening of the 155 cm^{-1} "barium" mode is more interesting. In accordance with the theories of Refs. 25 and 26, this mode should soften as a result of the appearance of the anomaly $2\Delta_1 \approx 310$ cm^{-1} at $T < T_c$ (dashed line in Fig. 10). On the basis of the model studied, this hardening of the "barium" mode indicates the appearance of a second anomaly of the density of states of free carriers $2\Delta_2 \leqslant 153/1.06 \approx 144$ cm^{-1} at $T < T_c = 80$ K.

The observed irregularity $2\Delta_1 \approx 310$ cm^{-1} agrees satisfactorily with the position of the superconducting gap for $\mathbf{E} \perp \mathbf{C}$ polarization, discovered by the Raman scattering method,[28,29] and with the result of the investigation of the temperature dependence of the frequencies of Raman-active phonons.[23,24] One possible reason for the anomaly $2\Delta_2$ could be the anisotropy of the superconducting gap of free carriers in CuO_2 planes relative to the **C** axis of the crystal. In this case one would expect the reflection coefficient in $\mathbf{E} \| \mathbf{C}$ polarization to increase at $\nu \approx 140$ cm^{-1}. However, investigation of the reflection spectra of the single crystal with $T_c = 80$ K in $\mathbf{E} \| \mathbf{C}$ polarization showed that the reflection coefficient decreases at $T < T_c$ in the spectral region $\nu \geqslant 100$ cm^{-1}. Thus the $2\Delta_2$ anomaly most likely corresponds to $\mathbf{E} \perp \mathbf{C}$ polarization. In this case, since for $\mathbf{E} \perp \mathbf{C}$ the reflection coefficient $R(\nu)$ is close to 100% for $\nu \leqslant 108$ cm^{-1}, it should apparently be assumed that $2\Delta_2 \geqslant 108$ cm^{-1}, i.e., $1.8 \leqslant 2\Delta_2/kT_c < 2.4$. We note that two similar anomalies, interpreted correspondingly as superconducting gaps in the spectra of free carriers in CuO_2 planes and CuO chains, were observed in $YBa_2Cu_4O_8$ by the Raman-scattering method.[28]

The appearance of two anomalies in the density of states of free carriers at $T < T_c$ can be explained with the help of the model developed in Ref. 30. In Ref. 30 it was assumed that a high-T_c superconductor consists of alternating superconducting (S) CuO_2 layers and normal (N) BaO_2 layers and CuO chains. In addition, Cooper pairing occurs only in the S layers, and the S and N layers are coupled, the coupling being described by the hopping integral t. The calculation of the density of states at temperatures $T < T_c$, taking into account only the order parameter Δ ($t = 0$), gives the standard BCS anomaly in the density of states of free carriers at energies shifted by Δ away from the Fermi energy. However, when both Δ and $t > 0$ are taken into account, a step appears at the "true" value of Δ and two anomalies $\Delta_1 > \Delta$ and $\Delta_2 < \Delta$ in both the superconducting and normal layers. As an illustration, Fig. 11a shows the qualitative spectral dependence of the density of states constructed for $t \approx kT_c$ on the basis of the calculation in Ref. 30. In addition, the anomaly at Δ_2 is maximum in the normal layers, which actually corresponds to an induced quasigap. In accordance with Ref. 30, the experimental results obtained in the present work for a 123 single crystal with $T_c = 80$ K can be interpreted as a quasigap of superconducting CuO_2 layers $2\Delta_1 \approx 5.3kT_c$ and an induced quasigap of normal O1–Cu1–O4 chains $2\Delta_2 \approx 2kT_c$ with the "true" value $2\Delta \approx 3.7kT_c$. In this case the hopping integral is equal to $t \approx 0.8kT_c$.

It is known, however, that the surface of 123 crystals contains a "dead" layer, in which the oxygen content varies from that typical of the superconductor up to $x = 0$ of the dielectric state.[31] The single crystals studied can also contain inclusions of the normal phase N, whose dimensions are equal to several superconducting correlation lengths. In this case, on the basis of a theoretical calculation of the density of states for macroscopic $SNIS$ structures, in which the interaction of neighboring SN boundaries was neglected,[32] it can be expected that two gap features will appear in the reflection spectra of the single crystal. The qualitative energy dependences of the density of states, which are constructed on the basis of the calculations in Ref. 32, are shown in Fig. 11b. One feature of the density of states Δ_1 should be observed near the "true" value Δ typical of the superconductor. The second feature, $\Delta_2 < \Delta$, is the quasigap induced in the N region.

4. CONCLUSIONS

Investigations of the IR reflection spectra of $YBa_2Cu_3O_{6+x}$ single crystals with light polarization $\mathbf{E} \perp \mathbf{C}$ and $\mathbf{E} \| \mathbf{C}$ revealed fine structure in the spectra which were measured in $\mathbf{E} \perp \mathbf{C}$ polarization at low temperatures. Investigation of crystals with different oxygen content showed that

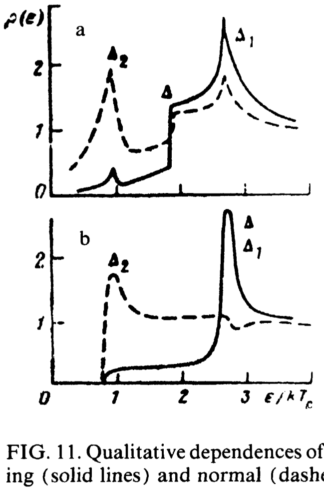

FIG. 11. Qualitative dependences of the density of states of superconducting (solid lines) and normal (dashed lines) layers of high-T_c superconductor based on the theoretical calculations in Refs. 30(a) and 32(b).

this structure is the result of direct excitation of optical phonons, an electronic transition by the electromagnetic field, as well as, and most likely, the result of scattering of free carriers in O1–Cu1–O4 chains by optical phonons. Thus at frequencies in the range $\nu \geqslant 110\ \mathrm{cm}^{-1}$ the IR reflection spectrum of superconducting 123 single crystals in $\mathbf{E}\perp\mathbf{C}$ polarization cannot be interpreted on the basis of simple ideas about the reflection of light by free carriers. The observed structure of the reflection spectra makes it much more difficult to observe directly the superconducting gap 2Δ in 123 crystals with high T_c and can result in incorrect interpretation of spectral features as a manifestation of the superconducting gap 2Δ.

The use of a direct method for measuring 2Δ, namely, the method of the temperature dependence of optical phonon frequencies, showed that two anomalies appear in the density of states of free carriers at the transition of the crystal with $T_c = 80$ K into the superconducting state: $2\Delta_1 \approx 5.3kT_c$ and $2\Delta_2 \approx 2kT_c$. The existence of two such anomalies agrees satisfactorily with the theoretical models of Refs. 30 and 32. In accordance with Ref. 30, the high-T_c superconductor is a system of alternating superconducting (S) and normal (N) layers, the interaction between the S and N layers being determined by the hopping integral t. In this case the superconductivity is actually of a gapless character. The feature $2\Delta_1 \approx 5.3kT_c$ can be interpreted as a quasigap in the superconducting $\mathrm{CuO_2}$ layers and the feature $2\Delta_2 \approx 2kT_c$ can be interpreted as an induced quasigap in the system of free carriers of the normal layers O1–Cu1–O4. The "true" gap is $2\Delta \approx 3.7kT_c$. However, the crystals investigated can contain regions of normal metal with dimensions equal to several superconducting correlation lengths. Then, in accordance with Ref. 32, the singularity $2\Delta_1$ is close to the gap 2Δ of the superconductor S and $2\Delta_2$ is the induced gap in N regions. Further investigations are required in order to determine which of these two models is realized in 123 crystals. We note that both of the models considered here also make it possible to explain, at least qualitatively, the long-wavelength broadening of the gap feature in the Raman-scattering spectra.[28–29]

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