Influence of a photoexcited electron-hole plasma on the Raman scattering spectra of $YBa_2Cu_3O_x$ single crystals

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The Raman spectra of tetragonal $YBa_2Cu_3O_x$ crystals in the region of $\sim 500\ \text{cm}^{-1}$ were determined using different power densities I_0 of the exciting radiation of wavelengths 4880, 5145, 5321, and 6471 Å at temperatures 80–300 K. An increase in I_0 revealed changes in the spectra due to interference of the electron continuum with a $470\ \text{cm}^{-1}$ phonon and also due to activation of $560–590\ \text{cm}^{-1}$ dipole vibrations because of interaction of photocarriers with the crystal lattice. An analysis of the spectra yielded the electron-phonon interaction constant. The changes in the spectra were of resonant nature, but they were absent in the case of the excitation wavelengths 5321 and 6471 Å. A triple multichannel Raman spectrometer, developed by the authors, made it possible to record simultaneously a spectral interval of $500\ \text{cm}^{-1}$ in the range $\geqslant 25\ \text{cm}^{-1}$ on excitation with cw laser radiation. The reflection spectra of polarized light were determined for single crystals of the tetragonal and orthorhombic phases at wavelengths in the range 360–990 nm.

There have been very numerous investigations of the Raman scattering spectra of $YBa_2Cu_3O_x$ ($6 \leqslant x \leqslant 7$) materials (see, for example, Refs. 1–12). These compounds are attracting interest because, depending on the oxygen content x, they may exhibit a number of phase transitions: structural (tetragonal → orthorhombic phase), antiferromagnetic (in the range $x < 6.5$), superconducting (in the range $x > 6.5$ at temperatures $T \lesssim 90$ K), and also semiconductor-metal. The Raman spectra of these materials provide an informative method for investigating lattice dynamics, phase transitions, magnon[11] and electron (see Ref. 12 and the literature cited there) excitations, structure characteristics, and nature of the interatomic and electron-phonon interactions, which is essential for the understanding of the mechanism of the superconducting transition that occurs in these compounds. Moreover, the Raman spectra provide a good method for checking the quality and composition of synthesized $YBa_2Cu_3O_x$ compounds. The presence of even a small amount ($\sim 1\%$) of concomitant phases ($BaCuO_2$, Y_2BaCuO_5, etc.) distorts significantly the nature of the spectrum of $YBa_2Cu_3O_x$ (Ref. 4). This can account for the clear contradictions between the Raman spectra of $YBa_2Cu_3O_x$ samples given in the literature (particularly ceramic samples). It is therefore especially important to investigate the Raman spectra of $YBa_2Cu_3O_x$ single crystals which can provide the most reliable information on the crystal lattice dynamics.

The $YBa_2Cu_3O_x$ compounds absorb light strongly in the visible part of the spectrum (and the depth of penetration of light into a crystal is ~ 1000 Å). The absorption of light which excites the Raman spectra may not only result in resonances in these spectra, but may also create electron-hole pairs in a crystal, and the influence of these pairs on the Raman spectra is sensitive to the electron-phonon interaction and to characteristics of the density of electron states. Studies of resonant changes in the Raman spectra with the excitation wavelength can provide information on the structure of the electron energy bands of crystals,[13] especially as investigations of this structure on the basis of optical characteristics have failed to give reliable data because of lack of oriented $YBa_2Cu_3O_x$ single crystals of sufficient size.[14] One can expect the efficiency of formation of electron-hole plasma to depend on the oxygen content of $YBa_2Cu_3O_x$. In fact, according to Ref. 15, carriers in a semiconducting crystal of $YBa_2Cu_3O_x$ ($x < 6.5$) are most likely to be localized because of the random potential of impurities and defects. However, an increase in x ensures that the density of the intrinsic carriers becomes sufficient to screen the random potential, so that the mobility of carriers increases and the conductivity of a $YBa_2Cu_3O_x$ crystal with $x > 6.5$ (orthorhombic phase) becomes metallic; this makes it difficult to form a photoinduced electron-hole plasma. In general, the efficiency of formation of photoinduced electron-hole pairs depends on the absorption of light and is proportional to the peak intensity of the exciting radiation and to the lifetime of electron-hole pairs. We investigated for the first time the influence of the power density of the exciting radiation at different wavelengths on the polarized Raman scattering spectra of $YBa_2Cu_3O_x$ single crystals and also recorded the polarized reflection spectra of these crystals in the wavelength range 330–990 nm.

Since the conventional methods for recording the Raman spectra are not very effective in the case of $YBa_2Cu_3O_x$ materials (for example, double spectrometers can be used to study these spectra only at frequencies in excess of $150\ \text{cm}^{-1}$ and the time taken to record the spectrum is $\gtrsim 10$ h), we developed a triple multichannel Raman spectrometer constructed entirely from solid components, which made it possible to record simultaneously a spectral interval of $\sim 500\ \text{cm}^{-1}$ in a time of the order of 10 min when the Raman spectra were excited with radiation from a cw laser. The optical part of this spectrometer was described by us in Ref. 16. The low level of the stray scattered light at the exit from this spectrometer made it possible to investigate the Raman spectra of $YBa_2Cu_3O_x$ at frequencies in the range $\geqslant 25\ \text{cm}^{-1}$ using an exciting line with a resolution of $\sim 4\ \text{cm}^{-1}$. Since

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the study of the Raman spectra of $YBa_2Cu_3O_x$ single crystals was possible only in the "reflection" geometry and the intensity in the spectrum was relatively low, monochromatization of the exciting radiation was important in order to avoid the appearance in the spectrum of plasma lines due to the gas discharge of the laser. The effectiveness of the three-prism monochromatizing system was insufficient for this purpose and in the final variant we used a concave holographic grating (2000 lines/mm, $F = 50$ cm) with a metal stop ($D = 0.5$ mm) in the focal plane of the grating.

Since the multichannel recording system used by us earlier[17] was designed only for operation with a pulsed laser, we developed a new multichannel detector based on an image converter with a microchannel amplifier plate and a supervidicon image tube (a Soviet analog of an SIT tube), which made it possible to use pulsed and cw lasers. The supervidicon and the image amplifier were coupled by fiber-optic face plates. In view of the high sensitivity of the supervidicon, the image amplifier was used under low-load conditions which had a favorable influence on the noise characteristics of the system as a whole (see below). When the image amplifier gain was $\sim 10^3$ (corresponding to a voltage of 700 V across the microchannel plate), the signal/noise ratio for single photoelectrons from the entry photocathode reached 30. The systems for reading and analyzing the signal were the same as in Ref. 17, except that the height h in photometry of the lines was variable (0.3–3 mm). This control was provided by varying the amplitude of the scan in the direction of the amplitude of the spectral lines. This made it possible to minimize the recorded level of the noise from the input photocathode by selecting the optimal ratio of the height of the spectral lines to the height h of the actual sensitive area of the detector. The main characteristics of the microchannel system using cw laser radiation were as follows.

Spectral range, nm	380–850
Working area ($l \times h$, mm)	22×0.3–3
Resolving power, line pairs/mm	~ 10
Noise level from the whole working area for $h = 1$ mm, photoelectrons/s	~ 20
Dynamic range (linear region)	> 200

We investigated oriented single crystals for which the Raman spectra were determined by us earlier[7] at low power densities of the excitation. The spectra were excited with focused radiation from an argon-krypton laser ($\lambda_i = 4880$, 5145, and 6471 Å) and with the second harmonic of a pulsed YAG:Nd laser ($\lambda_i = 5321$ Å). In these experiments the power density of the exciting radiation I_0 was varied by altering the peak intensity. The average power was kept constant (~ 20 mW) by rotating sector-type choppers. The off-duty factor of the pulses ranged from 1 to 10 for the Ar-Kr laser radiation to $\sim 2 \times 10^3$ for the pulsed laser. The process of heat transfer was improved by embedding a sample in indium, so that apart from the investigated face, all the others were in contact with a bulk metal.

The reflection spectra were recorded using a reflecting microscope with light incident normally on freshly cleaved surfaces of single crystals. This incident light was focused down to a spot 20 μm in diameter and light reflected at an angle of 180° was collected within an angle of $\sim 40°$. The spectra were recorded employing an automated KSVU-23 spectrometer with a resolution of ~ 10 Å.

The Raman spectra of tetragonal crystals, both in the original state and after annealing in helium,[7] exhibited major changes (in the *zz* scattering geometry) on increase in I_0, as manifested by broadening, shift toward lower frequencies, and reduction in the intensities of the bands, and also by the appearance of some additional bands. This effect appeared most clearly in the spectral range near 500 cm^{-1} and below 200 cm^{-1}.

Figure 1 shows the spectra of a tetragonal crystal annealed in helium and recorded in the range 500 cm^{-1}. When the average power of the incident radiation was 8 mW, only one band at 470 cm^{-1} was observed and it was accompanied by a weak structure-free wing (curve 1 in Fig. 1); at 200 mW there were major changes in the spectrum: the 470 cm^{-1} band shifted toward lower frequencies and the wing was replaced with a strong asymmetric band at 590 cm^{-1} (curve 2 in Fig. 1). In the *zx* geometry the 590 and 470 cm^{-1} bands were absent when the power was 8 or 200 mW (curves labeled 3 in Fig. 1). In the spectral range below 200 cm^{-1} new bands appeared at 80 and 100 cm^{-1} when the excitation power was high.

The changes in the spectra in Fig. 1 (curve 2) could be due to laser heating of a sample or photoinduced effects of the radiation I_0. We estimated the likely temperature rise in a crystal due to high-power laser radiation at T_{room}: this was done by measuring the ratio of the intensity of the 470 cm^{-1} band in the Stokes and anti-Stokes Raman spectra when the power density of the exciting radiation was 3.8 and 38 kW/cm^2 and the average power was 20 mW in both cases ($\lambda_i = 5145$ Å). When the power density was 3.8 kW/cm^2, the temperature rise was 10 ± 5 °C, whereas for 38 kW/cm^2 the temperature of the crystal rose by 50–60 °C. Since heating of a sample in an oven from T_{room} to 100 °C had practically no effect on the Raman spectra in the region of ~ 500 cm^{-1} when the exciting power density was 3.8 kW/cm (Fig. 2), we concluded that the main changes in the spectra due to an increase in I_0 (Figs. 1 and 2) were not due to laser heating, but due to the influence of an electron-hole plasma consisting of photocarriers the number of which increased on increase in I_0.

We shall now consider changes in the Raman spectra of the original tetragonal crystal excited using $\lambda_i = 4880$ Å ra-

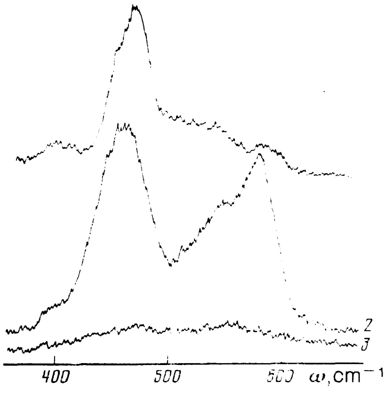

FIG. 1. Raman spectra of a tetragonal $YBa_2Cu_3O_x$ crystal annealed in helium and excited with radiation of average power 8 mW (1) and 200 mW (2, 3) in the following scattering geometries: 1), 2) *zz*; 3) *zx*; $\lambda_i = 5145$ Å.

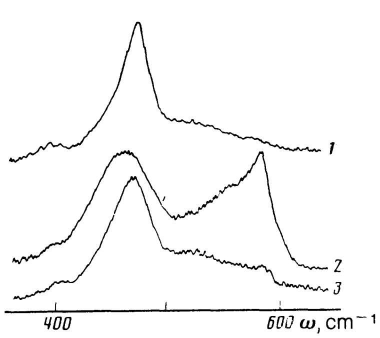

FIG. 2. Raman spectra of a tetragonal $YBa_2Cu_3O_x$ crystal excited using radiation of average power 20 mW and of power density 3.8 kW/cm^2 (1, 3) and 38 kW/cm^2 (2). 1), 2) Room temperature; 3) 100 °C; $\lambda_i = 5145$ Å.

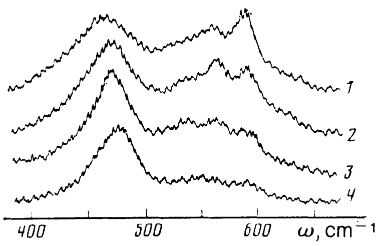

FIG. 4. Raman spectra of a tetragonal $YBa_2Cu_3O_x$ crystal obtained using exciting radiation of 38 kW/cm^2 power density ($\lambda_i = 5145$ Å) at different temperatures (K): 1) 300; 2) 200; 3) 150; 4) 80. Scattering geometry *zz*.

diation at $T_{\rm room}$ (Fig. 3). If $I_0 \lesssim 4$ kW/cm^2, in addition to the main band at 480 cm^{-1}, we observed only a weak wide band at 590 cm^{-1} due to the lattice disorder.[7] An increase in I_0 gave rise to bands at 560 and 590 cm^{-1} and increased their intensities. In the range $I_0 > 10$ kW/cm^2 the intensities of these bands no longer increased and a further rise of I_0 produced an additional shift, broadening, and weakening of the main band at 480 cm^{-1}. The changes observed in the spectra in the range $I_0 \leqslant 64$ kW/cm^2 were found to be fully reversible. The bands at 560–590 cm^{-1}, like the band at 480 cm^{-1}, appeared only in the *zz* geometry.

Approximately the same changes in the Raman spectra were observed on increase in I_0 at $\lambda_i = 5145$ Å. However, at $\lambda_i = 5321$ and 6471 Å the spectra were practically independent of I_0 and were similar to the spectrum labeled 1 in Fig. 3, although at $\lambda_i = 5321$ Å the value of I_0 was varied from 10 to 100 kW/cm^2.

When samples were cooled to 80 K the Raman spectra ($\lambda_i = 4880$ Å) exhibited on the whole the same dependence on I_0 as at $T_{\rm room}$, but the rise and saturation of the intensity of the 560–590 cm^{-1} bands occurred at higher values of I_0. At $\lambda_i = 5145$ Å there was a significant weakening of the influence of laser excitation on the nature of the spectrum as temperature was lowered (Fig. 4) and at 80 K the 560–590 cm^{-1} bands were practically undetectable at the maximum power I_0 and the 480 cm^{-1} band had the same profile as at low values of I_0.

In view of the resonant nature of the observed singularities in Raman spectra, we determined the polarized-light reflection spectra $R(\lambda)$ of tetragonal and orthorhombic single crystals (Fig. 5). We found that in the $E \parallel z$ case all the samples exhibited a reflection in the dependence $R(\lambda)$ at $\lambda \approx 5000$ Å, which was most likely due to interband transitions responsible for the resonant nature of the changes in the Raman spectra. The stronger features in the spectral dependences $R(\lambda)$ at $\lambda \approx 8000$ Å ($E \parallel z$) and 4500 Å ($E \perp z$) were probably due to plasmons. This interpretation was in agreement with calculations of the energy band structure reported in Ref. 18, which also indicated the possibility of low-energy electron transitions in $YBa_2Cu_3O_x$ crystals. These transitions should give rise to an electron continuum in the Raman spectra with which the scattering by phonons could interfere. The Raman scattering due to electron transitions was supported by some increase in the background in the spectra of the tetragonal phase of $YBa_2Cu_3O_x$ when I_0 was increased. Interference was observed earlier in the Raman spectra of heavily doped *p*-type semiconductors and was described within the framework of the Fano resonance[13] which increased the damping ($\Delta\Gamma$) and shifted the frequency ($\Delta\omega$) of phonons.

A distinguishing feature of the Fano resonance in the Raman spectra is the dependence of the interference and, consequently, of the profile of the phonon band on the wavelength of the exciting light, usually attributed to the characteristics of the energy band structure. Therefore, the observed resonant nature of changes in the parameters of the 480 cm^{-1} band allowed us to consider such changes as a consequence of the Fano resonance. An analysis of the Fano resonance yielded

$$\Delta\Gamma=4\pi V^2\rho, \qquad \Delta\omega=\frac{2V^2(R^2+\pi^2\rho^2)}{R}, \tag{1}$$

where V is the matrix element of the anharmonic interaction

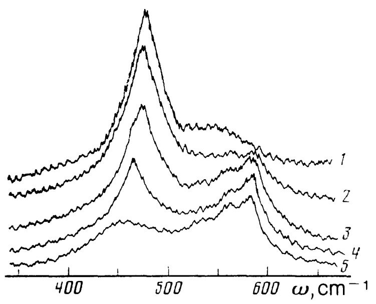

FIG. 3. Raman spectra of a tetragonal $YBa_2Cu_3O_x$ crystal recorded using exciting radiation ($\lambda_i = 4880$ Å) of different power densities (kW/cm^2): 1) 3.8; 2) 6.5; 3) 9.2; 4) 24; 5) 64. Scattering geometry *zz*; $T_{\rm room}$.

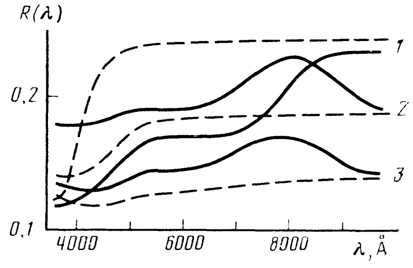

FIG. 5. Reflection spectra of $YBa_2Cu_3O_x$ single crystals: 1) orthorhombic crystal; 2) original tetragonal crystal; 3) tetragonal crystal annealed in helium. The continuous curves correspond to $E \parallel z$ and the dashed curves to $E \perp z$.

of a phonon with the continuum, $\rho(\omega)$ is the density of states in the electron continuum, and

$$R=\int \frac{\rho(\omega')\,d\omega'}{\omega-\omega'}. \qquad (2)$$

It follows from Eq. (1) that the ratio $\Delta\Gamma/\Delta\omega$ is independent of V and is governed only by the frequency distribution $\rho(\omega)$:

$$\frac{\Delta\Gamma}{\Delta\omega}=\frac{2\pi\rho R}{R^2+\pi^2\rho^2}. \qquad (3)$$

If we use the values of $(\Delta\Gamma/\Delta\omega)_{\rm exp}$ taken from the experimental spectra and if, for the sake of simplicity, we assume that the electron continuum extends from 0 to a certain frequency ω_c with $\rho = \text{const}$, we can determine ω_c satisfying Eq. (3) for a given value of $(\Delta\Gamma/\Delta\omega)_{\rm exp}$ and then use Eq. (1) to estimate V.

We can find from Fig. 3 that in the case of the 480 cm^{-1} band, due to the nondipole totally symmetric vibration A_g of the axial Cu-O bond,[7] we have $(\Delta\Gamma/\Delta\omega)_{\rm exp} \approx -1$ at 24 kW/cm^2. This provides an estimate of the magnitude of the electron-phonon interaction $V = 10^2$–10^3 cm^{-1}.

The appearance of the 560–590 cm^{-1} bands on increase in I_0 could be due to the Raman scattering by dipole vibrations, which became allowed in the centrosymmetric crystal because of the effects of the interaction of photoinduced carriers with defects.[13,19] In view of this we should point out that the infrared absorption spectra have a strong band at 592 cm^{-1}. Within the framework of this interpretation of the appearance of the 560–590 cm^{-1} bands, their intensity should be correlated with the density of a photoinduced plasma and bands should be active only in the parallel polarization (for example, in the *zz* geometry),[20] as observed experimentally. The observation of photoinduced bands at 560–590 cm^{-1} implies the presence of an induced structural deformation of the lattice near photocarriers, indicating also the occurrence of a fairly strong interaction of photocarriers with the lattice.

As expected, the Raman spectra of orthorhombic crystals ($T_c = 90$ K) were practically unaffected by I_0 at all the wavelengths λ_i and this could be attributed to a high density of free carriers in the orthorhombic phase.

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[1] R. M. Macfarlane, H. Rosen, and R. Seki, Solid State Commun. **63**, 831 (1987).

[2] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **58**, 2340 (1987).

[3] A. Yamanaka, F. Minami, K. Watanabe, K. Inoue, S. Takekawa, and N. Iyi, Jpn. J. Appl. Phys. **26**, L1404 (1987).

[4] H. Rosen, E. M. Engler, T. C. Strand, V. Y. Lee, and D. Bethune, Phys. Rev. B **36**, 726 (1987).

[5] V. D. Kulakovskiĭ, O. V. Misochko, V. B. Timofeev, G. A. Emel'chenko, and V. A. Tatarchenko, Pis'ma Zh. Eksp. Teor. Fiz. **46**, 460 (1987) [JETP Lett. **46**, 580 (1987)].

[6] A. V. Bazhenov, L. V. Gasparov, V. D. Kulakovskiĭ, O. V. Misochko, Yu. A. Osip'yan, and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 162 (1988) [JETP Lett. **47**, 198 (1988)].

[7] I. V. Aleksandrov, A. B. Bykov, A. F. Goncharov, V. N. Denisov, B. N. Mavrin, O. K. Mel'nikov, and V. B. Podobedov, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 184 (1988) [JETP Lett. **47**, 223 (1988)].

[8] C. Thomsen, R. Liu, M. Bauer, A. Wittlin, L. Genzel, M. Cardona, E. Schonherr, W. Bauhofer, and W. Konig, Solid State Commun. **65**, 55 (1988).

[9] D. N. Mirlin and N. I. Reshina, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 315 (1988) [JETP Lett. **47**, 378 (1988)].

[10] D. M. Krol, M. Stavola, W. Weber, L. F. Schneemeyer, J.V. Waszczak, S. M. Zahurak, and S.G. Kosiński, Phys. Rev. B **36**, 8325 (1987).

[11] K. B. Lyons, P. A. Fleury, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **60**, 732 (1988).

[12] K. B. Lyons, S. H. Liou, M. Hong, H. S. Chen, J. Kwo, and T. J. Negran, Phys. Rev. B **36**, 5592 (1987).

[13] A. Abstreiter, M. Cardona, and A. Pinczuk, in: *Light Scattering in Solids IV* (ed. by M. Cardona and G. Güntherodt), Springer Verlag, Berlin (1984), p. 5.

[14] I. I. Mazin, E. G. Maksimov, S. N. Rashkeev, S. Yu. Savrasov, and Yu. A. Uspenskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 94 (1988) [JETP Lett. **47**, 113 (1988)].

[15] A. Aharony, R. J. Birgeneau, A. Coniglio, M. A. Kastner, and H. E. Stanley, Phys. Rev. Lett. **60**, 1330 (1988).

[16] V. N. Denisov, B. N. Mavrin, and V. B. Podobedov, Zh. Eksp. Teor. Fiz. **92**, 1855 (1987) [Sov. Phys. JETP **65**, 1042 (1987)].

[17] V. N. Denisov, B. N. Mavrin, and V. B. Podobedov, Phys. Rep. **151**, 1 (1987).

[18] G. L. Zhao, Y. Xu, W. Y. Ching, and K. W. Wong, Phys. Rev. B **36**, 7203 (1987).

[19] A. A. Gogolin and E. I. Rashba, Solid State Commun. **19**, 1177 (1976).

[20] J. Menendez and M. Cardona, Phys. Rev. B **31**, 3696 (1985).

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