Ultrafast relaxation in Y-Ba-Cu-O and Ni thin films studied by nonlinear spectroscopy technique

V.N.Bagratashvili, V.A.Lobastov, A.N.Zherikhin

Scientific Research Center for Technological Lasers,
USSR Academy of Science, Troitsk, Moscow Region, 142092

V.M.Petnikova, V.V.Shuvalov

Moscow State University, Moscow, 119899

ABSTRACT

By picosecond spectrometer with two tunable dye lasers high temperature superconducting (HTSC) (monocrystal Y-Ba-Cu-O with critical temperature T_c = 87 K) and metal (Ni) thin films has been investigated. A selfdifraction process efficiency η vs biharmonic pumping component detuning Ω has been measured at the temperature Θ = 300 and 80 K. It is found, that there is a well-defined dip on the dispersion curve $\eta(\Omega)$ for the HTSC films at Θ = 80 K and -10 cm^{-1} > Ω > -50 cm^{-1}. This region upper limit corresponds to a superconducting energy gap value 2Δ. At 10 cm^{-1} < Ω < 50 cm^{-1} any distinction of the same type is absent. In other respects all obtained dispersion curves are resemble. They consist of the central peak ($\eta \approx 10^{-7}$, $|\Omega| < 10$ cm^{-1}) and wide wings ($\eta \approx 10^{-9}$, $|\Omega| > 10$ cm^{-1}) with interference structure. Y-Ba-Cu-O film resonances are coincided with the phonon mode frequencies (120, 335 and 580 cm=-1). It is shown that photoexcitation kinetics (the sample "darkening") must be consist of some components. A characteristic time of the most "ultrafast" component below then 5 fs has been estimated and a complex subpicosecond quantum beats presence has been predicted.

1. INTRODUCTION

A HTSC breakthrough had stimulated an active study of metal- oxide compound physical properties[1]. At once by IR spectroscopy methods the first attempts to measure a superconducting energy gap value and to obtain a reliable information about carrier coupling mechanism have been made. A number of investigations of a band structure, phonon modes and other characteristics that determine HTSC film optical properties have been performed.

Not long ago some reports about investigations of a HTSC bolometer unit-step response and frequency response have been published[2-5]. Because of the relative simplicity and high sensitivity these photodetectors are competitive with semiconducting ones. The first experiments have shown that a transition to a resistive phase caused by the ultrashort laser pulse action doesn't be explained only by a sample heating. At least two different relaxation mechanisms with essential different characteristic times — thermal (> 1 μs) and nonequilibrium electronic (< 100 ps) ones — become apparent. However an electrical response is detected in all such experiments usually. Thus their time resolution is defined only by recording device characteristics and doesn't be in excess of 50-100 ps.

A registration of the HTSC film optical response to the laser pulse and effective nonlinear spectroscopy method application enable a new information about this phenomenon to obtain[6-8]. Both the unit-step response and frequency response of such photodetectors may be investigated by this technique. The time resolution up to 10 fs may be reached.

2. METHOD OF RESEARCH

Four-photon spectroscopy methods based on cubic nonlinear susceptibility $\chi^{(3)}$ investigations are a powerful tools for the condensed matter spectroscopy[9]. In these methods three electromagnetic waves with frequencies ω_{1-3} and wave vectors k_{1-3} are mixed in a sample and give rise to some new waves with frequencies $\omega_4 = (\omega_i - \omega_j + \omega_k)$ and wave vectors $k_4 = (k_i - k_j + k_k)$, where i,j,k = 1,2,3. The spectral (Fourier) analysis of this nonlinear process dispersion curve $\eta(\omega_4;\omega_i,-\omega_j,\omega_k) \approx |\chi^{(3)}(\omega_4;\omega_i,-\omega_j,\omega_k)|^2$ is an efficient way for the subpicosecond phenomena main

 0-8194-1068-3/92/$4.00

feature understanding[10-13]. The normal technique is to excite in medium some electronic state spectrum by two laser pulses with different frequencies ω_1 and ω_2. These states correlation is established only due to electron-electron (e-e), electron-phonon (e-p) and other relaxation interactions, so the wave of intraband polarization at the difference frequency $\Omega = (\omega_1 - \omega_2)$ with wave vector $K = (k_1 - k_2)$ may be efficiently induced[10]. In our case $\omega_1 = \omega_3$, $k_1 = k_3$ and we have the so called selfdifraction process with $\omega_4 = (\omega_1 - \omega_2 + \omega_1)$, $k_4 = (k_1 - k_2 + k_1)$. This technique has been named a biharmonic pumping (BP)[11]. The selfdifraction process efficiency η vs Ω is usually measured in such experiments[11-13].

It must be mentioned, that the results given by BP technique are completely equivalent to the results obtained by nonstationary four-photon experiments with subpicosecond pulses[10-13]. This statement results from the functional relationship given by $\chi^{(3)}$ Fourier transform. In real measurements the tuning range of Ω may be above 1000 cm^{-1} and corresponding equivalent time resolution may be so high as 5 fs[10].

This work seeks to investigate HTSC (Y-Ba-Cu-O) and metal (Ni) thin film by BP and saturation spectroscopy[10] technique. For these subjects e-e type relaxation processes must be attach great importance because of high free carrier density. One can expect that the superconductive transition will be accompanied by a modification of the nonlinear process efficiency frequency dependence $\eta(\Omega)$. Really when the frequency Ω is less than superconducting energy gap 2Δ the exited electronic state correlation can't be caused by e-e interaction processes, and one can expect that the dispersion curve $h(\Omega)$ will fall down in this region.

3. EXPERIMENTAL SET UP

Our experimental set up is a modified version of a picosecond spectrometer that has been described in detail in references[12,13] and has been successful for semiconductor and dye solution research. Its block-diagram is shown in fig.1. We used a second harmonic of passive mode locking Nd:YAG laser pulses for two dye laser pumping. Their tunable range was about 590-645 nm, pulse duration — 20 ps, peak power — 50 kW, spectral width — 1,5 cm^{-1}. The delay time $\Delta\tau$ between dye laser pulses was controlled by optical path length variation. In present experiments we didn't used this possibility and $\Delta\tau = 0$. Both laser beams was focused on the sample surface at the same position. The focal spot dimension was about 50 μm, the angle between beams — 7°. The sample was placed within optical cryostat.

A registration system included some photodiodes for energy control of Nd:YAG laser, second harmonic and both dye laser pulses. The energy of selfdifraction radiation was measured by a photomultiplier. To eliminate the noise connected with light scattering process by sample inhomogeneities a spatial filter was used. The registration system sensitivity run into 10^{-16} J per pulse. To obtain the mean value of efficiency η the averaging over some laser shot series was produced. Only laser pulses with energy deviation below 10% were taking into account.

We used a laser deposition technique for Y-Ba-Cu-O thin film production . Monocrystal $SrTiO_3$ substrata were used. KrF eximer laser pulses were focused on the target surface. Light energy density was about 2 J/cm^2, the substratum temperature — Θ = 1050 K. Oxygen pressure within the chamber during deposition process was p = 5 10^{-2} Torr. Obtained film critical temperature T_c is about 87 K and their thickness is varied from 0,2 to 1,0 μm. The Ni films were deposited by the same technique. Polished glass plates were used as substrata. Obtained film transmittance T is about 1,5% at λ = 620,4 nm.

4. RESULTS AND DISCUSSION

The dispersion curves $\eta(\Omega) \propto |\chi^{(3)}(\Omega)|^2$ are shown in fig.2a-d, where $\Omega = (\omega_1 - \omega_2)$, ω_1 = const and corresponds to λ_1 = 620,4 nm. The dispersion curves for Ni film obtained at Θ = 300 K and 80 K (fig.2 a,b) are resemble to each other. They include a central peak ($|\Omega| < 10$ cm^{-1}) with Lorentzian approximation $\eta_0 \propto [1 - (\Omega/\Omega_0)^2]^{-2}$ where $\Omega_0 = (5{,}1 \pm 0{,}6)$ cm^{-1}. At the wings (10 $cm^{-1} < |\Omega| < 700$ cm^{-1}) the mean level of the efficiency η is approximately 10^{-2} from its maximum value ($\eta_0 \approx 10^{-7}$ at $\Omega = 0$). There is a characteristic structure on the wings, which we connect with interference of $\chi^{(3)}$ resonant phonon and nonresonant electron partials[10,13]. The sample cooling

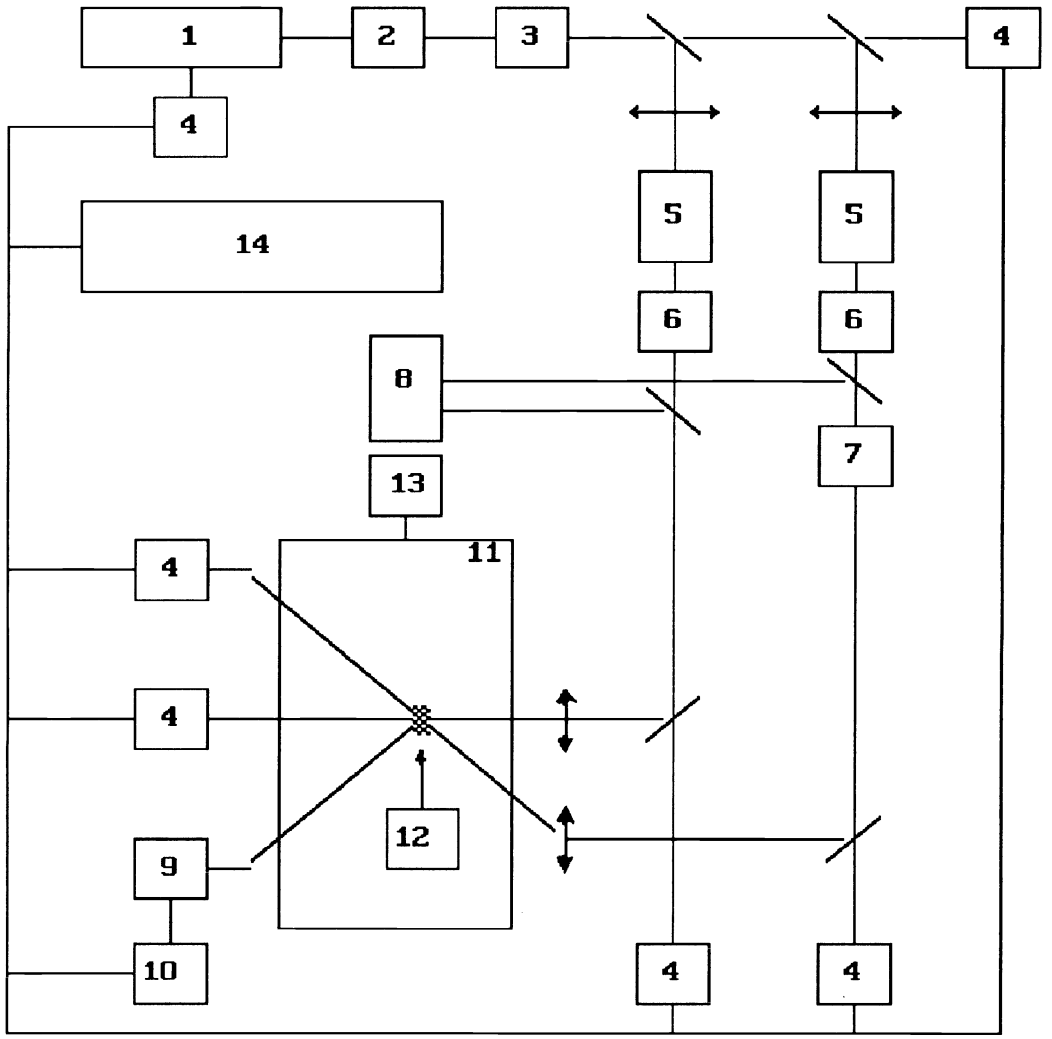

Fig. 1. Experimental set-up: 1- Nd:YAG laser, 2- frequency doubler, 3- dye laser, 4- delay line, 5- optical cryostat, 6- sample, 7- temperature control system, 8- photodiod, 9- space filter, 10- photomultiplier, 11- frequency control system, 12- computer.

doesn't caused any change in the central peak region (fig.2b), but the wing structure becomes "smoother" at Θ = 80 K than at Θ = 300 K.

The dispersion curve $\eta(\Omega)$ for Y-Ba-Cu-O film (T = 1,5%) at Θ = 300 K (fig.2c) is resemble to the same dependence for Ni film. Its central peak ($\eta_0 \approx 10^{-7}$ at Ω = 0) has the same Lorentzian approximation with Ω_0 = (7,2±1,2) cm^{-1}. There are similar side-peaks on the wings, their positions correspond to well-known phonon mode frequencies 120, 335 and 580 cm^{-1} measured by Raman spectroscopy experiments[15]. The Y-Ba-Cu-O film cooling causes essential change of dispersion curve and in the frequency range -10 cm^{-1} > Ω > -50 cm^{-1} a well-defined dip is really formed (fig.2d). This region upper limit (50 cm^{-1}) corresponds to a superconducting energy gap value 2Δ measured by other scientific groups at the same temperature[16]. In the frequency range 10 cm^{-1} < Ω < 50 cm^{-1} any distinction of the same type is absent. The central peak and the wing structure are also changed. The central peak width decreases because of its shape can't be approximated by Lorentzian and the side-peak positions are shifted. We believe, that the origin of this dip formation and the central peak distortion is connected

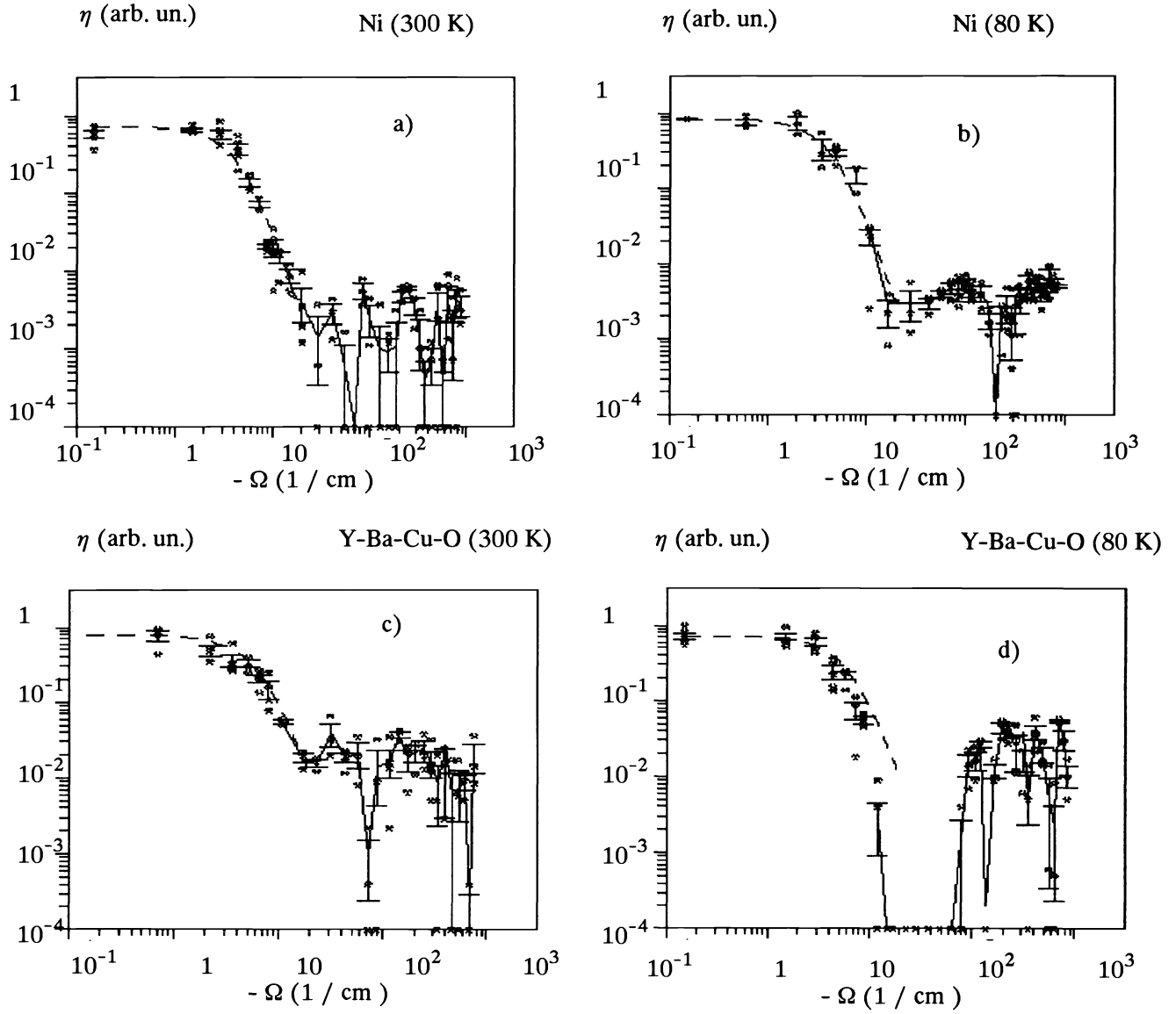

Fig. 2. Selfdifraction process efficiency η vs biharmonic pumping component frequency detuning $\Omega = (\omega_1 - w_2)$.

with allowed electronic state spectrum transformation — with the superconducting energy gap appearance. A reason of such dispersion curve trend must be analogous to the origin of Y-Ba-Cu-O Raman spectrum "asymmetrical feature" formation[16,17].

It is of interest to discuss a possible nonstationary experiment result. Obtained dispersion curve $h(\Omega)$ complex trend indicates that in the metal (Ni) and HTSC (Y-Ba-Cu-O) films a relaxation kinetics must be consist of some "slow", "fast" and "ultrafast" components. These components correspond to the dispersion curve central peak and its wings with interference structure. Therefore the one- or two-exponential simplest models of photoexcitation decay can't be used. Correct description must include some interfering resonant phonon and nonresonant electron partials. A characteristic time of the most "ultrafast" component may be estimated as below than 5 fs. In addition the some side-peak ($\Omega \neq 0$) presence means that the complex subpicosecond quantum beats must be observed. These beats

pattern must be changed by the sample superconductive transition and their characteristic frequency 2Δ as well as phonon mode frequencies must be observed. Our conclusions following from the experimental data analysis are in agreement with qualitative theory predictions not long ago published in reference[6].

Our experiments have shown that the efficiency maximum value $\eta 0$ at $\Omega = 0$ is proportional to the Y-Ba-Cu-O film transparency. It can be explained by the following mechanism. The absorptance α of Y-Ba-Cu-O film is high enough so $\alpha^{-1} < h$, where h is the film thickness. In this case the wave ω_4 can be generated only near the input film surface and its intensity decreases during propagation due to the film absorption. So, the output intensity must be proportional to the film transmittance.

We have measured the Y-Ba-Cu-O film transmittance T at $\Theta = 300$ K and $\lambda_1 = 620{,}4$ nm vs the incident laser pulse energy — a saturation spectroscopy[9,13] ($\omega_4 = \omega_1 - \omega_1 + \omega_1$, $k_4 = k_1 - k_1 + k_1$). Within the limits of experimental accuracy (about 2-3%) we didn't found any saturation of the absorptance a for the all investigated films. However application of pump-probe version of this nonlinear spectroscopy method[9,13] ($\omega_4 = \omega_1 - \omega_1 + \omega_2$, $k_4 = k_1 - k_1 + k_2$) have made possible to obtain some additional useful information. In this case the sample has been excited by sufficiently powerful (with energy about 0,2 μJ) pump pulse at a fixed wavelength l (595, 600, ..., 630 nm). Simultaneously ($\Delta\tau = 0$) by a comparative weak (with respect to pumping) probe pulse at tunable wavelength λ_2 its transmission spectrum has been measured. Then the same procedure has been repeated when the excited pulse is absent. As before at any experimental "point" $\lambda_2 = \text{const}$ the sample transmittance value T exhibit an error of 2-3%, but application of the whole measured dependence approximation methods is possible now. By a least-square procedure every experimental dependence has been approximated by the expansion into series of orthogonal polynomials up to some power. The optimal (6-8) power of this expansion has been determined by preliminary fit statistics. It was found, that a relative deviation of approximated functions corresponding to any realizations obtained independently at the same experimental conditions and stopped λ_2 is never more than 0,3-0,4%. At the same time into some spectral regions an excited sample "darkening" is always observed. In this case the relative change of transmittance approximated function value is never more than 1,0-1,2%. And what is more into spectral region 630 nm $\leq \lambda_2 \leq$640 nm for $\lambda_1 = 610$ nm the pattern of these changes caused by pump pulse action is in qualitative agreement with experimental data presented in reference[8]. So if the application of this procedure is correct and our measurement accuracy is really improved then some modification of transmission spectrum of Y-Ba-Cu-O films by picosecond pulse action have been really recorded. For Ni films any changes of the same type are absent.

5. CONCLUSION

Our experiments have demonstrated that the four-photon spectroscopy methods are a powerful tools for the metal and superconductor research. In addition a biharmonic pumping technique has some substantial merits: a) it is the most "direct" procedure for measurements of bath "noise" spectrum. So this technique is an efficient way for the electron subsystem allowed state spectrum investigation for those subjects where e-e relaxation processes are very important; b) it is the most convenient procedure for indirect measurements of ultrafast relaxation process rates. Its equivalent time resolution may be so high as 5 fs, and high sensitivity is supported by the spatial filter application possibility.

Our conclusions about subpicosecond relaxation kinetics are only qualitative as we have no phase information about $\chi^{(3)}$ pattern. If we could obtain this information by BP method, our prediction of the results obtained by the nonstationary experiment with femtosecond pulses would have been definitive. Really for that it is necessary to built some theoretical model that will take into account correct contribution of all interaction processes or to carry out such experiment.

6. REFERENCES

1. "Physical properties of high temperature superconductors", ed. by D.M.Ginsberg, *World Scientific*, New Jersey, 1989.

2. W.S.Brocklesby, Don Monroe, A.F.J.Levi et al. "Electrical response of superconducting YBa Cu O to light", *Appl. Phys. Lett.*, vol.54, N12, pp.1175-1177, 1989.

3. H.S.Kwok, J.P.Zheng, Q.Y.Ying, "Nonthermal optical response of Y-Ba-Cu-O thin films", *Appl. Phys. Lett.*, vol.54, N24, pp.2473-2475, 1989.

4. E.M.Gershenson, M.E.Gershenson, G.N.Gol'tsman et al. "Ultra fast electron bolometers using Nb and YBa Cu O thin films", *ISEC-89*, pp.214-218, Tokyo, 1989.

5. J.Talvacchio, M.G.Forrester, A.I.Braginski, "Photodetection with high-T superconducting films", *Science and technology of thin-film superconductors*, pp.152-161, Plenum, New York, 1989.

6. B.D.Fainberg, "Real time optical spectroscopy of superconducting-gap excitations", *Phys. Stat. Sol.* (b), vol.160, N2, pp.169-172, 1990.

7. S.D.Brorson, J.G.Fujimoto, E.P.Ippen. "Femtosecond thermomodulation study of high-T superconductors", *Solid State Communs*, vol.74, N12, pp.1305-1308, 1990.

8. M.E.Gershenson, V.V.Golovlev, I.B.Kedich et al. "Femtosecond laser spectroscopy of nonequilibrium electronic processes in YBa Cu O ", *preprint*, Troitsk, 1990 (in Russian).

9. S.A.Akhmanov, N.I.Koroteev, "Methods of nonlinear optics in light-scattering spectroscopy", *Nauka*, Moscow, 1981 (in Russian).

10. V.M.Petnikova, B.A.Grishanin, V.V.Shuvalov, "Nonstationary semiconductor spectroscopy", *Itogi nauki i techniki, Sovremennie problemi lasernoi fisiki*, vol.2, pp.7-81, VINITI, Moscow, 1990 (in Russian).

11. T.Yajima, "Nonlinear optical spectroscopy of an inhomogeneously broadened resonant transition by means of three-wave mixing", *Opt. Communs*, vol.14, N3, pp.309-323, 1975.

12. V.M.Petnikova, S.A.Pleshanov, V.V.Shuvalov, "Identification of relaxation mechanisms in nonlinear spectroscopy of electron resonances of semiconductors", *Sov. Phys. JETP*, vol.61, N2, pp.211-217, 1985.

13. V.M.Petnikova, M.A.Kharchenko, V.V.Shuvalov, "Stationary and nonstationary spectroscopy of GaSe", *Phys. Lett. A*, vol.125, N6,7, pp.347-353, 1987.

14. V.N.Denisov, V.N.Mavrin, V.B.Podobedov et al. "Diagnostics of the high temperature superconducting YBa Cu O films by Raman spectroscopy", *Solid State Communs*, vol.69, N7, pp.743-746, 1989.

15. V.D.Kulakovskii, O.V.Misochko, V.B.Timofeev, "Phonons in orthorombic YBa Cu O monocrystals", *Fizika tverdogo tela*, vol.31, N9, pp.220-230, 1989 (in Russian).

16. K.B.Luons, S.H.Liou, M.Hong et al., "Raman detection of the superconducting gap in Ba-Y-Cu-O superconductors", *Phys. Rev. B*, vol.36, N10, pp.5592-5594, 1987.

17. V.P.Gnezdilov, V.V.Eremenko, V.S.Kurnosov, A.V.Peschansky, V.I.Fomin, "Raman studies of superconducting energy gap in YBa Cu O superconductors", *Fizika nizkikh temperatur*, vol.15, N8, pp.823-827, 1989 (in Russian).