Nonlinear spectroscopy of Y–Ba–Cu–O and Ni thin films by a biharmonic pumping technique

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1. Introduction

Four-photon spectroscopy methods based on the investigation of the cubic nonlinear susceptibility \(\chi^{(3)}\) are powerful tools in condensed matter spectroscopy [1]. In these methods three electromagnetic waves with frequencies \(\omega_{1-3}\) and wave vectors \(\mathbf{k}_{1-3}\) 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 \(\mathbf{k}_4=(\mathbf{k}_i-\mathbf{k}_j+\mathbf{k}_k)\), where \(i, j, k=1, 2, 3\). The spectral (Fourier) analysis of the dispersion curve of this nonlinear process,

\[
\eta(\omega_4; \omega_i, -\omega_j, \omega_k) \sim |\chi^{(3)}(\omega_4; \omega_i, -\omega_j, \omega_k)|^2,
\]

is an efficient way to reveal the main features of the subpicosecond phenomena [2–5]. The usual technique is to excite in a medium a spectrum of some electronic states by two laser pulses with different frequencies \(\omega_1\) and \(\omega_2\). Correlation of excited states is established only due to electron–electron (e–e), electron–phonon (e–p) and other relaxation inter-

actions, so the wave of intraband polarization at the difference frequency \(\Omega=\omega_1-\omega_2\) with wave vector \(\mathbf{K}=\mathbf{k}_1-\mathbf{k}_2\) may be efficiently induced. In our case with \(\omega_1=\omega_3\) and \(\mathbf{k}_1=\mathbf{k}_3\) we have a so-called selfdiffraction process with \(\omega_4=2\omega_1-\omega_2\) and \(\mathbf{k}_4=2\mathbf{k}_1-\mathbf{k}_2\). This technique has been named biharmonic pumping (BP) [2]. The selfdiffraction process efficiency \(\eta\) versus \(\Omega\) is usually measured in such experiments [3–5].

It must be mentioned that the results obtained by the BP technique are completely equivalent to the results obtained by nonstationary four-photon experiments with subpicosecond pulses [2–5]. This statement results from the functional relationship given by the Fourier transform of \(\chi^{(3)}\). In real measurements the tuning range of \(\Omega\) may be above 1000 cm\(^{-1}\) and the corresponding equivalent time resolution may be as high as 5 fs [3–5].

This work seeks to investigate HTSC (Y–Ba–Cu–O) and metal (Ni) thin films by the BP technique. For these objects the e–e type relaxation processes...
are of great importance due to the high free carrier density. One can expect that the superconductive transition will modify the dependence of the nonlinear process efficiency versus the frequency detuning, \( \eta(\Omega) \). In fact, when the frequency \( \Omega \) is less than the superconducting energy gap \( 2\Delta \), the excited electronic state correlation cannot be caused by e-e interaction processes, and one can expect that the dispersion curve \( \eta(\Omega) \) will decrease in this region.

### 2. Experimental setup

Our experimental setup is a modified version of a picosecond spectrometer which has been used successfully in semiconductor and dye solution research as described in detail in refs. [3–5]. Its block diagram is shown in fig. 1. We used the second harmonic of passive mode locking Nd: YAG laser pulses for the two dye laser pumping. Their tunable range was about 590–645 nm, the pulse duration 20 ps, the peak power 50 kW, the spectral width 1.5 cm\(^{-1}\). The delay time \( \Delta \tau \) between the dye laser pulses was controlled by optical path length variation. In the present experiments we did not use this possibility and \( \Delta \tau = 0 \). Both laser beams were focused on the sample surface at the same position. The focal spot dimension was about 50 \( \mu \)m, the angle between the beams 7\(^\circ\). The sample was placed into an optical cryostat.

The registration system included some photodiodes for the energy control of the Nd: YAG laser, the second harmonic and both dye laser pulses. The energy of the selfdiffraction radiation was measured by a photomultiplier. To eliminate the noise connected with the light scattering process by sample inhomogeneities a spatial filter was used. The registration system’s sensitivity ran to \( 10^{-16} \) J per pulse.

To obtain the mean value of the efficiency \( \eta \) averaging over some laser shot series was performed. Only laser pulses with an energy deviation below 10\% were taken into account.

We used a laser deposition technique for the Y–Ba–Cu–O thin film production [6]. Monocrystal SrTiO\(_3\) substrates were used. KrF excimer laser pulses were focused on the target surface. The light energy density was about 2 J/cm\(^2\), the substrate temperature \( \Theta = 1050 \) K. The oxygen pressure within the chamber during the deposition process was \( p = 5 \times 10^{-2} \) Torr. The obtained critical film temperature \( T_c \) was about 87 K and their thickness varied from 0.2 to 1.0 \( \mu \)m. The Ni films were deposited by the same technique. Polished glass plates were used as substrates. The obtained film transmittance \( T \) was about 1.5\% at \( \lambda = 620.4 \) nm.

### 3. Experimental results and discussion

The dispersion curves \( \eta(\Omega) \sim |\chi^{(3)}(\Omega)|^2 \) are shown in figs. 2a–2d, where \( \Omega = \omega_1 - \omega_2, \omega_1 = \text{const} \) and corresponds to \( \lambda_1 = 620.4 \) nm. The dispersion curves for the Ni film obtained at \( \Theta = 300 \) and 80 K (figs. 2a, 2b) resemble each other. They include a central peak (\( |\Omega| < 10 \) cm\(^{-1}\)) with a Lorentzian approximation \( \eta \sim [1 - (\Omega/\Omega_0)^2]^{-2} \) where \( \Omega_0 = 5.1 \pm 0.6 \) cm\(^{-1}\). At the wings (\( 10 < |\Omega| < 700 \) cm\(^{-1}\)) the mean level of the efficiency \( \eta \) is approximately \( 10^{-2} \) of its maximum value (\( \eta_0 \approx 10^{-7} \) at \( \Omega = 0 \)). There is a characteristic structure on the wings, which we connect with the interference of \( \chi^{(3)} \) resonant phonon and nonresonant electron partials [3–5]. The sample cooling does not cause any change in the central peak region (fig. 2b), but the wing structure becomes “smoother” at \( \Theta = 80 \) K than at \( \Theta = 300 \) K.
The dispersion curve for the Y–Ba–Cu–O film ($T = 1.5\%$) at $\Theta = 300\,\text{K}$ (fig. 2c) resembles the dependence for the Ni film. Its central peak ($\eta_0 \approx 10^{-7}$ at $\Omega = 0$) has the same Lorentzian approximation with $\Omega_0 = 7.2 \pm 1.2\,\text{cm}^{-1}$. There are similar side-peaks on the wings, and their positions correspond to the well-known phonon mode frequencies 120, 335 and 580 cm$^{-1}$ measured by Raman spectroscopy experiments [7]. The Y–Ba–Cu–O film cooling causes an essential change of the dispersion curve and in the frequency range $-10 > \Omega > -50\,\text{cm}^{-1}$ a well-defined dip is formed (fig. 2d). The upper limit of this region (50 cm$^{-1}$) corresponds to a superconducting energy gap value $2\Delta$ measured by other researchers at the same temperature [8]. In the frequency range $10 < \Omega < 50\,\text{cm}^{-1}$ no such effect is found. The central peak and the wing structure are also changed. The central peak width decreases as its shape cannot be approximated by a Lorentzian and the side-peak positions are shifted. We believe, that the origin of this dip formation and the central peak distortion is connected with the allowed electronic state spectrum transformation - with the superconducting energy gap appearance. The reason of such a dispersion curve trend must be analogous to the origin of the Y–Ba–Cu–O Raman spectrum "asymmetrical feature" formation [8,9].

It is of interest to discuss a possible nonstationary experiment result. The complex trend of the dispersion curve $\eta(\Omega)$ indicates that in the metal (Ni) and
HTSC (Y–Ba–Cu–O) films a relaxation kinetics must consist of some “slow”, “fast” and “ultrafast” components. These components correspond to the dispersion curve’s central peak and its wings with interference structure. Therefore the one- or two-exponential simplest models of photo-excitation decay cannot be used. A correct description must include some interfering resonant phonon and nonresonant electron partials. The characteristic time of the most “ultrafast” component may be estimated below 5 fs. In addition, the presence of some side-peak (Ω\neq0) means that the complex subpicosecond quantum beats must be observed. These beat patterns must be changed by the sample superconductive transition and their characteristic frequency 2Δ. Also phonon mode frequencies must be observed.

Our experiments have shown that the maximum efficiency value \(\eta_0\) at \(Ω=0\) is proportional to the Y–Ba–Cu–O film transparency. It can be explained by the following mechanism. The absorptance \(\alpha\) of the Y–Ba–Cu–O film is high enough, so \(\alpha^{-1} \ll h\), where \(h\) is the film thickness. In this case the wave \(\omega_4\) can be generated only near the film interface and its intensity decreases during the propagation due to the film absorption. So the output intensity must be proportional to the film transmittance.

Also, we measured the Y–Ba–Cu–O film transmittance at \(\lambda=620.4\) nm versus the incident laser pulse energy. Our measurement accuracy was about 2%. For all investigated films we found no saturation of the absorptance \(\alpha\).

4. Conclusions

Our experiments have demonstrated that the four-photon spectroscopy methods are powerful tools for metal and superconductor researches. In addition, the biharmonic pumping technique has some substantial advantages:

(a) It is the most “direct” procedure for measurements of a bath “noise” spectrum. So, for the objects where e–e relaxation processes are very important this technique is an efficient way to investigate the spectrum of the allowed states of the electron subsystem.

(b) It is the most convenient procedure for “indirect” measurements of ultrafast relaxation process rates. Its equivalent time resolution may be as high as 5 fs, and high sensitivity is supported by the possibility of spatial filter applications.

Obviously, our conclusions about subpicosecond relaxation kinetics are mainly of qualitative character due to the lack of phase information about the \(\chi^{(3)}\) pattern. Having had such an information by the BP method, the predicted results obtainable by the nonstationary experiment with femtosecond pulses would be definitive. For this purpose it is necessary to work out a theoretical model which would take into account correctly the contribution of all interaction processes or to carry out such an experiment.

References