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PACS numbers: 42.62.Fi; 78.47.+p; 78.20.-e; 78.20.Bh
DOI: 10.1070/QE2003v033n11ABEH002538

Interference of nonlinear response components in degenerate four-photon spectroscopy of ultrathin metal films

Yu.V. Bobyrev, V.M. Petnikova, K.V. Rudenko, A.Yu. Shipova, V.V. Shuvalov

***Abstract*. It is shown that a specific dip in the spectral dependence of the nonlinear response of ultrathin metal films observed by the method of degenerate four-photon spectroscopy is caused by a change in the phases of interfering components of the electron nonlinear susceptibility. This allows one to measure the time scale of subpicosecond intraband processes using picosecond light pulses.**

Keywords: *degenerate four-photon spectroscopy, ultrathin metal films, interference of nonlinear susceptibility components.*

1. Introduction

The ultrafast relaxation kinetics of electronic excitation in metals is usually studied by the pump-probe pulse method [1 – 10]. The change in the reflection $[\Delta R(\tau, \lambda)]$ and (or) transmission $[\Delta T(\tau, \lambda)]$ coefficients of an ultrathin metal film induced by an ultrashort pump pulse is monitored with a probe pulse of the same ultrashort duration. The probing is performed with a variable time delay τ with respect to the pump pulse in a broad spectral range either in succession (the wavelength of the probe pulse is changed successively) or in parallel (using a broadband probe pulse). Then, information on the kinetics $\Delta\varepsilon(\tau, \lambda)$ of the complex permittivity ε is obtained from the experimental data using standard procedures (see, for example, Refs [1, 3, 6 – 9]). The time evolution of nonequilibrium states is described in terms of thermodynamic parameters (temperatures T_e and T_p of the electron and phonon subsystems, respectively, the Fermi level E_F, etc.), whose instantaneous values are calculated from $\Delta\varepsilon(\tau, \lambda)$ using certain models [6 – 9, 11, 12]. In the method of degenerate four-photon spectroscopy (DFPS), the nonequilibrium spatially inhomogeneous distributions (gratings) of $\Delta\varepsilon$ are probed simultaneously ($\tau \equiv 0$) with their excitation [13 – 16]. The gratings are recorded in a sample by the interference field of two comparatively long (picosecond) pulses of the same wavelength λ propagating at an angle to each other. The dependence of the diffraction efficiency η of one of these pulses (self-diffraction) on λ is measured. Note that the DFPS method was developed for studying the resonance mechanisms of nonlinearity, i.e., for the measurements of the frequency and width of the resonance lines separated in the nonlinear response and the ratio of their amplitudes [17].

Already first pump-probe pulse experiments with Cu and Y – Ba – Cu – O films and fullerenes revealed a strong dependence of $\Delta\varepsilon$ on λ [6 – 9]. It is shown that there exist points on the axis λ at which $\Delta\varepsilon \equiv 0$ for any τ. These data were interpreted assuming a dominant role of interband electronic transitions in the formation of the nonlinear response of a metal. The authors of paper [18], who studied thin W and Al films using other variants of the pump-probe pulse method, made the same conclusion. A drastic decrease in the amplitude of the nonlinear response η for Ni and Pt films in the vicinity of certain points on the axis λ was also discovered by the DFPS method [13 – 16]. The authors showed that the model of a nonlinear response [19], which takes into account the saturation of interband electronic transitions in a real (see below) band structure, very accurately describes the experiments using a minimal number of fitting parameters.

Below, we will show, using the model [19] for the DFPS of Pt films, that due to the interference of two components of a nonlinear response there exist points on the axis λ at which both the real ($\mathrm{Re}\chi_{ee}^{(3)}$) and imaginary ($\mathrm{Im}\chi_{ee}^{(3)}$) parts of the electron nonlinear susceptibility vanish simultaneously. This not only explains the results of all experiments [6 – 9, 13 – 16] but also permits the measurements of the characteristic times of subpicosecond intraband processes by the DFPS method using comparatively long (picosecond) light pulses.

2. Structure of a nonlinear response in DFPS

Within the framework of the model [19], the structure of the electron part $\chi_{ee}^{(3)}$ of the nonlinear susceptibility (nonlinear response) of an ultrathin metal film can be represented in the form typical for nonlinear spectroscopy

$$\chi_{ee}^{(3)} \propto P_0(K_+P_+ + K_-P_-), \tag{1}$$

where P_0, $P_\pm$, and $K_\pm$ are the resonance factors describing the probabilities of all possible one- and two-photon electronic transitions and depending on the frequency detunings of resonances. It follows from the expressions for P_0, $P_\pm$, and $K_\pm$ presented in Ref. [19] that in the DFPS

Yu.V. Bobyrev, V.M. Petnikova, K.V. Rudenko, A.Yu. Shipova, V.V. Shuvalov International Teaching and Research Laser Center, M.V. Lomonosov Moscow State University, Vorob'evy gory, 119992 Moscow, Russia

Received 26 March 2003
Kvantovaya Elektronika **33** (11) 998 – 1000 (2003)
Translated by M.N. Sapozhnikov

method, when the frequencies ω of all the interacting waves are the same,

$$P_+ = P_-^* = P_0^* = \sum_{i,i'} \int\int \frac{d_{i,i'}(\boldsymbol{k},\boldsymbol{k}')n_i(\boldsymbol{k})[1-n_{i'}(\boldsymbol{k}')]}{[\omega-\Omega_{i,i'}(\boldsymbol{k},\boldsymbol{k}')+\mathrm{i}\Gamma_{i,i'}(\boldsymbol{k},\boldsymbol{k}')]^2}\,\mathrm{d}\boldsymbol{k}\mathrm{d}\boldsymbol{k}', \quad (2)$$

$$K_+ = K_-^* = \sum_{i,i'} \int\int \frac{d_{i,i'}(\boldsymbol{k},\boldsymbol{k}')n_i(\boldsymbol{k})[1-n_{i'}(\boldsymbol{k}')]}{-\Omega_{i,i'}(\boldsymbol{k},\boldsymbol{k}')+\mathrm{i}\Gamma_{i,i'}(\boldsymbol{k},\boldsymbol{k}')}\,\mathrm{d}\boldsymbol{k}\mathrm{d}\boldsymbol{k}'. \quad (3)$$

Here, i and i' are the numbers of the initial and final bands involved in the $(i,\boldsymbol{k}) \to (i',\boldsymbol{k}')$ electronic transition with the dipole moment $d_{i,i'}(\boldsymbol{k},\boldsymbol{k}')$ and the rate $\Gamma_{i,i'}(\boldsymbol{k},\boldsymbol{k}')$ of intraband ($i = i'$) or interband ($i \neq i'$) relaxation; $\boldsymbol{k}$ is the electron wave vector; $n_i(\boldsymbol{k})$ is the occupation number of the $(i,\boldsymbol{k})$ electronic state, which is specified in the thermodynamic equilibrium by the Fermi–Dirac distribution. The integration over $\boldsymbol{k}$ and $\boldsymbol{k}'$ is performed within the first Brillouin zone, and summation is performed over i and i' in all the state bands. Below, taking into account that the photon momentum is small, we will assume that all the $(i,\boldsymbol{k}) \to (i',\boldsymbol{k}')$ electronic transitions are 'direct' ($\boldsymbol{k} \equiv \boldsymbol{k}'$) and, therefore, we will pass in (2) and (3) to one-dimensional integrals over $\boldsymbol{k}$, assuming that $d_{i,i'}(\boldsymbol{k},\boldsymbol{k}') \equiv d_{i,i'}(\boldsymbol{k})$ and $\Gamma_{i,i'}(\boldsymbol{k},\boldsymbol{k}') \equiv \Gamma_{i,i'}(\boldsymbol{k})$. The transition frequencies will be described by the expressions $\Omega_{i,i'}(\boldsymbol{k},\boldsymbol{k}') \equiv \Omega_{i,i'}(\boldsymbol{k}) = E_{i'}(\boldsymbol{k}) - E_i(\boldsymbol{k})$, where $E_i(\boldsymbol{k})$ is the electron energy in the (i, $\boldsymbol{k}$) state normalised to Planck's constant $\hbar$.

As in Ref. [19], we will determine frequencies $\Omega_{i,i'}(\boldsymbol{k})$ in all our subsequent calculations by interpolating the known data on the band structure of massive Pt samples [20] over the entire Brillouin zone, taking into account the size renormalisation of the band structure [19, 21]. This allows us to include a real (known from the literature) band structure of an object under study to model (1)–(3), thereby drastically reducing the number of free (fitting) parameters of the model. These parameters in our subsequent calculations are the temperature T_e of the electron subsystem and the characteristic time scale $\Gamma_{i,i'}^{-1}(\boldsymbol{k})$ of relaxation processes. However, here we will consider only a much more important and general result, which directly follows from relations (1)–(3). Indeed, by introducing the notation

$$P = P_+ = |P|\exp(\mathrm{i}\varphi_P), \quad K = K_+ = |K|\exp(\mathrm{i}\varphi_K), \quad (4)$$

we can easily write expression (1) in the form

$$\chi_{ee}^{(3)} \propto |P|^2|K|\cos(\varphi_P+\varphi_K)\exp(\mathrm{i}\varphi_P). \quad (5)$$

It follows from (5) that, if the frequencies of interacting pulses are degenerate, the electron nonlinear response vanishes not only when either $|P|$ or $|K|$ vanishes (which is, in our opinion, unlikely) but also when $\varphi_P + \varphi_K = (2k+1)\pi/2$, where k is any integer. It is remarkable that this conclusion remains valid even without any other assumptions on the type of dependences $d_{i,i'}(\boldsymbol{k})$, $n_i(\boldsymbol{k})$, $E_i(\boldsymbol{k})$, and $\Gamma_{i,i'}(\boldsymbol{k})$ because it requires no specifying of these dependences. That is why, in our opinion, this quite general effect should explain experimental results of papers [6–9, 13–16], where the vanishing (or reduction down to the noise level) was observed simultaneously both for the real ($\mathrm{Re}\chi_{ee}^{(3)}$) and imaginary ($\mathrm{Im}\chi_{ee}^{(3)}$) parts of the electron nonlinear susceptibility.

3. Numerical simulation

Below, we used the following simplifications in our calculations. We assumed, as in Ref. [19], that $d_{i,i'}(\boldsymbol{k}) \equiv d$ and $\Gamma_{i,i'}(\boldsymbol{k}) \equiv \Gamma$ are constants independent of i, i', and $\boldsymbol{k}$. Corrections $\delta n_i(\boldsymbol{k})$ (for saturation), caused by the action of pump light fields at the frequency ω, to the equilibrium values $n_i^{\mathrm{F}}(\boldsymbol{k})$ of the occupation numbers given by the Fermi–Dirac distribution were assumed small (the maximum saturation level was $\delta n_i(\boldsymbol{k})[n_i^{\mathrm{F}}(\boldsymbol{k})]^{-1} \simeq 0.01$). They were calculated using the approach [19] based on the modified density matrix for the effective two-level system in the dipole approximation [22]. The frequency $\Omega_{i,i'}(\boldsymbol{k})$ was calculated by interpolating the data on the band structure of Pt [20] over the entire Brillouin zone taking into account the requirements of symmetry and periodicity. The interpolation and subsequent integration were performed for the bands covering the ±2.5-eV range from the Fermi level. The free parameters of the model (1)–(3) were not varied but fixed at values providing good agreement between the calculated dependence $\eta(\lambda)$ and experimental results [16]. We assumed that the Pt film thickness L, determining a total number of subbands of size quantisation, was 5 nm, the electron subsystem was 'heated' by pump pulses up to $T_e = 600$ K, and the relaxation time of interband polarisation was $\Gamma^{-1} = 180$ fs.

As expected, our calculation confirmed that $|P(\lambda)|$ changes monotonically in the spectral region 620–640 nm of interest to us (see Ref. [16]) and $|K(\lambda)|$ is almost constant and never vanishes (Fig. 1). A simultaneous continuous change in φ_P at φ_K being constant (Fig. 2a) leads to the vanishing of $\cos(\varphi_P+\varphi_K)$ at $\lambda \simeq 635$ nm (Fig. 2b). For this reason, in complete agreement with the experiment and calculation [16], the electron part of the nonlinear response $\eta(\lambda) \propto |\chi_{ee}^{(3)}|^2$ of the Pt film also vanishes at this point (Fig. 3).

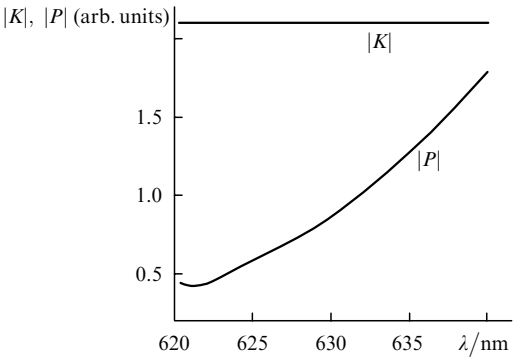

Figure 1. Dependences $|P(\lambda)|$ and $|K(\lambda)|$ calculated for the 5-nm thick Pt film for $T_e = 600$ K and $\Gamma^{-1} = 180$ fs.

4. Conclusions

The results obtained in our paper show that the spectral feature of the nonlinear response of ultrathin metal films – the dip in the dependence $\eta(\lambda)$, discovered recently by the

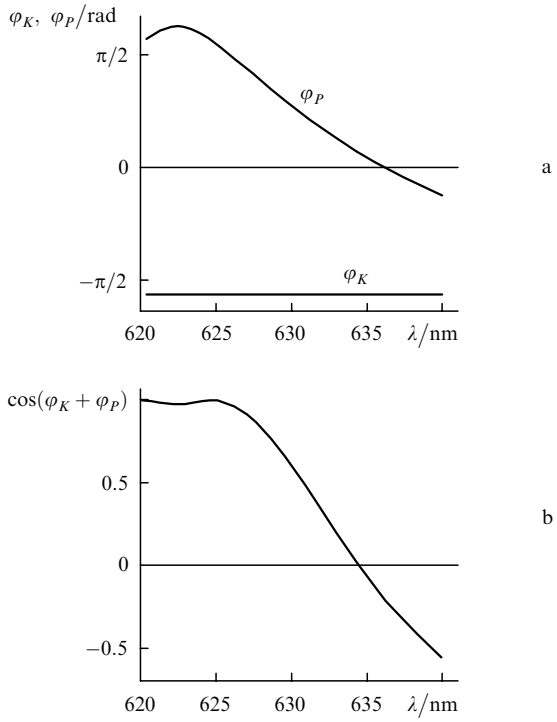

Figure 2. Wavelength dependences of φ_P and φ_K (a) and $\cos(\varphi_P + \varphi_K)$ calculated for the 5-nm thick Pt film for $T_e = 600$ K and $\Gamma^{-1} = 180$ fs.

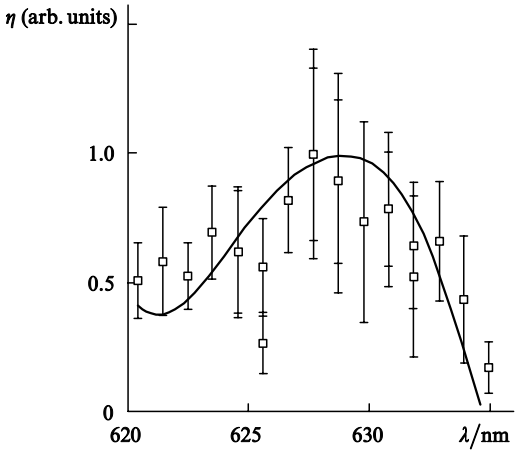

Figure 3. Experimental data [16] (squares) and the dependence $\eta(\lambda)$ (solid curve) calculated for the 5-nm thick Pt film for $T_e = 600$ K and $\Gamma^{-1} = 180$ fs.

DFPS method, appears most likely due to a change in the phase relations between two interfering components of the electron nonlinear susceptibility. Note that the existence of these two components in expression (1) for $\chi_{ee}^{(3)}$ is associated with commutation relations in the Liouville equation for the density matrix (see, for example, Refs [17, 22]) and is inevitable in this sense within the framework of any description. This effect is independent of the type of dependences $d_{i,i'}(\boldsymbol{k})$, $n_i(\boldsymbol{k})$, $E_i(\boldsymbol{k})$, and $\Gamma_{i,i'}(\boldsymbol{k})$ and is caused only by the degeneracy of the frequencies of interacting waves. Therefore, the mechanism, which we described above, should be also valid for the pump-probe method [1–10], where the variations in the reflection $[\Delta R(\tau, \lambda)]$ and transmission $[\Delta T(\tau, \lambda)]$ coefficients of metal films are probed and, hence, the frequency-degenerate nonlinear response of the films is studied. This mechanism can also explain the data obtained in papers [6–9]. Note that out treatment is substantially simpler and, in our opinion, more realistic than that proposed in Ref. [9]. First of all, this is explained by the fact that we did not use the assumption that intraband relaxation is completely frozen on the Fermi surface because, in our opinion, is not adequate to the problem, taking into account high temperatures realised in such experiments.

Our treatment also explains the fact that the DFPS method allows one to determine the characteristic time scale of subpicosecond intraband processes using comparatively long (picosecond) light pulses [13–16]. In essence, this is possible because there exist peculiar points on the axis λ at which the electron nonlinear response of metal films vanishes. The spectral positions of these points are very sensitive to the phases of the components $\chi_{ee}^{(3)}$ and, hence, to the rates of intraband processes of interest to us. Our preliminary analysis also confirms that the DFPS data can be quite informative indicator of the appearance of energy gaps in the spectra of electronic states, which are related to phase transitions and, in particular, to the superconducting transition. However, a detailed analysis of these possibilities of the DFPS method is outside the scope of this paper and will be considered elsewhere.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Grant No. 02-02-16603) and the Federal Specific Scientific and Technical Program on the Investigations and Developments in Priority Directions of Science and Technology.

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