Source of a strong anisotropy of quadrupole-allowed second-order nonlinear polarizability of the noble-metal surfaces

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(Received 6 June 1990)

The experimentally observed strong anisotropy of reflected second-harmonic (SH) generation at the copper crystal surface has previously been explained as the result of interband electron transitions. In the present paper the first calculation of the quadrupole-allowed second-order nonlinear polarizability of an anisotropic electron plasma has been produced using the kinetic equation without taking into account interband transitions. The previously neglected anisotropy of the nonlinear response of noble-metal electrons near the Fermi surface has been found to be essential. The strong SH anisotropy experimentally observed by some authors at the silver and gold crystal surfaces might prove the principal role of the anisotropy source considered here.

Second-harmonic generation (SHG) is extensively used for the investigation of centrosymmetric media surfaces (see Ref. 1 and references therein). SHG has been found to be a sensitive probe of adsorbate-induced changes in the electronic properties of surfaces,[2] microroughness,[3] and other parameters of metal and semiconductor surfaces. Recently, the high rotational anisotropy of the second-order nonlinear response at cubic $m3m$ crystals has been experimentally observed.[4-9] This allows the use of SHG for the study of structural symmetry changes of the silicon surface during its reconstruction.[10] For the first time, strong rotational anisotropy has been found at a semiconductor surface.[4,5] Later the same dependence was obtained at noble-metal crystals: Cu(111),[6] Ag(111),[7,8] and Au(111).[7] The strong SH anisotropy has been observed also at the aluminum crystal surface.[9] Detailed phenomenological analysis of SH anisotropy for $m3m$ crystals has been performed,[11,12] but the source of the strong anisotropy of a metal nonlinear polarizability has not been investigated seriously. Knowledge about these sources could help us to understand what kind of information on the metal surface might be obtained from the experimental study of SH anisotropy. Tom and Aumiller[6] made an assumption that "in metals we would expect electrons to be nearly free, and we would thus expect the nonlinear polarizability of the surface to be isotropic." Observed strong SH anisotropy has been explained by these authors as a contribution of interband transitions. In the present work, the nonlinear response of electrons of noble metals (Cu,Ag,Au) is analyzed without taking into account interband transitions. Nevertheless, it is shown here that an essential anisotropy of the nonlinear polarizability of electrons near the Fermi surface does take place in these metals.

SHG at a metal surface is known to originate from two types of sources: (i) quadrupole-allowed nonlinear current in a uniform electron plasma (bulk sources), and (ii) dipole-allowed nonlinear response of a thin nonuniform layer at a metal surface with a thickness of about the Thomas-Fermi screening length λ_{TF} (surface sources).[13] Both bulk and surface sources may lead to SH anisotropy.[11,12] In the case of the $Si(111)/SiO_2$ interface, the anisotropy in SHG arising from the bulk is the same order of magnitude as that arising from the interface.[5] The analogous relation for metals is not established. In the present work an anisotropy of nonlinear response of noble-metal electrons is analyzed for bulk sources excited in uniform plasma.

Below we will use the kinetic equation for distribution function $f(\mathbf{p},\mathbf{r},t)$ of a metal electron plasma with dispersion law $E=E(\mathbf{p})$ placed in an electromagnetic wave with frequency ω:

$$\frac{\partial f}{\partial t}+\frac{\partial E}{\partial \mathbf{p}}\frac{\partial f}{\partial \mathbf{r}}=e\left[\mathbf{E}+\frac{1}{c}\left[\frac{\partial E}{\partial \mathbf{p}}\times\mathbf{B}\right]\right]e^{-i\omega t}\frac{\partial f}{\partial \mathbf{p}}\ , \tag{1}$$

where $\mathbf{p}$, $\mathbf{r}$, and $-e$ are quasimomentum, coordinate, and charge of electrons; $\mathbf{E}$ and $\mathbf{B}$ are amplitudes of electric and magnetic pump fields. The collision term in the kinetic equation (1) was assumed to be equal to zero so that both scattering and interband transitions of electrons would be neglected. The solution of (1) will be taken in the form

$$f(\mathbf{p},\mathbf{r},t)=f^{(0)}(\mathbf{p})+f^{(1)}(\mathbf{p},\mathbf{r})e^{-i\omega t}+f^{(2)}(\mathbf{p},\mathbf{r})e^{-2i\omega t}+\cdots\ ,$$

where $f^{(0)}(\mathbf{p})$ is the equilibrium distribution function of electrons, and $f^{(1)}(\mathbf{p},\mathbf{r})$ and $f^{(2)}(\mathbf{p},\mathbf{r})$ are amplitudes of linear and second-order corrections to $f^{(0)}(\mathbf{p})$. They may be found from the relation

$$f^{(n)}(\mathbf{p},\mathbf{r})=e\left[-in\omega+\frac{\partial E}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{r}}\right]^{-1}\times\left[\mathbf{E}+\frac{1}{c}\left[\frac{\partial E}{\partial \mathbf{p}}\times\mathbf{B}\right]\right]\frac{\partial f^{(n-1)}}{\partial \mathbf{p}}\ ,$$

where $n=1,2$. The inverse operator may be written in the form

$$\left[-in\omega+\frac{\partial E}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{r}}\right]^{-1}=\frac{i}{n\omega}\left[1-\frac{i}{n\omega}\frac{\partial E}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{r}}-\frac{1}{(n\omega)^2}\left[\frac{\partial E}{\partial \mathbf{p}}\frac{\partial}{\partial \mathbf{r}}\right]^2+\cdots\right]$$

because of a small nonlocality parameter in SHG experiments $\xi=v_F/l_s\omega\sim 10^{-1}$, where v_F is the electron speed at Fermi level and l_s is spatial scale of pump-field variation (skin-layer thickness). In the first order in ξ and $\mathbf{E}$ the correction to distribution function is equal to

$$f^{(1)}(\mathbf{p},\mathbf{r})=\frac{ie}{\omega}\frac{\partial f^{(0)}}{\partial p_j}\mathcal{E}_j+\frac{e}{\omega^2}\frac{\partial E}{\partial p_k}\frac{\partial f^{(0)}}{\partial p_j}\frac{\partial \mathcal{E}_j}{\partial r_k},$$

where $\mathcal{E}_j$ is the component of $\mathbf{E}$. Here it has been taken into account that $f^{(0)}(\mathbf{p})$ depends only on kinetic electron energy: $f^{(0)}(\mathbf{p})=f^{(0)}(E(\mathbf{p}))$, hence $(\partial E/\partial \mathbf{p}\times\mathbf{B})\partial f^{(0)}/\partial \mathbf{p}=0$. In the same way, using the relation between $\mathbf{B}$ and $\mathbf{E}$ in the form $\mathbf{B}=(c/i\omega)\mathrm{rot}\mathbf{E}$, the amplitude of second order in $\mathbf{E}$ and first order in ξ corrections to distribution function may be obtained:

$$f^{(2)}(\mathbf{p},\mathbf{r})=-\frac{e^2}{2\omega^2}\frac{\partial^2 f^{(0)}}{\partial p_j\partial p_k}\mathcal{E}_j\mathcal{E}_k+\frac{ie^2}{2\omega^3}\left[\frac{\partial^2 E}{\partial p_j\partial p_k}\frac{\partial f^{(0)}}{\partial p_l}+\frac{\partial E}{\partial p_k}\frac{\partial^2 f^{(0)}}{\partial p_j\partial p_l}+\frac{\partial E}{\partial p_l}\frac{\partial^2 f^{(0)}}{\partial p_j\partial p_k}\right]\mathcal{E}_j\frac{\partial \mathcal{E}_l}{\partial r_k}. \quad (2)$$

The nonlinear current amplitude at double frequency is equal to

$$\mathbf{j}^{(2)}(\mathbf{r})=-e\int\frac{\partial E(\mathbf{p})}{\partial \mathbf{p}}f^{(2)}(\mathbf{p},\mathbf{r})d^3p,$$

where integration is over the first Brillouin zone. For centrosymmetric dispersion law $E(\mathbf{p})=E(-\mathbf{p})$, a contribution to $\mathbf{j}^{(2)}$ from the first term of (2) is equal to zero. The second term of (2) describes quadrupole-allowed nonlinear current. Since the equilibrium distribution function is a Fermi function,

$$f^{(0)}(\mathbf{p})=\frac{2}{(2\pi\hbar)^2}\left[\exp\frac{E(\mathbf{p})-E_F}{kT}+1\right]^{-1},$$

the main contribution to the nonlinear current is made by the electrons with energies $E(\mathbf{p})$ that are close to the Fermi level E_F. For low temperatures $kT\ll E_F$ the integral over E can be taken. As a result the integral over quasimomentum space transforms into one over the Fermi surface. For quadrupole-allowed second-order nonlinear polarizability defined by the expression $j_i^{(2)}=\chi_{ijkl}\mathcal{E}_i(\partial/\partial r_j)\mathcal{E}_k$, we obtain

$$\chi_{ijkl}=-\frac{ie^3}{2\omega^3}\frac{2}{(2\pi\hbar)^3}\left[2\oint_{S_F}\frac{\partial E}{\partial p_n}n_in_jn_kn_l\left[\Delta_pE-2\frac{\partial^2 E}{\partial p_n^2}\right]dS+2\oint_{S_F}\frac{\partial E}{\partial p_n}\left[n_jn_kn_ln_m\frac{\partial^2 E}{\partial p_i\partial p_m}+\text{c.p.}\,i\to j\to k\to l\right]dS-\oint_{S_F}\frac{\partial E}{\partial p_n}\left[2n_in_l\frac{\partial^2 E}{\partial p_j\partial p_k}+n_in_k\frac{\partial^2 E}{\partial p_j\partial p_1}\right]dS\right], \quad (3)$$

where $\hat{\mathbf{n}}=(\partial E/\partial \mathbf{p})|\partial E/\partial \mathbf{p}|^{-1}=(\partial E/\partial \mathbf{p})(\partial E/\partial p_n)^{-1}$ is the unit vector of a normal to the Fermi surface, $p_n=(\mathbf{p}\cdot\mathbf{n})$ and $\Delta_pE=\sum_i\partial^2E/\partial p_i^2$. For a free-electron gas with dispersion law $E(\mathbf{p})=p^2/m$, Eq. (3) leads to

$$\mathbf{j}_{\mathrm{fe}}^{(2)}=-\frac{ie^3N}{m^2\omega^3}[\mathbf{E}(\mathrm{div}_r\mathbf{E})+\tfrac{1}{4}\mathrm{grad}_r\mathbf{E}^2], \quad (4)$$

where N is the equilibrium electron concentration. The same result has been obtained earlier with the help of the hydrodynamic model.[13] It should be mentioned that expression (4) is not only valid for the $T\to 0$ limit but for any temperature. Moreover, the nonlinear current in a free-electron gas is determined by (4) for any function $f^{(0)}(\mathbf{p})=f^{(0)}(E(\mathbf{p}))$.

Let us estimate an anisotropy of quadrupole-allowed second-order nonlinear polarizability obtained for noble metals within the framework of the present model. The Fermi surface of these metals is unclosed. It may be approximately considered as spheres with centers coinciding with those of Brillouin zones and connected with each other by small necks along eight directions in quasimomentum space: [111], [11$\bar{1}$], ..., [$\bar{1}\bar{1}\bar{1}$]. At the significant distance from the necks, Fermi electron properties are expected to be close to properties of free electrons. As we approach the [111] direction, the absolute value of Fermi velocity $v_F=\partial E/\partial p_n$ is decreased since a distance between isoenergetic surfaces $E(\mathbf{p})=E_F$ and $E(\mathbf{p})=E_F+\delta E$ is increased, where δE is a small increment in electron kinetic energy. There is a region in the vicinity of the [111] direction which gives no contribution to (3) since the Fermi surface is absent there (region inside necks). So for the estimation of $\hat{\chi}$ component magnitudes we will replace the real Fermi surface in the first Brillouin zone with the sphere of radius p_F assuming that

an expression under the integral in (3) is equal to zero in a certain region around [111] and equivalent directions. In the remaining part of the sphere we substitute for values of the quasimomentum derivatives of E their typical values. Let these values be equal to those in free-electron plasma: $\partial E/\partial p_n = p_F/m^*$, $\Delta_p E = 3/m^*$, $\partial^2 E/\partial p_n^2 = 1/m^*$, $\partial^2 E/\partial p_j \partial p_k = \delta_{jk}/m^*$, where m^* is a constant with the mass dimension, $\delta_{jk}=1$ for $j=k$ and $\delta_{jk}=0$ for $j\neq k$. In this way, we obtain the following estimate for χ_{ijkl}:

$$\chi_{ijkl} = -\frac{ie^3}{2\omega^3}\frac{2}{(2\pi\hbar)^3}\frac{p_F^3}{(m^*)^2}\left[10\int\Theta(\tau,\hat{\mathbf{n}}^s)n_i^s n_j^s n_k^s n_l^s d\Omega - \int\Theta(\tau,\hat{\mathbf{n}}^s)(2n_i^s n_l^s\delta_{jk}+n_i^s n_k^s\delta_{jl})d\Omega\right]$$
$$= -\frac{ie^3}{2\omega^3(m^*)^2}\frac{2}{(2\pi\hbar)^3}\frac{4\pi}{3}p_F^3 X_{ijkl}(\tau)\ , \tag{5}$$

where integration is over the full solid angle 4π, $\hat{\mathbf{n}}^s$ is the unit vector of a normal to the sphere, and $\Theta(\tau,\hat{\mathbf{n}}^s)=0$ if the angle between $\hat{\mathbf{n}}^s$ and [111], [11$\bar{1}$], etc., directions is smaller than τ, and $\Theta(\tau,\hat{\mathbf{n}}^s)=1$ in other cases. When taking into account the above consideration, the value of τ must be taken equal or slightly more than angle τ' determining typical radius $r=(\sqrt{3}\pi/a)\tan\tau'$ of the circle, which is cut by the Fermi surface at the Brillouin-zone boundary, where a is the lattice parameter. Tensor $\hat{X}$ determined by (5) (and, hence, $\hat{\chi}$) meets the requirements of face-centered-cubic crystal symmetry ($m3m$ symmetry): nonzero components of $\hat{X}$ in coordinate systems with axes along fourfold crystallographic systems have an even number of each of the Cartesian indices, which are included in Eq. (5) symmetrically due to $\Theta(\tau,\hat{\mathbf{n}}^s)$ function properties:

$$\int\Theta(\tau,\hat{\mathbf{n}}^s)n_i^s n_j^s d\Omega = \delta_{ij}\int\Theta(\tau,\hat{\mathbf{n}}^s)(n_i^s)^2 d\Omega\ .$$

The amplitude of p-polarized SH light excited by a p-polarized plane wave (p,p second harmonic geometry) at the (111) $m3m$ crystal face may be expressed in the following form:[11,12]

$$\mathcal{E}_{pp}(2\omega) = a_{pp} + b_{pp}\cos(3\phi)\ ,$$

where ϕ is the angle between the plane of incidence and the (0$\bar{1}$1) crystallographic plane, and a_{pp} and b_{pp} are isotropic and anisotropic SH components. For noble metals the dielectric constant at a pump frequency $|\epsilon(\omega)|\gg 1$, so in the case of bulk nonlinear current excitation their relation is approximately equal to

$$\frac{b_{pp}}{a_{pp}} \simeq \frac{\sqrt{2}}{6}\frac{\sqrt{\epsilon(2\omega)}}{\sin\theta}\frac{\chi_{an}}{\chi_{xyxy}+\frac{1}{3}\chi_{an}}\ ,$$

where θ is the angle of incidence and $\chi_{an}=\chi_{xxxx}-\chi_{xxyy}-\chi_{xyxy}-\chi_{xyyx}$.

In SHG experiments,[6-8] YAG:Nd laser beam with wavelength 1.06 μm has been used as a pump radiation (where YAG denotes yttrium aluminum garnet). The dielectric constant of noble metals $\epsilon(2\omega)$ at the double frequency is of order 10, so for $\theta=\pi/4$ the anisotropy of p,p-SH light will be essential ($b_{pp}\simeq a_{pp}$) if $\chi_{an}\simeq\chi_{xyxy}$. The values of X_{an} and X_{xyxy} determined by expression (5) are shown in Fig. 1 versus τ. For copper, silver, and gold the angle $\tau'=10°-11°$ (Ref. 14), and for realistic values of $\tau=10°-15°$ $X_{an}/X_{xyxy}=\chi_{an}/\chi_{xyxy}=0.5-1$. For more exact calculation of $\hat{\chi}$ components the real topography of the Fermi surface should be considered. Nevertheless, estimations presented here show the strong anisotropy of second-order quadrupole-allowed polarizability of noble-metal electrons without taking into account the interband transitions. Also it should be noted that for these values of τ the total square of the regions where $\theta(\hat{n}^s)=0$ makes up 6–14 % of the full sphere square $4\pi p_F^2$.

In conclusion, in the present paper a strong anisotropy of quadrupole-allowed second-order nonlinear polarizability of noble-metal electrons near the Fermi surface has been found. We did not analyze here the contribution of interband transitions to SH anisotropy. It should be noted however, that in noble metals their contribution to electronic response would be expected to be considerably different. For example, in copper the contribution of interband transitions to linear response at the double frequency ($\lambda_{2\omega}=532$ nm) is significant: $\epsilon_{Cu}(2\omega)=-5.6+i5.4$. In silver the electron transition at the same wavelength from the d zone over the Fermi level is minor: $\epsilon_{Ag}(2\omega)=-11.8+i0.37$. On the other hand, the Fermi-

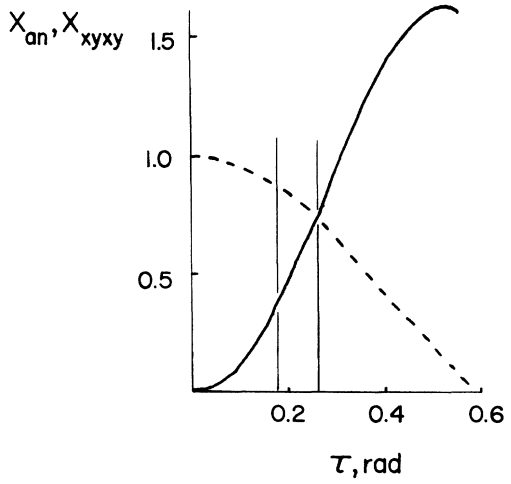

FIG. 1. The values of X_{an} (solid line) and X_{xyxy} (dashed line) determined by (5) vs τ. The range of τ values used for the estimate of X_{an} and X_{xyxy} in noble metals is marked by vertical lines.

surface topography is very close for all metals considered. Therefore, experimentally observed strong SH anisotropy for Cu, Ag, and Au may be considered as indirect proof of the principal role of conduction electrons near the Fermi level in second-order response anisotropy. The Fermi surface of metals such as aluminium is significantly more complex than that of noble metals. Therefore we would expect the SH response of these metals to be strongly anisotropic too.

It is a pleasure to acknowledge discussions with O. A. Aktsipetrov, Yu.A.Il'inksii, and I. M. Sokolov. I especially wish to thank P. V. Elyutin for some notes about this work.

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