Anisotropy of nonlinear-optics response of aluminum single crystal

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A pronounced anisotropy has been observed in the nonlinear-optics response of $3s$ and $3p$ electrons in an aluminum single crystal. A corresponding theory is derived.

1. This letter reports an experimental and theoretical study of a nonlinear-optics response, quadratic in the field, of an aluminum single crystal. This response has proved to be highly anisotropic and relatively strong: 1.5 orders of magnitude stronger than that of silicon. We offer a quantitative interpretation of the experimental data based on a quantum-mechanical calculation of the response of nearly free $3s$ and $3p$ electrons. This observed anisotropy of the nonlinear response opens up new opportunities for studying the dynamics of the electronic structure of normal metals and superconductors.

2. The first experiments on optical harmonic generation upon reflection from the surface of metals were carried out in the mid-1960s (see Ref. 1 and the bibliography there). For a long time, the theoretical interpretation of these experiments was dominated by a hydrodynamic model of an isotropic plasma of free carriers near the surface of the metal.[2] Only recently was it pointed out that the intensity of the second harmonic depends on the orientation of the crystallographic axes during reflection from copper[3] and silver[4] single crystals. This fact was interpreted by Tom and Aumiller,[3] who invoked a component of the nonlinear response due to d electrons which are tightly bound to the atomic framework.

As the subject of the present study we selected aluminum, whose optical response is determined by s and p electrons. Our study included experiments on the nonlinear reflection of picosecond pulses and a quantitative interpretation of the data.

3. In our experiments we studied the generation of the reflected second harmonic of the beam from a Nd:YAG laser with a pulse length of[5] 3×10^{-11} s. The laser beam struck the surface of the crystal at an angle of 45° from the normal. We measured the intensity of the second harmonic as we rotated the single crystal around the normal to the surface. The surface was prepared by mechanical polishing (with a grain size down to 0.25 μm) followed by electrochemical polishing. The use of picosecond pulses resulted in a second-harmonic signal which could be detected quite well at light intensities one or two orders of magnitude below the threshold for damage to the Al. Figure 1 shows the intensity of the second harmonic versus the angular position of the Al crystal during reflection from a (110)-cut surface. The symmetry of this dependence corresponds to the crystallographic symmetry of the (110) cut of Al; the lattice structure determines the anisotropy of the nonlinear response. The intensity of the second

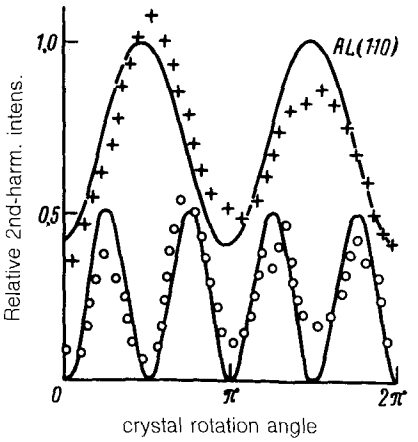

FIG. 1. Orientation dependence of the intensity of the second harmonic for the Al(110) surface. The points are experimental. + —The light at the fundamental frequency and that in the second harmonic are polarized in the plane of incidence; O—the light in the second harmonic is polarized perpendicular to the plane of incidence. The solid lines are calculated from the equations of Ref. 9 under the assumption $|\xi/\chi^{(2)}_{1212}Q| = 1$.

harmonic in the maxima exceeds that of the quadrupole second harmonic from the surface of silicon by a factor of more than 20.

4. The linear optical properties of Al, like those of any crystal of cubic symmetry, are isotropic. The effect of an anisotropy in the crystal structure on the nonlinear-optics response of Al can be dealt with systematically by summing the contributions from intraband and interband transitions of electrons, with allowance for the anisotropy of the band structure. We have carried out a numerical calculation of the optical quadrupole susceptibility of aluminum on the basis of a quantum-mechanical model of the susceptibility.[6] The pseudopotential method was used to calculate the band structure and wave functions of the electrons.[7] In the one-particle approximation, we find the following expression for the electron current at the doubled frequency in the case of interband transitions, using a time-dependent perturbation theory:

$$\mathbf{j}_Q(2\omega) = -\frac{e^2}{2q^2\hbar^3c^2}\sum_{P,\mathbf{k},b,b',b''} P(b,b',b'')R(\omega,\mathbf{k},\mathbf{q})\mathbf{q}(\mathbf{A}\mathbf{q})^2(E_{b''}-E_b)$$

$$\times (E_{b''}-E_{b'})(E_{b'}-E_b)\left(\langle b|\frac{\partial^2|b''\rangle}{\partial\mathbf{k}^2}\right)\left(\frac{\partial\langle b''|}{\partial\mathbf{k}}|b'\rangle\right)\left(\frac{\partial\langle b'|}{\partial\mathbf{k}}|b\rangle\right).$$

Here E_b and $|b\rangle$ are the energy and wave function of an electron in band b, with wave vector $\mathbf{k}$; $\mathbf{A}$ is the vector of the incident electromagnetic wave, with frequency ω and wave vector $\mathbf{q}$ in the medium; $R(\omega,\mathbf{k},\mathbf{q})$ is a resonant factor which incorporates the state density; and $P(b,b',b'')$ is the permutation operator. A corresponding expression has been derived for intraband transitions.

Figure 2 shows the Al band structure which we calculated from the model of Ref. 7. The energies at the principal points of the Brillouin zone agree well with the published data. The integration over the Brillouin zone was carried out by means of an

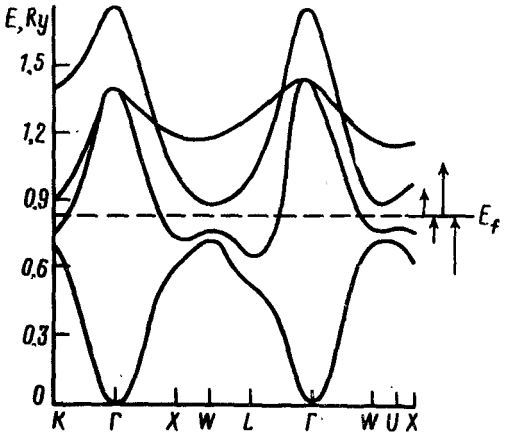

FIG. 2. The calculated band structure of Al. Shown for comparison by the arrows at the right are the photon energies $\hbar\omega$ and $2\hbar\omega$ and the Fermi level E_F.

approximate tetrahedron method.[8] As a result, we found the following values for the components of the nonlinear quadrupole susceptibility tensor of Al [in electrostatic units; $\lambda(\omega) = 1.06\,\mu$m]: $\chi^{(2)Q}_{1111} = 7\times10^{-13}$, $\chi^{(2)Q}_{1212} = 4\times10^{-13}$, $\chi^{(2)Q}_{1122} = 3\times10^{-13}$. The anisotropy of the nonlinear susceptibility tensor is detemined by the parameter $\xi = \chi^{(2)Q}_{1111} - (2\chi^{(2)Q}_{1212} + \chi^{(2)Q}_{1122})$. In an isotropic medium we would have $\xi = 0$, while in an anisotropic medium the value of ξ determines the angle-dependent component of the orientation dependence.[9] In our calculation we have $|\xi/\chi^{(2)Q}_{1212}| = 1$, in good agreement with the experimental dependence (Fig. 1).

5. In summary, it has been shown theoretically and experimentally that an Al single crystal has a strongly anisotropic nonlinear response. This anisotropy stems from an interaction of nearly free $3s$ and $3p$ electrons of Al with the internal field in the crystal.

Consequently, even in the absence of a contribution of d electrons, the nonlinear electronic response of a metal single crystal contains information about the crystal structure. This circumstance can be utilized for picosecond and femtosecond diagnostics of structural conversions in single crystals of normal metals and superconductors. The nonlinear-optics diagnostic procedure can thus compete successfully with picosecond electron diffraction, which has been used previously.[10]

Looking at the results of these experiments on metal single crystals and also experimental data on films of high-temperature superconductors,[11] we think it reasonable to suggest that nonlinear-optics methods might be used to analyze the dynamics of the electronic structure of high-temperature superconductors, which is presently the subject of vigorous discussion (e.g., Refs. 12 and 13).

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