Intrinsic Surface-Induced Optical Anisotropies of Cubic Crystals: Local-Field Effect

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We develop a simple local-field-effect theory in order to calculate the polarization near the surface and the surface dielectric response of crystals. We obtain a surface-induced anisotropy in all the optical properties of cubic crystals. A calculation of the reflectance anisotropy of a Ge(110) surface is in good agreement with recent measurements.

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The measurement of the anisotropies in the optical properties—such as reflectance, ellipsometric coefficients, and surface-plasmon–polariton dispersion relation—of different faces of cubic crystals[1,2] is an emerging tool for the investigation of surface structure, since in their bulk, cubic crystals are isotropic in the long-wavelength limit. Some of these anisotropies have an extrinsic origin such as anisotropic adsorbed films,[3] surface states,[4] and surface reconstruction.[5] However, in order to identify these extrinsic effects, one has to subtract the intrinsic anisotropies which may be allowed by the symmetry reduction near the surface. In some cases, these can only be obtained from theory. In this Letter we show that, even for a clean, bulk-truncated crystal, and with disregard of the modifications of the electronic structure near the surface, there is an important contribution to the intrinsic anisotropy which has as its origin the change in the local field near the surface: the surface local-field effect.[6]

There has been a prolonged interest in the local-field effect,[7] that is, the influence that the interaction between nearby points of a system through the spatial fluctuations of the electric field has on its macroscopic dielectric response.[8] Besides the textbook calculations of the bulk dielectric function of cubic crystals made up of point polarizable atoms,[9] much work has been done on the microscopic, quantum-mechanical formulation of the problem.[10,11] However, only few quantum-mechanical calculations of the local-field effect near crystal surfaces have been done,[5,12] since they are hindered by the loss of translational symmetry.[13] Yet, there are many calculations within the model of point polarizable atoms.[14] In the latter calculations, the optical properties of the system have usually been obtained directly from the microscopic Maxwell's equations. The main disadvantage of this approach is that each optical property requires a separate microscopic calculation. On the other hand, the macroscopic response of the crystal near its surface has usually been disregarded,[15] and few observable consequences of the surface local-field effect have been predicted.

In the present Letter we calculate the change in the macroscopic response produced by the change in the dipolar contribution to the local field near the surface of cubic crystals, within a model of point polarizable entities. With this macroscopic response, a perturbative solution[16] of the macroscopic Maxwell's equations can be used in order to calculate all the optical properties for different orientations of the surface and of the plane of incidence. In this way we obtain an intrinsic surface-induced anisotropy of the optical properties of cubic crystals which is in good agreement with recent experiments.[1]

We start by dividing the crystal into a lattice of polarizable entities with a polarizability α_{eff} defined through the equation

$$\mathbf{p}_i = \alpha_{\text{eff}}(\mathbf{E}_i^{\text{ex}} + \textstyle\sum_j{}' \mathbf{T}_{ij} \cdot \mathbf{P}_j), \tag{1}$$

where $\mathbf{p}_i$ is the dipole moment of the ith entity, $\mathbf{E}_i^{\text{ex}}$ is the external field, and $\mathbf{T}_{ij}$ is the dipole-dipole interaction tensor. If the crystal were made up of point polarizable atoms occupying the lattice sites and interacting between themselves through the dipolar field only, α_{eff} would be the atomic polarizability α. This identification fails even for the noble-gas solids, where α_{eff} is modified by the confinement of each atom by nearby atoms[17] and by the multipolar[18] and van der Waals interactions.[19] The interpretation of α_{eff} as an atomic polarizability is even worse for covalent crystals in which there is overlap between the electronic orbitals of nearby atoms, giving rise to an exchange interaction.[11]

However, α_{eff} may still be interpreted as an effective polarizability: $n_0\alpha_{\text{eff}}$ is the susceptibility that the crystal would have if the dipolar interactions between entities were turned off, where n_0 is the number density of entities. This interpretation, as well as a microscopic calculation of α_{eff} for a simple two-band semiconductor, has been discussed by Fiorino and Del Sole.[20] Notice that α_{eff} is a function of position since in general it depends on the density[21] and the geometrical arrangement of the nearby atoms. Because of the presence of nondipolar interactions, α_{eff} also depends on the spatial behavior of the fields, i.e., it is a nonlocal quantity.

Nevertheless, we remark that within the interpretation above, the bulk dielectric function ϵ of cubic crystals in the long-wavelength limit is given exactly by a relation of the Clausius-Mossotti type,[20]

$$(\epsilon-1)/(\epsilon+2)=\tfrac{4}{3}\pi n_0\alpha_{\mathrm{eff}}. \tag{2}$$

Therefore, α_{eff} can be obtained from the experimental measurements of ϵ, and the value thus obtained is dressed by the whole self-interaction of each entity, and by exchange, correlation, and any other nondipolar interaction between nearby entities.

Since α_{eff} depends on the environment of each entity, it is different for the entities near the surface. However, in order to investigate the effects of the change in the dipolar contribution to the local field near the surface of cubic crystals, we will neglect this change in α_{eff} and we will use its bulk value as given by Eq. (2). We expect the change in the local field to be confined within a region near the surface whose width is much smaller than the wavelength of light. Then, in this region we can ignore retardation and any slow variation of the external field.[22] Assuming that the system occupies the half space $z\geqslant 0$, we can write Eq. (1) as

$$\sum_{m\geqslant 0}\mathbf{M}_{nm}[\mathbf{P}_m-\mathbf{P}_B]=\sum_{m<0}\mathbf{M}_{nm}\mathbf{P}_B, \tag{3}$$

where $\mathbf{P}_m$ is the dipole moment of any entity in the mth plane $(m=0,1,2,\ldots)$ divided by its share of volume, $\mathbf{P}_B$ is the bulk polarization, $\mathbf{P}_B=(\epsilon-1)\mathbf{E}/4\pi=(\epsilon-1)\mathbf{D}/4\pi\epsilon$, and $\mathbf{M}_{nm}\equiv\delta_{nm}\mathbf{1}-n_0\alpha_{\mathrm{eff}}\mathbf{U}_{nm}$; negative values of m on the right-hand side refer to planes deleted to produce the semi-infinite crystal. Here,

$$\mathbf{U}_{nm}=\frac{1}{n_0}\sum_j{}'\nabla_i\nabla_i\frac{1}{|R_i-R_j|},$$

with i in plane n and j in plane m, is the planewise sum of the static dipolar interactions, whose efficient evaluation has been discussed in the literature.[23] This is an extremely fast decaying function of $|n-m|$, and so it can be truncated after a small number of planes. In order to arrive at Eq. (3) from Eq. (1) we have used the relation between the constant external field and the macroscopic electric $\mathbf{E}$ and displacement $\mathbf{D}$ fields: $\mathbf{E}^{\mathrm{ex}}=(E^x,E^y,D^z)$.

Following the perturbative approach of Ref. 16, an appropriate way of characterizing the macroscopic surface response is by means of the surface conductivities $\langle\langle\Delta\sigma^{xx}\rangle\rangle$, $\langle\langle\Delta\sigma^{yy}\rangle\rangle$, and $\langle\langle\Delta s^{zz}\rangle\rangle$, defined through

$$\begin{aligned}\Delta i^{\mu}&=\langle\langle\Delta\sigma^{\mu\mu}\rangle\rangle E^{\mu}(0),\quad \mu=x,y,\\ \Delta i^{z}&=\langle\langle\Delta s^{zz}\rangle\rangle D^{z}(0),\end{aligned} \tag{4}$$

where Δi is the surface current $\int dz[\mathbf{j}(z)-\mathbf{j}_B(z)]$. Here, $\mathbf{j}$ is the actual current density, and $\mathbf{j}_B=-i\omega\mathbf{P}_B$ is the current density of the bulk. Solving Eq. (3),[24] subject to the boundary condition $\mathbf{P}_m\rightarrow\mathbf{P}_B\rightarrow 0$ as $m\rightarrow\infty$, for the change in polarization near the surface of the crystal, we can calculate

$$\begin{aligned}\langle\langle\Delta\sigma^{\mu\mu}\rangle\rangle&=-i\omega a\frac{\epsilon-1}{4\pi}\sum_{n\geqslant 0}\frac{P_n^{\mu}-P_B^{\mu}}{P_B^{\mu}},\quad \mu=x,y,\\ \langle\langle\Delta s^{zz}\rangle\rangle&=-i\omega a\frac{\epsilon-1}{4\pi\epsilon}\sum_{n\geqslant 0}\frac{P_n^{z}-P_B^{z}}{P_B^{z}},\end{aligned} \tag{5}$$

where a is the distance between crystal planes and we assume that the principal axes of $\langle\langle\Delta\sigma\rangle\rangle$ point along the x and y directions.

Finally, these surface conductivities can be substituted in Eqs. (31)–(33) of Ref. 16 in order to obtain the surface impedance of the system. By substituting this in equations such as (37) and (41) of Ref. 16, we can immediately calculate all the optical properties of the system.

Since there are recent measurements[1] of the normal-incidence reflectance anisotropy on a Ge(110) surface, we calculate the normalized change in reflectance,

$$\frac{\Delta R}{R}\equiv\frac{R^x-R^y}{R}=\frac{16\pi}{c}\,\mathrm{Re}\left[\frac{\langle\langle\Delta\sigma^{xx}\rangle\rangle-\langle\langle\Delta\sigma^{yy}\rangle\rangle}{\epsilon-1}\right], \tag{6}$$

when the polarization direction rotates from the x ($\langle 1\bar{1}0\rangle$) to the y ($\langle 001\rangle$) direction. The inputs to our calculation are the bulk response ϵ, taken from the measurements of Aspnes and Studna,[25] and the lattice structure, and there are no adjustable parameters. However, we must choose our polarizable entities.

Since Ge has a diamond structure, we choose as polarizable entities tetrahedra, each with a Ge ion at its center, four shared Ge ions at the vertices, and four doubly occupied electronic orbitals joining the center to the vertices. These tetrahedra are arranged in an fcc lattice with lattice constant 5.658 Å.[26] With this choice we minimize the nondipolar interactions between nearby entities since there is only a small overlap between the four orbitals that meet at each tetrahedron vertex. The sharing of the vertex ions between four tetrahedra should be of no concern at relatively low frequencies, for which the polarization is dominated by the motion of the valence electrons and not by those in the ionic cores.

In Fig. 1, we show the normalized change in polarization along the (110) surface as a function of the crystalline plane number n, for a frequency of 4.3 eV where the imaginary part of ϵ peaks. Notice that at the surface, the polarization along the $\langle 001\rangle$ direction differs by more than 60% from its bulk value.[24] Although the change in polarization at the surface is

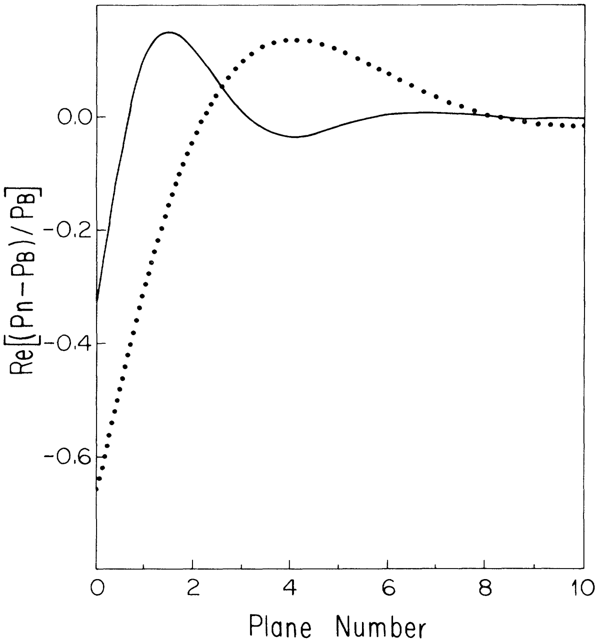

FIG. 1. Real part of the normalized change in polarization along the $\langle 1\bar{1}0\rangle$ (solid curve) and $\langle 001\rangle$ (dotted curve) directions near a Ge(110) surface vs crystal plane number. The frequency is 4.3 eV.

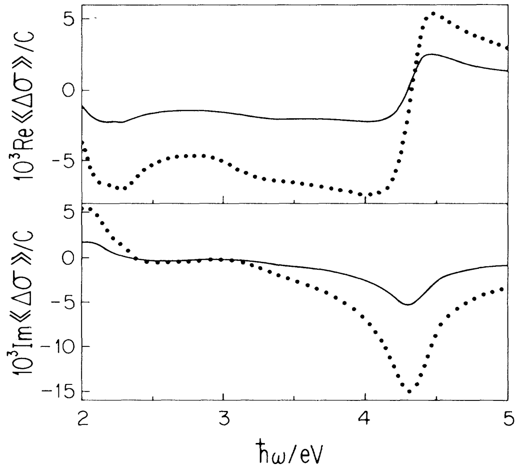

FIG. 2. Real and imaginary parts of the Ge(110) surface conductivity along the $\langle 1\bar{1}0\rangle$ (solid curves) and $\langle 001\rangle$ (dotted curves) directions vs frequency.

very large, it is confined to within the first ~10 planes, so that the perturbative formulas of Ref. 16 can be used. In the cases where the polarization does not decay rapidly enough,[27] a different approach based on an expansion in bulk normal modes (i.e., classical Frenkel's excitons[28]) and the introduction of additional boundary conditions might be used.[6] Notice also the difference between the polarization along the $\langle 1\bar{1}0\rangle$ and the $\langle 001\rangle$ directions.

In Fig. 2, we show the real and imaginary parts of the surface conductivities $\langle\langle\Delta\sigma^{xx}\rangle\rangle$ and $\langle\langle\Delta\sigma^{yy}\rangle\rangle$ as functions of frequency. These were used in order to calculate the reflectance anisotropy, shown in Fig. 3, together with the experimental results of Ref. 1. Our calculation predicts a reasonable line shape and is of the correct order of magnitude. As could be expected, we overestimate the surface local-field effect since we replace every two finite-sized Ge atoms by one point polarizable entity. Using a generalization of the formalism above, we have also included in Fig. 3 a calculation of the reflectance anisotropy choosing single Ge atoms occupying a diamond lattice as polarizable entities. The striking discrepancy with experiment shows that this is not a fortunate choice. The reason for this is that the interaction between neighboring Ge atoms is dominated by the covalently shared electrons, and is therefore mostly nondipolar. Notice also that our results are very sensitive to the crystal structure. We have corroborated this sensitivity by repeating our calculations assuming an sc and bcc lattice.

In conclusion, we have shown that the local-field effect induces a change in the macroscopic dielectric response of cubic crystals near their surface. This change depends on the orientation of the surface and of the plane of incidence, so that the optical properties such as reflectance, ellipsometric coefficients, and surface-plasmon–polariton propagation also depend on orientation. A calculation of the reflectance anisotropy for normal incidence on a Ge(110) surface is in good agreement with experiment, indicating that the surface local-field effect accounts for most of the intrinsic surface-induced anisotropies; other contributions to the intrinsic anisotropy have been recently estimated by Aspnes.[1] We have performed similar calculations

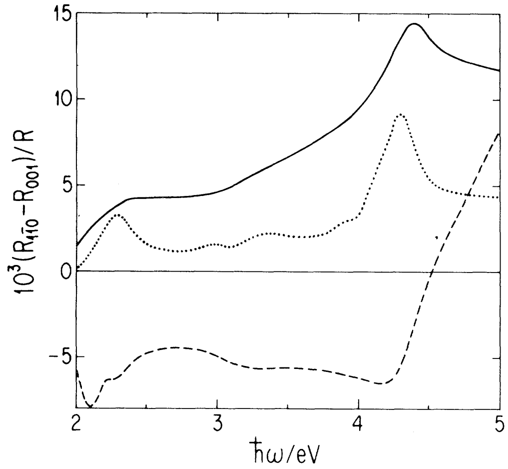

FIG. 3. Normal-incidence reflectance anisotropy of a Ge(110) surface vs frequency: fcc calculation (solid curve), diamond-lattice calculation (dashed curve), and experimental result (dotted curve).

for the reflectance anisotropy of Si(110) and for the anisotropy induced by the local field on the dielectric response of a monolayer of randomly oriented Br_2 molecules physisorbed on a Ge(110) surface. The agreement with experiment is similar to what we have shown here. Although more elaborate calculations are needed, they will have to take the surface local-field effect into account. We believe that a microscopic calculation of the change in α_{eff} near the surface, followed by a local-field calculation such as ours, might be a more feasible project than present attempts[5,13] to obtain the macroscopic response at crystal surfaces from the microscopic, spatially fluctuating dielectric response. We hope that this paper will stimulate work in that direction.

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