VOLUME 63, NUMBER 19 PHYSICAL REVIEW LETTERS 6 NOVEMBER 1989

Photon–Single-Phonon Coupling at Polar Crystal Surfaces

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(Received 20 April 1989)

We calculate the direct coupling among long-wavelength photons and single short-wavelength phonons at the surface of semi-infinite polar crystals. This coupling is allowed due to the loss of momentum conservation at interfaces. The ir reflectance shows deviations of order 10^{-4} from the Fresnel spectrum, with a rich structure related to the detailed ionic motions in regions of the phonon dispersion relations commonly regarded as inaccessible to light. The reflectance depends on polarization and crystal orientation, suggesting a new ir optical-anisotropy spectroscopy which is expected to be surface sensitive.

PACS numbers: 78.65.Fa, 71.36.+c, 78.20.Ci, 78.30.Fs

The energy- and quasimomentum-conservation laws within a periodic lattice impose severe restrictions on the coupling among photons and phonons. Since the wavelength of photons is typically much larger than interatomic distances, only phonons with wave vectors in a small region near the center of the Brillouin zone $k \simeq 0$ can participate in one-phonon scattering.[1] Long-wavelength photons and short-wavelength phonons may still couple in the presence of spatial inhomogeneities such as impurities[2] or within disordered materials[3] for which phonons with all possible k's contribute to the photon scattering. In order to optically probe short-wavelength phonons in crystalline materials artificial periodicities have been introduced. As a result of Brillouin-zone folding, Raman scattering by small-k phonons in a superlattice yields kinematical information on large-k phonons of the homogeneous crystal.[4]

The most simple inhomogeneity is the presence of a single interface. Near a low-index flat surface, a crystal losses translational symmetry in one direction, but retains two-dimensional periodicity. Hence, long-wavelength light may interact with phonons whose wavelength is smaller by several orders of magnitude, although quasimomentum along the surface remains a conserved quantity. The strength of this interaction is sensitive to the microscopic atomic motions which give rise to the surface-induced phonon-photon coupling. The spectra dependent on this coupling is expected to yield information on the surface dynamics.

The purpose of the present Letter is the calculation of one such spectra. Using a simple microscopic model for the lattice dynamics of a semi-infinite cubic crystal, and including the interaction between the atomic displacements and the radiation field, we calculate the far-infrared reflectance R of a polar semiconductor. The results deviate from the reflectance R^0 as calculated with the Fresnel theory[5] in terms of its macroscopic dielectric response ϵ. The origin of this discrepancy is the surface-induced coupling among the incident light and phonons, some of which have wave vectors at the edge of the Brillouin zone and have been commonly regarded as optically inaccessible. The corrections to the Fresnel formulas depend on the relative orientation between the polarization vector and the principal directions of the surface, giving rise to an anisotropy spectra of order $\sim 10^{-4}$, which may be observed using differential-reflectance techniques.[6-13]

Similar anisotropy spectra have been calculated[6] and measured[7] recently for visible and near-ultraviolet light. They have shown a remarkable sensitivity to the geometrical[8] and the chemical[9] state of the surface, to the position and orientation of adsorbates,[10] to surface states,[11] to surface-state–induced electric fields,[12] and to the spatial distribution of the electronic polarizability.[13] Therefore, optical anisotropy is a very useful surface probe, with the added benefit that light does not require a vacuum to propagate, so it can even by employed in hostile environments.[9] In this paper we explore the anisotropy spectra in the far infrared, where the polarization is determined by the atomic motions rather than electronic transitions.

We begin our calculation with the equations of motions for the atoms, which we write as

$$-m_\alpha \omega^2 \mathbf{u}_{i\alpha} = e_\alpha \mathbf{E}^T(\mathbf{R}_{i\alpha}) + \sum_{j\beta}{}' \mathbf{U}_{i\alpha j\beta}(\mathbf{u}_{j\beta} - \mathbf{u}_{i\alpha}) , \qquad (1)$$

where m_α and $\mathbf{u}_{i\alpha}$ are the mass and the displacement from the equilibrium position $\mathbf{R}_{i\alpha}$ of the atom α in the ith primitive cell of the crystal, and $\mathbf{U}_{i\alpha j\beta} = \mathbf{K}_{i\alpha j\beta} + e_\alpha \mathbf{T}_{i\alpha j\beta} e_\beta / \epsilon_\infty$ is the total interaction matrix between atoms $i\alpha$ and $j\beta$. This includes a short-range mechanical term $\mathbf{K}_{i\alpha j\beta}$ and a screened long-range unretarded Coulomb interaction proportional to the dipolar tensor $\mathbf{T}_{i\alpha j\beta} = \nabla_{i\alpha} \nabla_{i\alpha} |\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta}|^{-1}$ and to the effective charges e_α and $e_\beta \equiv \pm e^*$. Here, ϵ_∞ is the contribution of the valence electrons to the dielectric function.

We also included in Eq. (1) an interaction with the retarded transverse field $\mathbf{E}^T$ radiated by the atoms which vibrate with frequency ω within a medium with response ϵ_∞. This field obeys Maxwell's equations and therefore satisfies the wave equation

$$\nabla^2\mathbf{E}^T(\mathbf{r})+\epsilon_\infty q^2\mathbf{E}^T(\mathbf{r}) = -4\pi q^2\mathcal{P}^T\sum_{j\beta}e_\beta\mathbf{u}_{j\beta}\delta(\mathbf{r}-\mathbf{R}_{j\beta}) , \qquad (2)$$

where $q=\omega/c$, $\delta(\mathbf{r})$ is the Dirac delta function, and the operator $\mathcal{P}^T$ is the transverse projector.

In summary, our model consists of rigid ions immersed in a dielectric medium, interacting through short-range mechanical forces as well as long-range Coulomb and radiation fields. For simplicity, Eq. (1) is written within the harmonic approximation and incorporates only two-body mechanical forces, although realistic calculations require many-body forces.[14] Photon extinction[15] and nonharmonic phonon scattering are accounted for by adding a damping term to $\mathbf{K}_{i\alpha j\beta}$.

Within the bulk, the equations of motion have Bloch-type solutions[16] $\mathbf{u}_{i\alpha}=\psi_{\mathbf{k}\alpha}e^{i\mathbf{k}\cdot\mathbf{R}_{i\alpha}}$ for which Eq. (1) becomes

$$\sum_\beta\left[\left(m_\alpha\omega^2-\sum_\gamma\mathbf{U}_{\alpha\gamma}(\mathbf{0})\right)\delta_{\alpha\beta}+\mathbf{U}_{\alpha\beta}(\mathbf{k})+\mathbf{U}^R_{\alpha\beta}(\mathbf{k})\right]\psi_{\mathbf{k}\beta}=0 . \qquad (3)$$

Here

$$\mathbf{U}_{\alpha\beta}(\mathbf{k})\equiv\sum_j\mathbf{U}_{i\alpha j\beta}e^{-i\mathbf{k}\cdot(\mathbf{R}_{i\alpha}-\mathbf{R}_{j\beta})} \qquad (4)$$

is the Fourier transform of the nonretarded interaction tensor, and

$$\mathbf{U}^R_{\alpha\beta}(\mathbf{k})=\frac{4\pi q^2 n}{k^2-q^2\epsilon_\infty}e_\alpha e_\beta(1-\hat{\mathbf{k}}\hat{\mathbf{k}}) \qquad (5)$$

is the interaction between sublattices α and β through the radiation field when $q\ll 1/a$; a is the lattice parameter and n is the lattice site density.

Equation (3) would usually be solved for ω given a Bloch vector $\mathbf{k}$ within the first Brillouin zone, yielding the bulk phonon-polariton-photon dispersion relations.[17] However, we are interested in the excitation of these normal modes at surfaces upon which monochromatic light is incident at a given angle θ. Therefore we give real values to ω and to the parallel projection $\mathbf{k}_\parallel=\mathbf{Q}$, and we solve Eq. (3) for the normal component $k_\perp=k_z$. We assumed that the crystal occupies the $z>0$ region. In this case Eq. (3) has many solutions: a long-wavelength polariton mode, some short-wavelength propagating bulk phonons, and many complex k_z's which correspond to evanescent phonons. The latter are not truly bulk modes since they cannot be normalized in an infinite crystal, but they can be excited in finite or semi-infinite systems. The total number of solutions depends linearly on the number N of lattice planes after which the interaction $\mathbf{U}_{i\alpha j\beta}$ is neglected. We remark that although the Coulomb interaction between *atoms* has an infinite range, in the present problem it can be planewise summed exactly, and the Coulomb interaction between *planes* has a very fast exponential decay.[18]

The solution of Eq. (1) for a bulk-truncated semi-infinite crystal can be written as the superposition[19] $\mathbf{u}_{i\alpha}=\sum_{k_z}\eta_{\mathbf{k}}\psi_{\mathbf{k}\alpha}e^{i\mathbf{k}\cdot\mathbf{R}_{i\alpha}}$, which satisfies identically the equations of motion for all but the N planes closer to the surface of a semi-infinite one. Therefore the infinite system of equations for $\mathbf{u}_{i\alpha}$ in (1) can be simplified to the finite system

$$\sum_{k_z}\left[\sum_{j\beta}{}^{U}\mathbf{U}_{i\alpha j\beta}(\psi_{\mathbf{k}\alpha}e^{i\mathbf{k}\cdot\mathbf{R}_{i\alpha}}-\psi_{\mathbf{k}\beta}e^{i\mathbf{k}\cdot\mathbf{R}_{j\beta}})\right]\eta_{\mathbf{k}} =\sum_{j\beta}{}^{U}\mathbf{U}_{i\alpha j\beta}(\mathbf{u}_{i\alpha}-\mathbf{u}_{j\beta})=0 \qquad (6)$$

for the unknown $\eta_{\mathbf{k}}$, where the sum $\sum^U$ is performed only over the unoccupied sites $j\beta$ of the corresponding infinite crystal. There is one independent equation for i in each of the first N occupied planes and for each value of α. The system of equations (6) has a straightforward interpretation: The real semi-infinite crystal can be extended to an artificial infinite crystal by adding fictitious atoms. The correct superposition of the *normal modes* of this infinite crystal is that in which the fictitious atoms do not produce any (unretarded) force whatsoever on the real atoms. We close the system of equations by noticing that the transverse field at the surface,

$$\mathbf{E}^T(0)=\sum_{k_z\alpha}\eta_{\mathbf{k}}\frac{4\pi nq^2}{k^2-q^2\epsilon_\infty}e_\alpha\mathcal{P}^T\psi_{\mathbf{k}\alpha}=\mathbf{E}^i+\mathbf{E}^r , \qquad (7)$$

is a superposition of the incident field $\mathbf{E}^i$ plus the field radiated by all the atoms,

$$\mathbf{E}^r=\int d^2r'\,\mathbf{G}(0,\mathbf{r}')q^2e_\alpha\mathcal{P}^T\sum_{i\alpha}\mathbf{u}_{i\alpha}\delta(\mathbf{r}'-\mathbf{R}_{i\alpha}) , \qquad (8)$$

where $\mathbf{G}(\mathbf{r},\mathbf{r}')$ is the electromagnetic Green's function within a dielectric medium with response ϵ_∞. Finally, we solve for $\eta_{\mathbf{k}}$, we calculate $\mathbf{E}^r$, and we combine the contributions of the immersed ions to the reflection amplitude $r_i\equiv E^r/E^i$ with the contributions from the valence-electron polarization r_∞ to obtain the reflectance $R=|(r_\infty+r_i)/(1+r_\infty r_i)|^2$.

In Fig. 1 we show the normalized difference $\Delta R/R$ between the far-infrared normal-incidence reflectance $R(\omega)$ of the (110) face of a model zinc-blende crystal and Fresnel reflectance $R^0(\omega)=|(1-\sqrt{\epsilon})/(1+\sqrt{\epsilon})|^2$. We assumed mechanical interactions given by a nearest-neighbor Born[20] model adjusted to the sound velocities, high-frequency dielectric constant, effective charge, and ionic masses of a GaAs crystal.[21] In the figure we introduced $\omega_1=(ne_0^2/\mu)^{1/2}=9.2\times10^{12}\ \mathrm{s}^{-1}$ as a convenient unit of frequency, where μ is the reduced mass and e_0 is the electron charge.

Figure 1 shows a very rich structure for the difference between the ir reflectance calculated with our model and the Fresnel calculation. Furthermore, this spectrum differs when the polarization of light is along the bond chains, $\langle\bar{1}10\rangle$ or x direction, from the spectrum when the

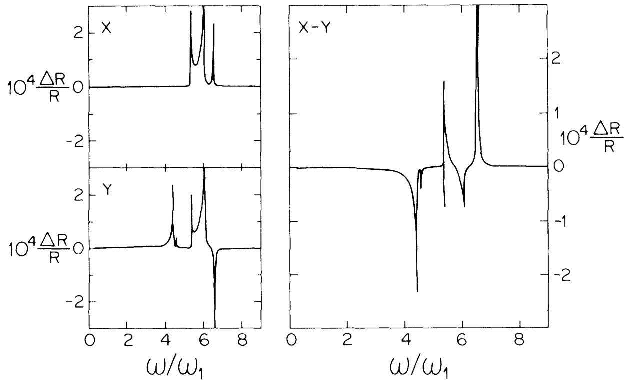

FIG. 1. Normal-incidence differential reflectance $\Delta R/R$ as a function of frequency ω for light shining on a model (110) GaAs crystal. The upper left panel corresponds to light polarized along the $\langle\bar{1}10\rangle$ direction, the lower left panel to the $\langle 001\rangle$ direction, and the right panel to the anisotropy spectrum.

light is polarized along the perpendicular $\langle 001\rangle$ or y direction. Therefore, by subtracting both spectra which could be done experimentally using differential-reflectance techniques, we eliminate all the contributions of the bulk to the reflected light and we obtain a large, surface-induced ir anisotropy signal. Similar anisotropy measurements have already been performed successfully in the visible and uv region[7–9,11,12] and have proved to be a very useful tool for the study of surfaces.

In order to understand the structure of our results, in Fig. 2 we show the phonon dispersion relations along the $\langle 110\rangle$ direction as calculated with the present model. There are acoustical and optical transverse modes (TA and TO) polarized along the x direction and coupled transverse-longitudinal (long elliptic) modes which oscillate in the y-z plane (labeled IA, IO, IIA, and IIO). Near the longitudinal frequency $\omega^L(\Gamma)$ the Fresnel reflectance has a sharp dip which approaches zero, yielding peaks in $\Delta R/R$ which can be seen in Fig. 1 for both x and y polarizations. There are also peaks near the transverse frequency $\omega^T(\Gamma)$ where the wave vectors of transverse phonons and those of photons approach each other, and therefore momentum conservation need not be violated to get photon-phonon coupling.

The remaining features of Fig. 1 are due to phonons near the edge X of the 1D Brillouin zone $k_z=\pi/d$ (d is the interplane distance). We discuss them here going from lower to higher frequencies. First, we notice that not all phonon branches contribute to the difference spectra. There is no peak associated to the x-polarized TA phonon for which each crystalline plane acquires a very small dipole moment. Similarly, the IA(X) phonon cannot couple to normally incident light since its polarization is longitudinal. On the other hand, there are features for y-polarized light when the branches IIA and IIO arrive at point X. For these, only one atom oscillates yielding a dipole along the y direction.

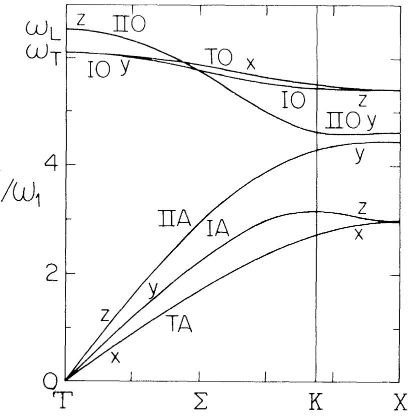

FIG. 2. Phonon dispersion relations for propagation along the $\langle 110\rangle$ direction. The modes labeled T are transverse and polarized along the $\langle\bar{1}10\rangle$ direction, and those labeled I (II) are polarized along $\langle 001\rangle$ at Γ (X) and along $\langle 110\rangle$ at X (Γ). Also shown are the longitudinal and transverse frequencies ω^L and ω^T.

The most remarkable peak is that coming from the IO mode, since its polarization at X is longitudinal and therefore it cannot couple directly to light. However, an indirect coupling to y-polarized light through evanescent long elliptical phonons is allowed since there is no $y \leftrightarrow -y$ reflection symmetry in the zinc-blende lattice. Finally, the TO phonon has a large dipole moment and gives rise to a peak for x polarization. Since the TO dispersion relation is always above the IO dispersion relation, the last two peaks differ slightly in frequency, originating a derivativelike structure in the anisotropy spectrum.

Similar calculations for (001) A and B surfaces and for different crystals yield ir anisotropies of the same order of magnitude as that for (110) GaAs. A full account of these results will be presented elsewhere.[22]

In summary, we have developed a microscopic theory to calculate the phonon-photon coupling at the surface of polar crystals and its contribution to the ir reflectance spectra. We illustrated the theory by applying it to the anisotropy spectra of a model semi-infinite GaAs crystal. We predicted deviations from the classical Fresnel reflectance which should be observable in differential-reflectance experiments. The normal-incidence reflectance anisotropy spectrum shows a remarkable structure. For instance, we found peaks related to the excitation of both acoustical and optical, and both transverse and longitudinal phonons.

There are previous calculations performed within elasticity theory and some experimental observations of the coupling between phonons and electromagnetic fields at piezoelectric crystal surfaces.[23] In comparison to those results, our microscopic calculations suggest a purely optical observation of that coupling and they predict much larger resonant structures which are related to the phonon band structure and the microscopic atomic motions near the surface. Therefore the ir anisotropy spectra should be quite sensitive to the surface structure. Our theory also predicts a photon-phonon coupling in centrosymmetric crystals, and we expect similar results in some faces of homopolar crystals when account is taken of charge transfers near the surface.

We are grateful to Rubén G. Barrera for his useful comments on the manuscript and to Rafael Barrio for stimulating discussions.

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