Dispersion of Surface Polaritons in GaP

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Surface polaritons are optically excited in semi-infinite crystals of GaP. Infrared radiation is coupled from silicon prisms into the sample via attenuated total reflection. The results give the first experimental dispersion relation for surface polaritons.

Surface phonons are a consequence of the finite extension of a crystal. Optical surface phonons have frequencies between ω_T and ω_L, as has been shown theoretically and experimentally by several authors.[1-3] In an ionic crystal whose size is small compared to λ_T (the wavelength at ω_T) only radiative surface modes exist, which have been detected directly by infrared absorption of light.[4-7] The resulting broad absorption bands above ω_T depend on the geometry of the crystallites.[4] Semi-infinite crystals and large, thin slabs have only nonradiative surface phonon modes with frequencies depending on wave vector $\vec{k}$. It has been shown theoretically that interaction between photons and surface phonons results in surface polaritons with remarkable dispersion in the long-wavelength region ("retardation region").[8,1] Excitation of nonradiative surface phonons has been observed by electron scattering experiments in thin films[9] and semi-infinite crystals.[10] Excitation occurred over a wide range of k values according to the angular distribution of the impinging electrons. Therefore, no dependence of frequencies on $\vec{k}$ could be observed directly. However, information as to the shape of the dispersion curve can be inferred from the line shape.[9]

In this paper we report the first optical excitation of nonradiative surface polaritons. We use an arrangement of attenuated total reflection (ATR), according to a suggestion of Ruppin.[11] Our experimental results give the dispersion of surface polaritons in the long-wavelength region for semi-infinite crystals of GaP.

Theoretical dispersion of surface polaritons for semi-infinite crystals is given by[11,1]

$$k(\omega) = \frac{\omega}{c}\left(\frac{\epsilon_1(\omega)\epsilon_M}{\epsilon_1(\omega)+\epsilon_M}\right)^{1/2}, \tag{1}$$

where k is the wave vector parallel to the surface, $\epsilon_1(\omega)$ the real part of the dielectric function of the crystal, and c the velocity of light in vacuum. ϵ_M is the dielectric constant of the surrounding medium. $\epsilon_1(\omega)$ is usually taken in the Lorentzian form for an ionic crystal.[1] For $k \gg \omega/c$ the dis-

persion approaches the maximum frequency[3,10]

$$\omega_S = \omega_T\left(\frac{\epsilon_0+\epsilon_M}{\epsilon_\infty+\epsilon_M}\right)^{1/2}, \tag{2}$$

with ϵ_0 and ϵ_∞ being the low- and high-frequency dielectric constants of the crystal. The nonradiative surface polaritons are TH waves with phase velocities always smaller than c. Therefore, direct coupling with incident light cannot occur. Excitation is, however, possible by ATR using a prism.[11,12] The principle is illustrated in the inset of Fig. 1. Reflectivity in a prism is reduced in the range of total reflection by lossy coupling of energy into a sample through a thin air gap of thickness d. Surface modes can be excited in the sample at wave vectors

$$k = k_0 n \sin\alpha, \tag{3}$$

where α is the angle of incidence in the prism, n the prism refractive index, and $k_0 = \omega/c$. The method is described in detail elsewhere.[13]

In our experiments we used silicon prisms shaped as parallelepipeds for use in a transmission arrangement. ATR spectra were taken by an infrared spectrometer with beam divergence reduced to 5 deg. As samples we investigated
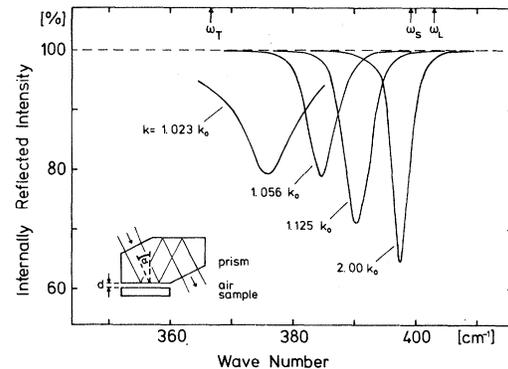

FIG. 1. Spectra of attenuated total reflection (parallel polarization) at room temperature. Different values of k according to Eq. (3). Spacings: $d = 40$, 25, 12, and 2.5μ m, ordered to increasing values of k. Inset shows experimental arrangement.

high-resistivity GaP with an area of about 1 cm^2.[14] The surface was optically polished. The spacing d between the prism surface and the sample was varied between 2.5 and 40 μm. All spectra were taken at room temperature.

Figure 1 shows four experimental ATR spectra at different values of k. We found loss of internally reflected energy in the frequency range between ω_T and ω_S for TH waves, in agreement with theoretical predictions.[11] For each curve k has been evaluated by Eq. (3) from the angle α of incidence. Additional spectra were taken at various values of k (not shown in Fig. 1). The frequency positions of the dips depend on k. The dips are experimentally broadened by averaging over a small range of k values because of nonvanishing beam divergence and by resolution of the spectrometer (≥ 2 cm^{-1}).

For evaluating the frequencies $\omega(k)$ of the surface polaritons from the observed minima, we calculated the loss of reflected intensity with a reflectivity formula[15] for the interfaces silicon/air/GaP. As input data we used the following:

For GaP, $\omega_T = 367.3$ cm^{-1}, $\omega_L = 403.0$ cm^{-1} (at room temperature),[16,17] $\epsilon_\infty = 9.091$,[18] $\epsilon_0 = 10.944$,[19] $\gamma = 0.0035\omega_T$ being the damping parameter for the TO phonon[20] as needed in the Lorentzian for $\epsilon(\omega)$; for air, $\epsilon_M = 1$; and for silicon, $n = 3.418$.[21,22]

For ω_T and ω_L of GaP we have chosen Raman data considered by us to be the most accurate ones. The results of the calculations show that only for vanishing loss of energy (corresponding to large spacings d) the frequencies of the minima agree with those of theoretical dispersion. Theory predicts for large spacings d the half-widths of the curves to be equal to the damping parameter γ of the TO bulk phonon. For decreasing d, loss of energy increases, the dips broaden and slightly shift towards lower frequencies. We therefore analyzed our experimental spectra and evaluated the frequency shifts of the minima for for each dip. We found corrections to be within 1.0 cm^{-1}. Figure 2 shows the corrected minima frequencies, which give the experimental dispersion $\omega(k)$. Experimental accuracy is indicated by the size of the rectangles. The solid line gives the theoretical dispersion for GaP calculated from Eq. (1).

The high experimental accuracy causes comparison with theoretical dispersion to be very sensitive to the input data of GaP. The good agreement, as seen in Fig. 2, confirms the set of input data. The agreement indicates that within experimental accuracy $\epsilon_1(\omega)$ of GaP obeys the
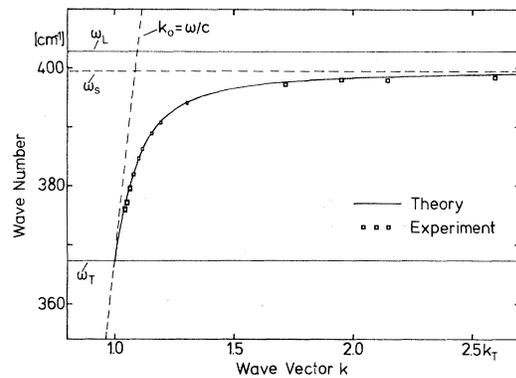

FIG. 2. Dispersion of surface polaritons in GaP. Experimental accuracy is given by size of rectangles. Theoretical curve is calculated from Eq. (1).

Lorentzian form in the range between ω_T and ω_S. The half-width of dips near ω_S with small loss of energy gave $\Delta\omega = 1.2 \pm 0.4$ cm^{-1}, which indeed agrees with previously reported TO bulk-phonon damping ($\gamma = 1.3$ cm^{-1},[20] $\gamma = 1.1$ cm^{-1},[18]). Our results show that ATR presents a good method to obtain the surface-polariton dispersion. For optically polished GaP crystals the surface phonons at long wavelengths are controlled by the bulk phonon parameters. A useful extension of the reported experiments should be to determine $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ between ω_T and ω_S with high accuracy directly from dispersion and linewidth.

Note added in proof.—A similar technique for excitation of surface modes was recently applied to ionic crystals.[23]

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Small-Polaron Hopping Motion in Some Chalcogenide Glasses*

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Unlike prior attempts to describe the motion of electronic charge carriers in disordered materials, we suggest that the (holelike) charge carriers may actually be self-trapped, i.e., small polarons. In support of our hypothesis, we discuss our measurements of the electrical conductivity, thermoelectric power, and Hall mobility on some chalcogenide glasses.

During the past few years a substantial experimental effort has been expended in characterizing the electrical transport properties of a wide variety of glassy chalcogenide systems. In attempting to understand and systematize the resulting observations the simple model initially proposed by Cohen, Fritzsche, and Ovshinsky, the so-called CFO model,[1] has been widely applied to such glasses. Consistent with the situation in most crystalline semiconductors, it was tacitly assumed in this model that the presence of charge carriers did not produce sufficiently large displacements of the atomic constituents so as to necessitate consideration of the possibility that the charge carriers could become self-trapped, i.e., form small polarons. It is the purpose of this Letter to first suggest reasons why one might expect the charge carriers in these glassy substances to be small polarons, and then to point out that such an *Ansatz* leads to predictions which are in agreement with our experimental observations on some chalcogenide glasses.

Let us begin our discussion by reviewing what is meant by a small polaron. Consider for the moment a charge carrier held fixed at a given position in a solid. The presence of the additional (stationary) charge would generally act as a substantial perturbation on its immediate environment, producing a displacement of atoms in its immediate vicinity and causing a reduction in the total energy of the system. The equilibrium positions which these atoms would assume in response to the added charge will be such as to produce a potential well for the carrier. In fact if the potential well associated with the local lattice distortion is sufficiently deep the carrier will occupy a bound state, being unable to move without an alteration of the positions of the neighboring atoms. Such a situation has been referred to as "self-trapping." The unit comprised of the localized charge carrier and its concomitant atomic deformation is termed a *small polaron* when the carrier is essentially confined to a single atomic site.

Clearly a small polaron can only be expected to form if an excess charge carrier will move sufficiently slowly so as to linger at a particular atomic position for time ample to permit the surrounding atoms to adjust to its presence. Since the time characterizing the establishing of new atomic equilibrium positions is a vibrational period ν^{-1}, one readily determines that the intrinsic mobility below which small-polaron formation would appear likely is $(e/kT)\nu a^2$, (~ 0.1 to 1