

$B(E)$  is determined by formula (12). The potential  $U(r)$  is given in this case by

$$U(r) = -\frac{e^2}{\kappa r} + \frac{e^2}{\kappa(r^2 + 2rd \cos \theta + d^2)^{3/2}}, \quad (\text{A1})$$

where  $d$  is the length of the dipole and  $\theta$  is the angle between the radius vector  $r$  and the dipole axis. Calculation for  $E < 0$  and  $|E| \ll e^2/\kappa d$  yields

$$B(E) = 2\pi(\ln 4 - 1)Nbd(2e^2/\kappa ms^2)^2, \quad (\text{A2})$$

where  $N$  is the dipole concentration and  $b$  is defined by formula (18). In this energy region,  $B$  does not depend on the energy. With the aid of (22) we obtain for the lifetime

$$\tau = \frac{1.1}{3(\ln 4 - 1)} \frac{\tau_0}{\alpha} \left( \frac{2e^2}{\kappa ms^2 d} \right) \left( \frac{2kT}{ms^2} \right)^{3/2}, \quad (\text{A3})$$

where  $\tau_0$  and  $\alpha$  are defined by formulas (4) and (6), in which  $N$  is the dipole concentration. Accordingly we have for the effective cross section for capture by a dipole

$$\sigma = [\tau N \langle v \rangle]^{-1} = 2^2 (2 \ln 8 - 3) \sigma_1 \left( \frac{ms^2}{2kT} \right)^3 \left( \frac{\kappa kTd}{e^2} \right) \approx \sigma_c \left( \frac{\kappa kTd}{2e^2} \right), \quad (\text{A4})$$

where

$$\sigma_1 = \frac{\pi}{6} \left( \frac{e^2}{\kappa ms^2} \right)^3 \frac{1}{\tau_0 s}, \quad \sigma_c = 2^2 \sigma_1 \left( \frac{ms^2}{2kT} \right). \quad (\text{A5})$$

For the dipole length  $d$  we can use the average distance to the nearest donor,  $d = 0.55N^{-1/3}$ .

<sup>1</sup>)Indeed, assume that the electron has an energy  $E \gg ms^2$ . We compare the probabilities of two processes: 1) the electron in the field of the center emits an acoustic phonon of high energy and is immediately captured by the center; 2) the electron "diffuses" from the energy  $E$  to the energy  $E_0$ . The electron lifetime  $\tau_1$  in the first process is

$$\tau_1^{-1} = 3\alpha(ms^2/\sqrt{EE_0})(kT/E+U)(ms^2/E+U)^2\tau_0^{-1}(E_0).$$

This expression was obtained from formula (21) of <sup>11</sup>. Here  $U$  is the binding energy, and the capture takes place when  $U \geq kT$ . Since  $\alpha \sim (E_0/ms^2)^3$ , and  $E > E_0$ , we see that the first process is less probable than the second ( $\tau_1 > \tau_c(E_0)$ ).

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## Resonance of a substrate surface polariton with a longitudinal phonon of a thin lithium-fluoride film

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We have investigated the spectra and the angular dependences of attenuated total internal reflection (ATIR) of surface polaritons of sapphire, rutile, and yttrium iron garnets with lithium-fluoride films 100-800 Å thick. The dispersion curves obtained at fixed incidence angles and at fixed frequencies are compared with the calculation. The thickness dependence obtained for the splitting in the ATIR spectrum agrees with the theoretical predictions.

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The extensive use of thin films in optics and electronics calls for knowledge of their properties, which in many cases differ from the properties of the bulk material from which these films are made. To investigate thin films deposited on a crystal it is possible to use, besides the traditional spectroscopic methods, also the surface polaritons of the crystal.<sup>[1]</sup> The dependence of the frequency  $\omega$  of a surface polariton on the wave vector  $k_x$  is given for the interface between two isotropic media with dielectric constants  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  by the formula

$$k_x = \frac{\omega}{c} \left( \frac{\epsilon_1(\omega)\epsilon_2(\omega)}{\epsilon_1(\omega) + \epsilon_2(\omega)} \right)^{1/2}. \quad (1)$$

Surface polaritons can exist at frequencies for which the dielectric constants of the media in contact have opposite signs. The field of a surface polariton is concentrated mainly near the surface, and decreases exponentially with increasing distance from the interface, so that surface polaritons are very sensitive to the properties of films on this interface. Consequently, the spectroscopy of surface polaritons can be a valuable source of information on thin films on crystal surfaces. If the frequency of the transverse or longitudinal oscillation of the dielectric film falls in the region of the existence of the substrate surface polariton, then a gap should be observed at this frequency in the dispersion curve of the

surface polariton and should depend on the thickness of the film.<sup>[1]</sup> For a very thick film, the surface polaritons on its two boundaries can be regarded as independent. If the region where the film has a negative dielectric constant lies inside the region of existence of the surface polariton of the substrate, then there three surface polaritons should be possible: one localized on the interface of the film and the external medium, at frequencies lying between the transverse and longitudinal phonons of the film, and the other two localized at the interface of the substrate and the film and with frequencies above the transverse frequency and below the longitudinal frequency of the film, respectively. The dispersion of all three surface polaritons is described by formulas of the type (1).

With decreasing film thickness, the surface polaritons cease to be independent, the calculation becomes complicated. Calculation and experiment, show, however, that for Zn and Se films with transverse and longitudinal phonons in the region where substrate surface plasmon exists, there are still three plasmon-phonon surface oscillations, but are now intermixed.<sup>[2]</sup>

In the other limiting case (very thin films), one can consider the resonance between the almost unperturbed substrate surface polariton and the longitudinal or transverse phonon of the thin film.<sup>[1,3]</sup>

In this approximation, the splitting of the surface-polariton line near the resonance is proportional to the square root of the film thickness. For a longitudinal phonon with macroscopic layer of thickness  $l$ , the splitting is equal to<sup>[1]</sup>

$$\Delta = \left( 2l|\epsilon_3| \frac{\epsilon_{02} - \epsilon_{\infty 2}}{\epsilon_{02}\epsilon_{\infty 2}} \omega_0 C(k_0) \right)^{1/2}, \quad (2)$$

where  $\omega_0$  is the frequency of the longitudinal phonon of the film,  $k_0$  is the substrate surface-polariton wave vector corresponding to this frequency,  $\epsilon_3$  is the dielectric constant of the substrate, and  $\epsilon_{02}$  and  $\epsilon_{\infty 2}$  are the static and high-frequency dielectric constants of the film. The functions  $C(k_0)$  are determined by the dielectric constant of the substrate and can be reduced, at  $|\epsilon_3| \gg 1$ , to the form

$$C \approx \frac{\omega_0}{|\epsilon_3|^{1/2} + |\epsilon_3|^{1/2} [(1 - \omega_{LO}^2/\omega_0^2)^{-1} - (1 - \omega_{TO}^2/\omega_0^2)^{-1}]}, \quad (3)$$

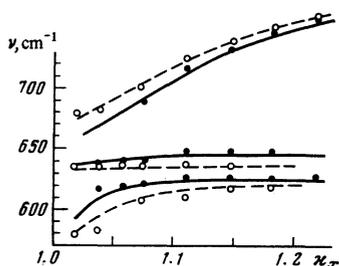


FIG. 1. Dispersion of ordinary surface polaritons of sapphire with lithium-fluoride film 200 Å thick (solid curves and points) and 800 Å thick (dashed curves and circles), calculated for a real reduced wave vector  $\kappa_x = ck_x/\omega$  and measured at fixed incidence angles.

where  $\omega_{LO}$  and  $\omega_{TO}$  are the frequencies of the longitudinal and transverse phonons of the substrate.

Using (2) and (3) we can calculate the gap in the spectrum of the attenuated total internal reflection (ATIR) of the crystal with the film. No account was taken here of the damping, which has little effect on the dispersion of the surface polaritons if the wave vector is real (measurements of the frequencies of the minima in the ATIR spectrum at fixed incidence angles), and allowance for the damping makes it possible to determine the widths of the ATIR spectral lines.

By measuring the angular dependence of the reflection in the ATIR prism at different fixed frequencies we can determine the dispersion of the surface polaritons at a real frequency<sup>[4]</sup> from the angular positions of the minima at different frequencies. The gaps in the dispersion curves should then give way to turning points.

We chose as the film material lithium fluoride with longitudinal-phonon frequency  $\sim 670 \text{ cm}^{-1}$ .<sup>[5]</sup> This frequency lies in the dispersion region of the surface polaritons of rutile,<sup>[6]</sup> sapphire, and yttrium iron garnet.<sup>[7,8]</sup> Lithium fluoride films 100–800 Å thick were deposited on these crystals by thermal evaporation in a vacuum  $\sim 10^{-6}$  Torr.

To investigate the ATIR spectra of the surface polaritons<sup>[1,2,6-8]</sup> we used Hitachi-225 and IKS-16 spectrophotometers with NPVO-1 (ATIR) attachments. The preliminary results were published in<sup>[9]</sup>. Splitting of the surface-polariton line in the ATIR spectrum was observed for the sapphire and rutile crystals, but the frequency near which the splitting was observed was shifted to  $650 \text{ cm}^{-1}$  (in place of  $670 \text{ cm}^{-1}$ ). The calculation of the dispersion curves of the surface polaritons sapphire (with oscillator parameters of<sup>[10]</sup>) with a lithium-fluoride film<sup>[5]</sup> do not agree with experiment.

To improve the agreement between calculation and experiment, we varied the lithium-fluoride oscillator strength obtained in<sup>[5]</sup> so as to make the longitudinal-phonon frequency  $650 \text{ cm}^{-1}$ . The experimental points for the dispersion of the surface polaritons at fixed incidence angles then agreed well with the calculated curves. Figure 1 shows a comparison of the calculation with experiment for 200 and 800 Å lithium-fluoride films on sapphire with substrate optical axis perpendicular to the plane of incidence (ordinary surface polariton). A low-frequency surface polariton exists also without a film, and is the result of the weak  $635\text{-cm}^{-1}$  vibration situated in the band of the residual rays and producing a gap in the substrate dispersion curve.<sup>[8]</sup> In the presence of a film, the high-frequency surface polariton of sapphire ( $635\text{--}820 \text{ cm}^{-1}$ ) splits, forming a gap, into two, one below  $650 \text{ cm}^{-1}$  and the other above this frequency.

The decrease of the frequency of the longitudinal phonon of a thin lithium-fluoride film explains the absence of splitting when the film is deposited on an yttrium-iron-garnet crystal. The  $650 \text{ cm}^{-1}$  frequency lies in the gap of the dispersion curve of the substrate,<sup>[7]</sup> a gap present even without the film. In this case, we observed only an increase of the gap, the upper branch

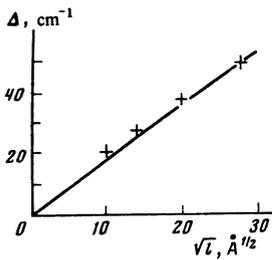


FIG. 2. Dependence of the splitting in the ATIR spectrum of surface polaritons on the thickness of the lithium fluoride film on sapphire (straight line—approximate calculation in accordance with<sup>[1,3]</sup>, crosses—experimental points; the dimensions of the crosses indicate the accuracy with which the distance between the minima in the ATIR spectrum is determined and the accuracy with which the film thickness is determined.)

rising and the lower dropping.

For lithium-fluoride films of different thicknesses, 100, 200, 400, and 800 Å, produced on sapphire under identical conditions, we determined the splitting at incidence angles corresponding to the wave vector  $k_0$ . The splitting was equal within the limit of the experimental error, for different orientations of the optical axis. To compare these results with those of<sup>[1,3]</sup> the dielectric constant of the sapphire was approximated by a single oscillator with transverse frequency  $\nu_{TO} = 570 \text{ cm}^{-1}$  and longitudinal frequency  $\nu_{LO} = 900 \text{ cm}^{-1}$ , in which case  $\epsilon_3(\nu_0) = -12.8$ , i. e.,  $|\epsilon_3| \gg 1$ . Assuming  $\epsilon_{\infty 2} = 1.9$  and  $\epsilon_{\infty 2} = 8.5$ , we obtain from (2) and (3)

$$\Delta \approx 1.8\sqrt{l} \quad (4)$$

for the gap width in  $\text{cm}^{-1}$  (the thickness is in Å). For a film 100 Å thick we obtain  $\Delta \approx 18 \text{ cm}^{-1}$ . The function (4) is compared with our results in Fig. 2. The agreement is good, despite the rough estimates used in the calculations (the use of a model with one oscillator for sapphire).

Figure 3 shows the dispersion of the surface polariton of a sapphire with an 800 Å film at fixed frequencies. The low-frequency turning point corresponds to the  $635 \text{ cm}^{-1}$  gap in Fig. 1 and exists without a film, while the high-frequency turning point appears when the lithium-fluoride film is deposited. The calculation was carried out with the same material oscillator parameters as used for the calculation of the curves in Fig. 1.

The decrease of the frequency of the longitudinal oscillations on going from bulk crystal to a thin film can be explained by assuming that the film consists of crystallites that are not close-packed. The porosity of thicker films (several microns thick) of lithium fluoride was reported in<sup>[11]</sup>. If the film consists of a mixture of lithium fluoride with bulk-crystal properties, occupying a fraction  $q$  of the volume, and air, then the dielectric constant of the film can be determined from the formula

$$\epsilon(\omega) = \epsilon(\omega)q + (1-q). \quad (5)$$

Calculation using the oscillator parameters of<sup>[5]</sup>

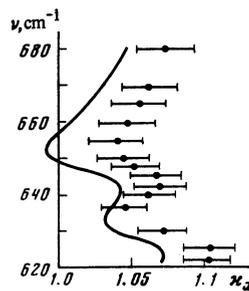


FIG. 3. Dispersion at a real frequency (calculation and experiment at fixed frequencies) for sapphire with a film of lithium fluoride 800 Å thick ( $\kappa_x = ck_x/\omega$ ).

shows the following: With decreasing filling coefficient  $q$ , the frequency for which  $\epsilon(\omega) = 0$  if no allowance is made for damping also decreases, and at  $q \approx 0.85$  the longitudinal frequency is equal to  $650 \text{ cm}^{-1}$ . This filling coefficient is close to the values obtained in<sup>[11]</sup>. Introduction of petrolatum oil into the clearance between the sample and the ATIR prism does not change the frequency of the gap in the spectrum of the sapphire surface polaritons. This indicates that the petrolatum oil does not penetrate into the pores of the film and does not change its dielectric constant.

We have thus obtained the splitting of the ATIR spectral line of a substrate surface polariton as a function of the film thickness; this function coincides with that predicted in<sup>[1,3]</sup>. This dependence ( $\propto \sqrt{l/\lambda}$ ) is slower than for most optical effects ( $\propto l/\lambda$ ), so that thinner films than those studied by ordinary methods can be investigated. The position of the gap turned out to be shifted towards lower frequencies, apparently because of the porosity of the lithium-fluoride films. The dispersion was obtained at fixed frequencies for sapphire with a lithium fluoride film. A turning point corresponding to the gap observed at fixed incidence angles was observed near  $650 \text{ cm}^{-1}$ .

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