

## Experimental Observation of Surface Exciton Polaritons

J. Lagois and B. Fischer

*Max-Planck-Institut für Festkörperforschung, D-7 Stuttgart 80, Germany*

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Surface exciton polaritons are observed in a semiconductor for the first time. The modes are excited in ZnO crystals by the method of attenuated total reflection. Changing the angle of incidence of the ultraviolet radiation gives an experimental dispersion relation for surface exciton polaritons.

Surface excitons have been treated theoretically by several authors.<sup>1-5</sup> Polariton dispersion relations and the reflectivity of crystals for the attenuated-total-reflection (ATR) method have been calculated.<sup>4,2</sup> The surface exciton frequencies always lie between the transverse and longitudinal resonance frequencies  $\omega_T$  and  $\omega_L$  of the bulk excitons for a given wave vector. Because of spatial dispersion, surface excitons have among surface excitations the unique property of coexistence with a bulk mode in the energy region between  $\omega_T$  and  $\omega_L$ . Consequently, energy transfer between these modes is possible.<sup>3</sup> Surface modes can be excited by an ATR arrangement. This method uses a prism to couple electromagnetic waves of wave vector  $k > \omega/c_{\text{vac}}$  across a thin spatial gap with the sample surface. The ATR method has been applied successfully to detect surface phonon polaritons and surface plasmons in various media.<sup>6</sup> Extending ATR to the shorter wavelengths of surface excitons is difficult because of the stringent requirements on control of the spacing between crystal and prism and because of exciton-free surface layers.<sup>4,7</sup> According to calculations by Maradudin and Mills,<sup>2</sup> the reflectivity changes  $\Delta R/R$  in an ATR experiment are expected to be of the order of  $10^{-5}$ . All these reasons may account for the fact that experiments on surface excitons have not been reported until now. However, a direct observation of surface excitons would offer new possibilities for obtaining information about exciton-free surface layers and spatial dispersion.

In this paper we report the first optical excitation of surface exciton polaritons in a semiconductor. We used an arrangement of attenuated total reflection at helium temperatures. Our experimental results give the dispersion relation of surface exciton polaritons in the short-wavelength region near the band gap of ZnO crystals.

A careful choice of the crystal material is necessary to obtain the best conditions for the experimental excitation and observation of surface

excitons. It is known for some materials that image charges or field-induced ionization of excitons creates an exciton-free surface layer at least 1 to 2 exciton Bohr radii thick.<sup>7,8</sup> The exciton-free surface layer has to be as thin as possible in order to excite excitons by an ATR technique which uses the evanescent waves "leaking out" of a prism while light is totally reflected inside. Only for thin exciton-free surface layers are the exponentially decaying electromagnetic waves still sufficiently intense at the crystal regions where excitons exist. From the free-exciton reflectance spectra it is known that the exciton-free surface layer of ZnO is less than about 30 Å,<sup>9</sup> probably the smallest one of the II-VI semiconducting compounds. For this reason we used ZnO crystals in our experiment.

ZnO has the wurtzite structure and therefore possesses three excitonic transitions at about 3.4 eV due to the upper two valence bands (*A* and *B* excitons, electric field  $\vec{E}$  perpendicular to the hexagonal  $\vec{c}$  axis) and to the third valence band (*C* excitons,  $\vec{E} \parallel \vec{c}$ ). The free *C*<sub>1</sub> excitons of the ground state of a hydrogenlike exciton model are separated by the crystal-field splitting of about 40 meV from the *A*<sub>1</sub> and *B*<sub>1</sub> excitons. Their longitudinal-transverse splittings are about 2 meV (*A*<sub>1</sub>) and 11 meV (*B*<sub>1</sub> and *C*<sub>1</sub>). The spin-orbit splitting of the *A*<sub>1</sub> and *B*<sub>1</sub> excitons is about -5 meV.<sup>9</sup> The relatively wide separation of differently polarized transitions facilitates the identification of the observed excitations as surface excitons.

The ZnO single crystals investigated were grown from the vapor phase.<sup>10</sup> The surfaces were optically polished parallel to the  $\vec{c}$  axis. Surface cleaning in a concentrated phosphoric acid etch is necessary to observe excitonic structures in an optical experiment.<sup>11</sup> Two samples of an area of about  $4 \times 13 \text{ mm}^2$  were cut from one single crystal of ZnO and pressed against two sides of a parallelepiped-shaped prism of Hera-sil glass. To increase the optical coupling to the

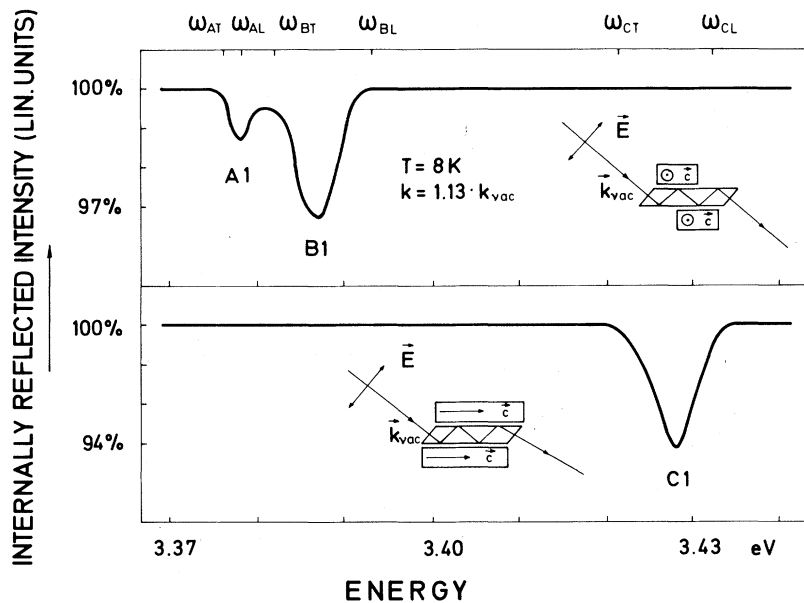


FIG. 1. Spectra of attenuated total reflection for surface excitons. The insets show the experimental arrangement. The actual percentage of the intensity loss depends on the details of area and coupling. Upper scale gives transverse and longitudinal frequencies of the A, B, and C excitons.

samples, we designed the prism for four internal reflections as indicated in the insets of Fig. 1. Since the gap thickness between prism and crystals has to be of the order of the wavelength of the exciting light (about 365 nm) we pressed the crystals without any spacing material against the prism. The slight surface irregularities of the crystals originating from etching limited the direct contact between prism and crystals to a few small spots. Around these spots the gap was of the order of about one wavelength as confirmed by interference fringes. Visual inspection gave a convenient control, since the total reflection of visible light was perturbed only at these few spots of direct contact between sample and prism. The holder for crystals and prism was manufactured to be suitable for a cryostat which was cooled down to about 8 K. The samples were in cold helium gas during the measurement. Light from a halogen lamp was filtered (300–440 nm), linearly polarized, and directed at the prism with a beam divergence of 0.3 deg. The spectra were taken with a grating spectrometer and a photomultiplier using a lock-in technique.

Figure 1 shows the experimental ATR spectra of the  $A_1$ ,  $B_1$ , and  $C_1$  excitons for two orthogonal orientations of the  $\vec{c}$  axis relative to the incoming light, as shown in the insets. We found a loss of several percent of the internally reflected light intensity in the frequency range between  $\omega_T$  and

$\omega_L$  of TM waves for light polarized parallel to the plane of incidence. The reflectance minima shift when the wave vector  $k$  is changed by variation of the angle of incidence at the prism-crystal interface. We observed the shift for the  $C_1$  exciton in detail and obtained the first part of a dispersion relation for surface excitons. Figure 2 shows the frequencies of the minima, which give the experimental dispersion relation  $\omega(k)$ . The solid lines display the theoretical dispersion relation for surface and bulk excitons.<sup>4,7</sup> (The symbols in Fig. 2 are identical to those of Ref. 4.) The parameters for ZnO were taken from Ref. 9. Extension to larger  $k$  values would require a prism of higher index of refraction.

We must establish that in fact surface excitons caused the decrease of the internally totally reflected light intensity. In the first place, the frequencies of the minima indeed lie between the transverse and longitudinal resonance frequencies of the corresponding bulk mode. Secondly, a crucial test was made by changing the polarization of the incoming light. We observed the reflectivity dips only for  $\vec{E}$  polarized parallel to the plane of incidence. For  $\vec{E}$  perpendicular to the plane of incidence there is no decrease of the intensity at the energy of *any* of the free excitons. This polarization dependence is in accordance with the properties of electromagnetic surface waves.<sup>6</sup> Finally, a direct coupling with bulk

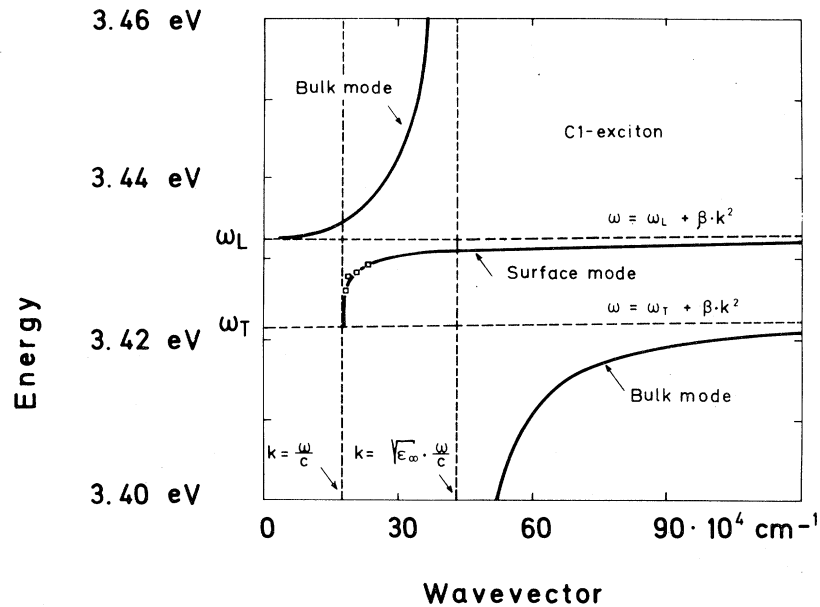


FIG. 2. Dispersion curves of surface and bulk excitons. The solid lines are calculated; the rectangles are experimentally determined. The experimental accuracy is approximated by the size of the rectangles.

waves which would superimpose the bulk reflectivity spectrum on the ATR spectrum could originate from the small spots of direct contact as well as from areas of thin gap between crystals and prism. Through control of the mounting, the areas of direct contact were limited to a few percent of the entire active area. Since we did not observe any influence of bulk reflectivity for light polarized either parallel or perpendicular to the plane of incidence, the direct coupling with bulk waves is obviously negligible. These considerations confirm our interpretation that the experimental spectra do in fact show the excitation of surface excitons.

The experimental points on the dispersion curve of Fig. 2 were obtained simply by using the energies of the reflectance minima. These experimental points are in remarkable agreement with the calculated dispersion curve. Note, however, that the exact energies can be derived only with precise knowledge of the thicknesses of the gaps between the prism and crystals. However, these thicknesses are inhomogeneous for our experimental conditions. Moreover, the spacing immediately around the points of contact is very small compared to the wavelength which leads to a broadening of the spectra as known from surface phonons and plasmons.<sup>12,13</sup> Therefore, it is as yet impossible to draw any conclusions about the lifetimes of surface excitons from the line shapes and widths of the experimental spectra.

It is surprising that the internally reflected light intensity is lowered by several percent, whereas the estimate for ZnSe of Maradudin and Mills<sup>2</sup> was only about  $10^{-5}$ . Since the difference cannot be due only to the different excitonic oscillator strengths of ZnSe and ZnO, these first experimental results should stimulate more theoretical and further experimental work. This should provide for instance more information about the existence of an exciton-free surface layer.

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*Note added.*—ATR spectra recently calculated by us are in good agreement with our experiments. These results will be published elsewhere.

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## Random-Walk Model of Energy Transfer in Cathodoluminescence

Lyuji Ozawa and Herbert N. Hersh

Zenith Radio Corporation Research Laboratories, Chicago, Illinois 60639

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The probability  $S$  of energy transfer from excited host lattice to activator ions can be calculated from experimental concentration-dependence data. It is 0.66 for  $Y_2O_2S:Eu$ ,  $S$  is the quantum efficiency for host-excited luminescence and can be used to calculate cathodoluminescence efficiency.

The mechanism of cathodoluminescence (CL) in inorganic phosphors is not completely understood. This is because the concepts of energy transfer from host lattice to the activator ions have so far been inadequate.<sup>1-3</sup> In this Letter, we shall report a new approach to determining the probability of the energy transfer from excited host lattice to activator ions.

Energy-transfer mechanisms in luminescent materials have been studied extensively by measuring luminescence intensities and lifetimes.<sup>4</sup> A point commonly overlooked in the measurements of luminescence intensities is the volume in which the excitation energy is contained. For phosphors in which the activator ions are excited only directly by the incident electrons (including internally generated secondary electrons<sup>5</sup>) the active volume  $V_a$  for directly excited phosphors is defined by the penetration depth of the incident electrons.  $V_a$  is thus a constant for a given cathode-ray (CR) voltage; the penetration depth of 10-kV electrons is  $0.4 \mu\text{m}$ .<sup>6</sup> If the energy of the incident electrons is scattered uniformly in  $V_a$  all of the lattice sites in  $V_a$  will have an equal chance of excitation. Therefore, the number of activator ions excited in  $V_a$ , which is proportional to the CL intensity, will be proportional to the activator concentration. Consequently, we expect the luminescence intensity as a function of activator concentration, i.e., the concentration dependence (CD), to have unit slope in a log-log plot at low activator concentrations where self-quench-

ing is negligible.<sup>7</sup> As an example of a directly excited phosphor, Fig. 1 shows the CD curves of  $Y_2O_2S:Ho$  under continuous (dc) CR excitation (10 kV,  $0.5 \mu\text{A}/\text{cm}^2$  were used throughout this report) and under direct  $Ho^{+3}$  excitation using 423-nm radiation. It is found that the slope is, as anticipated, unity.

For phosphors whose activator ions are excited by both incident electrons and excited host lattice (host excitation), the active volume ( $V_a$ ) is defined by the subsequent migration of the energy carriers<sup>8</sup> (ECs) created by the incident electrons in  $V_a$

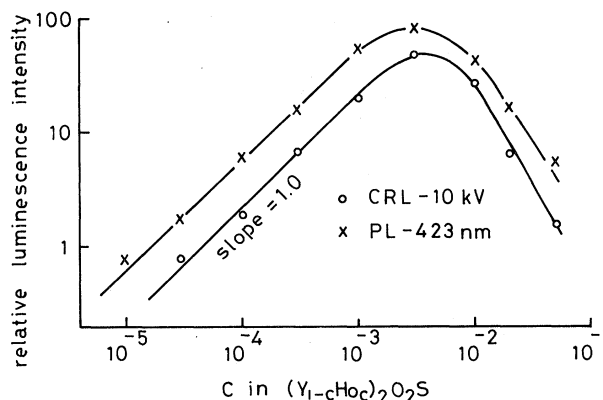


FIG. 1. Concentration-dependence curves of time-averaged  $Ho^{+3}$  luminescence at 544 nm of  $Y_2O_2S:Ho$  under continuous cathode-ray (CRL) and direct photoexcitation with 423-nm radiation (PL).