x_c. The critical-field experiments indicate that this feature should not be neglected in any realistic picture of the infinite cluster.

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Additional Boundary Conditions: Critical Comparison between Theory and Experiment

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A linear-response theory leads to a generalized additional boundary condition (ABC) which includes as special cases all the well-known ABC's. Calculations for the reflectivity are compared with an experimental spectrum of CdS. Strong evidence is found in favor of the Pekar ABC and against other ABC's. Comparison with an attenuated total reflectivity spectrum of ZnO suggests that a more sophisticated surface response is necessary for semiconductors with a small exciton-free surface layer.

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Certain semiconductors exhibit anomalous optical properties associated with excitonic transitions. These properties are a manifestation of the translational motion of the exciton. They are described by nonlocal models: Namely the dielectric function ϵ depends on the wave vector $\vec{q}$, as well as on the frequency ω. As a consequence calculations of optical properties of these materials necessitate an additional boundary condition (ABC) which supplements those normally applied for electromagnetic fields at the interface between spatially nondispersive (local) media. The nature of this ABC has been under intense discussion for the past ten years.

The ABC's are usually stated in terms of constraints on the excitonic polarization $\vec{P}(z)$ and its normal derivative $\vec{P}'(z)$ at the crystalline surface or at the interface between the bulk and an exciton-free surface layer. Pekar[1] originally suggested $\vec{P}=0$. Other frequently used ABC's are

$\vec{P}'=0$, due to Ting, Frankel, and Birman,[2] and $\vec{P}'+i\Gamma\vec{P}=0$, where $\Gamma^2=(\omega^2+i\nu\omega-\omega_T{}^2-Dq_x{}^2)/D$, $D=\hbar\omega_T/(m_e+m_h)$, ω_T and ν are the transverse and damping frequencies of the exciton, and m_e and m_h are the electron and hole masses. The last ABC has been given in different forms by Agarwal, Pattanayak, and Wolf, Birman and Sein, and Maradudin and Mills.[3] Two ABC's involve the parallel and perpendicular components of $\vec{P}$ distinctly. They are $\vec{P}_x'=P_z=0$, postulated by Kliewer and Fuchs[4] for metallic surfaces and $P_x=P_z'=0$, suggested by Rimbey and Mahan.[5] These ABC's become identical with the Ting-Frankel-Birman[2] and the Pekar[1] ABC's, respectively, for s polarization. On the basis of comparison between theory and experiment several groups[6] favored the Pekar ABC. Fukui, So, and Stegeman[7] found "reasonable agreement" with the Ting-Frankel-Birman ABC, Tokura *et al.*[8] were inclined in favor of the Rimbey-Mahan ABC, and recently Yu and Evangelisti[9] claimed "quantitative agreement" with the Agarwal-Pattanayak-Wolf ABC. Just which ABC is applicable? Moreover, "intermediate" (nameless) ABC's should not be ignored.

Further progress depends on (a) reliable exciton parameters and (b) parametrization of the ABC. As for the first requirement the recent advent of Brillouin[9] and Raman[10] scattering techniques has provided a breakthrough. The second requirement has been met in several works[11]; however, the procedures employed are not sufficiently general to cover all the ABC's listed in the preceding paragraph. Moreover, no careful comparison with experiments has been performed.

Our model involves three layers. The first is finite and is characterized by a local dielectric constant ϵ_1. The second layer occupies the region $-l\leq z\leq 0$ and has a local dielectric constant ϵ_2. The third layer is semi-infinite and is characterized by the Hopfield-Thomas[12] dielectric function

$$\epsilon(q_z)=\epsilon_0+(\epsilon_0/D)(\omega_L{}^2-\omega_T{}^2)/(q_z{}^2-\Gamma^2),$$

where ϵ_0 is the background dielectric constant and ω_L is the longitudinal exciton frequency. This model describes a semiconductor with an exciton-free surface layer if we select $\epsilon_1=1$ and $\epsilon_2=\epsilon_0$. It is also applicable to attenuated total reflectivity (ATR) experiments if we identify the first medium as a prism and the second medium as the gap ($\epsilon_2=1$). In both cases the linear response for the displacement vector (p polarization) in medium 3 is given by[13]

$$D_i(z)=\int_0^\infty[\epsilon(z-z')+U_i\epsilon(z+z')]E_i(z')dz', \quad (1)$$

$i=x,z$.

The functions $\epsilon(z\mp z')$ are Fourier transforms of $\epsilon(q_z)$ and U_x and U_z are phenomenological parameters. The translationally invariant first term describes the bulk response. The second term simulates the surface response: It corresponds to an excitation at $\vec{r}'$ being propagated to $\vec{r}$ *after being scattered at the interface* $z=0$. The parameters U_x and U_z describe the strength of this scattering. For elastic scattering $|U_i|=1$, and considerations based on energy conservation indicate that in general $|U_i|\leq 1$. Complex values of U_i correspond to a change of phase upon scattering. A sufficiently general description requires that in general $U_x\neq U_z$.

Our ignorance of the "correct" values of U_x and U_z corresponds exactly to our ignorance of the "correct" ABC. In fact, given the values of U_x and U_z the ABC is completely determined. It is obtained upon substitution of Eq. (1) in the wave equation:

$$(1+U_i)P_i'+i\Gamma(1-U_i)P_i=0, \quad (2)$$

where $i=x,z$. This *generalized* ABC describes the behavior of P_x and P_z at the interface 2|3. It reduces to the Pekar ABC for $U_x=U_z=-1$, to the Ting-Frankel-Birman ABC for $U_x=U_z=1$, to the Fuchs-Kliewer ABC for $U_x=-U_z=1$, to the Rimbey-Mahan ABC for $U_x=-U_z=-1$, and to the Agarwal-Pattanayak-Wolf ABC for $U_x=U_z=0$. By utilizing Eq. (2) we derive[14] a rather lengthy formula for the reflectivity R_p. It reduces to published expressions for particular values of U_x and U_z.

First we apply our formula[14] for R_p to compute the normal-incidence spectrum of the $A_{n=1}$ exciton of CdS. The parameters used have been measured by Yu and Evangelisti[9] for a sample designated 505/1. The technique employed was Brillouin scattering and therefore these parameters are free from implicit assumptions about ABC's. For normal incidence only one parameter U is required and we vary it from -1.0 to 1.0 in steps of 0.5. Figure 1 shows that $R(\omega)$ *changes continuously from the curve labeled* $U=-1.0$ *(Pekar ABC) to the curve labeled* $U=1.0$ *(Fuchs-Kliewer ABC).* The curve labeled $U=0.0$ (Agarwal-Pattanayak-Wolf ABC) occupies an intermediate position. Comparison with the local case indicates *that the importance of nonlocal effects increases as* U *is decreased from 1 to* -1. The crosses are

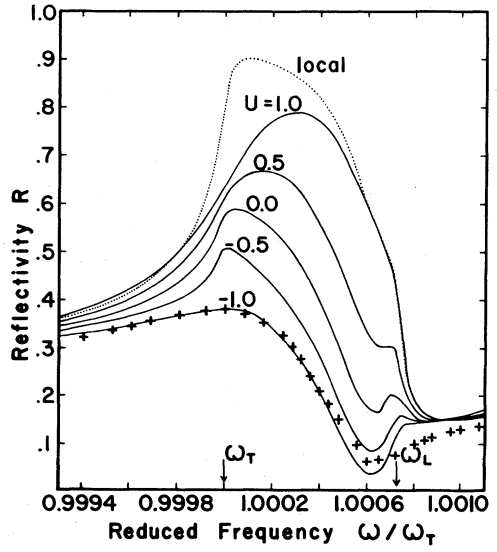

FIG. 1. Normal-incidence reflectivity for the $A_{n=1}$ exciton of CdS. The parameter U corresponds to a particular ABC, e.g., $U=-1$ describes the Pekar ABC. Thickness of exciton-free layer l = 100 Å. The experimental spectrum is due to Patella, Evangelisti, and Capizzi (Ref. 15).

results of measurements by Patella, Evangelisti, and Capizzi[15] *on the same sample 505/1 used later by Yu and Evangelisti*[9] to determine the exciton parameters. Agreement between the experimental crosses and the theoretical curve labeled $U=-1$ is excellent. We believe this to be the strongest evidence presented so far in favor of the Pekar ABC and against any other ABC covered by Eq. (2). Apart from U the only adjustable parameter in our calculation is the thickness l of the exciton-free layer. From Fig. 2 we see that $l=100$ Å is a reasonable choice. A comparison between Figs. 1 and 2 suggests that it is *not* possible to obtain agreement with experiment for $U \gtrsim -0.5$ and some suitable value of l. In order to shed light on the value of U_z a similar analysis with p-polarized light should be undertaken.

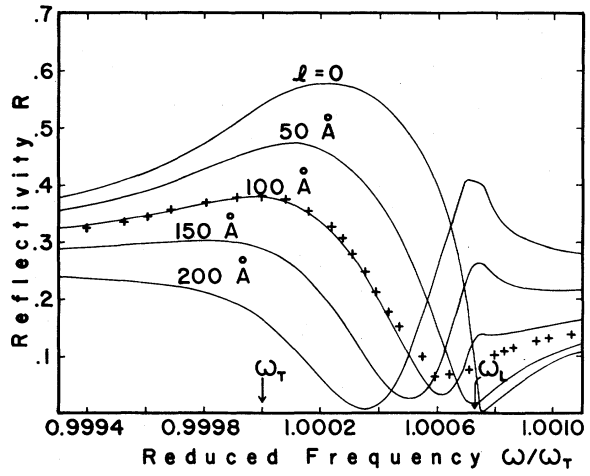

FIG. 2. As in Fig. 1, for various thicknesses of the exciton-free layer (Pekar ABC, $U=-1$).

Next we compute the ATR spectrum (for p polarization) of the $C_{n=1}$ exciton of ZnO. We have neglected the small (~ 30 Å) exciton-free layer and used the parameters measured by Lagois and Hümmer.[16] In Fig. 3 we show the resulting spectra for $U_z=-1$, $|U_x|=1$ (elastic scattering) and $U_z=-1$, $|U_x|=0.5$ (inelastic scattering). The phase φ of U_x is varied in steps of $\pi/4$. Thus the sixteen theoretical spectra correspond to sixteen different ABC's! The minima are associated with excitation of surface polaritons, as shown by Otto.[17] The depth and width of the spectral lines vary by as much as a factor of 4, depending on U_x. The dissipative mechanism stems principally from the fact that surface exciton polaritons are not true normal modes: Maradudin and Mills[3] showed that they decay into bulk polaritons even for $\nu=0$. As we increase φ from 0 to 2π the width (depth) increases (decreases) reaching a maximum (minimum) for $\varphi=\pi$, then gradually decreases (increases) to the initial value for $\varphi=2\pi$. The

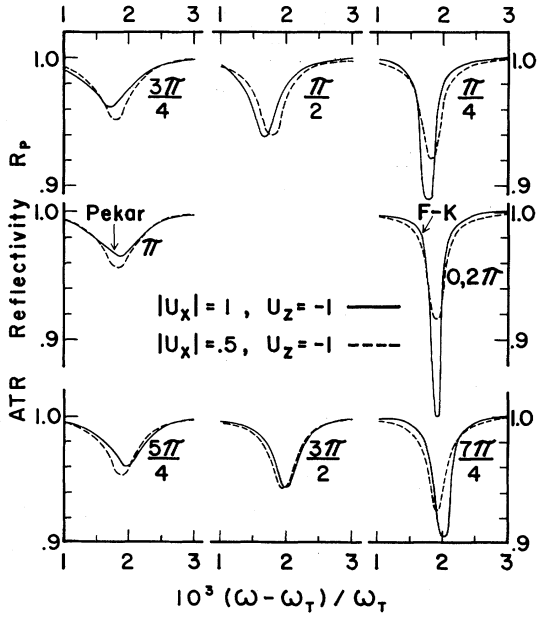

FIG. 3. Attenuated total reflectivity for the $C_{n=1}$ exciton of ZnO. The angle of incidence is 50° and the prism is separated by a 3600-Å gap from the surface of the crystal. The exhibited angles φ are the phases of the parameter U_x ($=|U_x|\exp i\varphi$).

width is thus greatest for the Pekar ABC, ~ 3 meV. About the same maximum width is obtained[14] for $U_z = 0$ and 1. On the other hand, the linewidth measured by Lagois[18] is ~ 6 meV. We conclude that for all values of U_x and U_z the theoretical linewidths fall short of the experimental one.

It should be noted that Lagois[18] got an excellent fit to his experimental ATR spectrum of ZnO on the basis of the Pekar ABC and a number of adjustable parameters. Lagois[18,19] argues that, as a result of band bending, ω_T, ω_L, and ν become depth dependent in the surface region.[20] This effect, however, is of consequence only for very few semiconductors with small exciton-free layers. In most cases excitons may exist only at distances ~ 100 Å from the surface where band bending is negligible and where surface excitations, if any, are extremely weak.

In conclusion, we have shown that a surface response based on the Pekar ABC and a simple exciton-free layer lead to excellent agreement with the normal-incidence reflectivity spectrum of a model semiconductor, namely CdS ($A_{n=1}$ exciton). This evidence weighs heavily in favor of the Pekar ABC and against any other ABC covered by Eq. (2). Similar comparisons between experiments on other semiconductors (including oblique incidence of light) and theory based on the generalized ABC, Eq. (2), should be undertaken before general conclusions can be drawn. In the case of ATR on semiconductors with a small exciton-free layer it seems that a more sophisticated surface response is required.

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