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Additional boundary conditions and surface exciton dispersion relations*

Peter R. Rimbey

Ames Laboratory-Energy Research and Development Administration, and Department of Physics, Iowa State University, Ames, Iowa 50011

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The surface-exciton dispersion curves in ZnO are derived from the surface impedances developed by Fuchs and Kliewer (FK) and Rimbey and Mahan (RM) including retardation. There exists a distinctive splitting between the two dispersions, the FK additional boundary conditions having longitudinal character, the RM additional boundary conditions being transverse. Surface-mode attenuation due to spatial dispersion is more pronounced in the RM formalism, although inclusion of a phenomenological damping parameter does not alter either dispersion curve.

Experimental results have recently begun to accumulate on a variety of substances whose reflectivity spectra exhibit structure attributable to surface-exciton resonances. Included in such crystal systems are semiconductors[1] (ZnO), ionic crystals[2] (CuBr), inert-gas crystals[3] (Xe), and molecular crystals[4] (tetracene). Formerly, observation of such excitations was viewed with some scepticism primarily because of the weak exciton-photon coupling and the possible decay into bulk mode states through the mechanism of spatial dispersion.[5,6] Concurrently, theoretical developments have been concerned with the effects of spatial dispersion on surface modes particularly as related to the question of additional boundary conditions.[6-11] It has been suggested that such experiments may elucidate the applicability of the various additional boundary conditions[5] (ABC's). In this paper we display certain ramifications of two ABC's as exhibited by their respective surface-exciton dispersion curves.

Previous theoretical work has suggested that the material polarization field $\vec{P}$ determines the ABC placed on the macroscopic Maxwell's equations for bounded media. In semi-infinite media these have usually taken a form where either $\vec{P}$ or its components vanish[12] (exciton ABC) at the surface or alternatively the derivatives of P_i have been the vanishing quantities[5] (plasmon ABC). In principle these two extreme cases can be generalized into a linear combination[6,13,14], e.g., $P(0^+) + \lambda[dP(0^+)/dz] = 0$ often interpreted as a Wannier exciton ABC. λ is a model-dependent parameter sometimes associated with the so-called dead layer or diffuse scattering. The nonlocal problem has also been solved for the half space and thin films utilizing certain symmetry conditions placed on the electric and magnetic fields. In the case of p-polarized light, Fuchs and Kliewer[15] (FK) initially proposed the symmetry conditions $E_x(z) = E_x(-z)$ and $H_y(z) = -H_y(-z)$, whereas Rimbey and Mahan[16] (RM) determined an alternative set given by $E_x(z) = -E_x(-z)$ and $H_y(z) = H_y(-z)$. Subsequently these specular scattering symmetry conditions were demonstrated to be tantamount to the ABC's $\partial P_x(0^+)/\partial z = 0$ and $P_x(0^+) = 0$, respectively.[14,16-18] The first has been extensively applied to metallic systems whereas the second was originally justified in terms of Frenkel excitons in molecular crystals.[17] A specular symmetry condition yielding a linear combination has not been derived although existence criteria have been investigated.[17,18]

Fischer and Quiesser[8] applied the Fuchs-Kliewer symmetry condition to a calculation of the surface Wannier exciton dispersion, however, a misprint is given in their Eq. (6) which would be important near the light line. Nonetheless, their dispersion curves were calculated with the proper dispersion relations and are correct. On the other hand, Rimbey's[9] calculation for the surface mode dispersion neglected retardation and no information was given about the small-q vector regime, again in the neighborhood of the light line. This is precisely the region where, to date, all experimental observations have been made. We wish to correct this discrepancy, in the approximation that a simple hydrodynamic (oscillator) dielectric function can be incorporated to describe a solid.

The procedure is to match the p-polarized surface impedances at the vacuum-solid interface and solve the nonlinear algebraic equations for the ω versus complex q dispersion curve. For the two mentioned symmetry conditions we have, respectively, the following:

Fuchs-Kliewer:

$$-\left(q_x^2 - \frac{\omega^2}{c^2}\right)^{1/2} = \frac{2\omega^2}{\pi c^2}\int_0^\infty \frac{dq_z}{q^2}\left(\frac{q_x^2}{(\omega^2/c^2)\epsilon_l(q,\omega)} + \frac{q_z^2}{(\omega^2/c^2)\epsilon_t(q,\omega) - q^2}\right); \tag{1a}$$

Rimbey-Mahan:

$$\left(q_x^2 - \frac{\omega^2}{c^2}\right)^{-1/2} = \frac{2}{\pi}\int_0^\infty dq_z \, \frac{\epsilon_t(q,\omega)}{(\omega^2/c^2)\epsilon_t(q,\omega) - q^2} \; . \tag{1b}$$

In the relaxation-time approximation the dielectric functions are given by

$$\epsilon_j^{\text{ex}} = \epsilon_0 + \frac{4\pi\alpha_0\omega_T^2}{\omega_T^2 - \beta_j q^2 - \omega\tilde{\omega}} \; , \tag{2}$$

with

$$\tilde{\omega} = \omega + i/\tau, \quad j = t, l \; .$$

Here the β_j coefficients differ essentially as to variation in the longitudinal and transverse effective masses. Substituting Eq. (2) into Eqs. (1) and integrating yields the following dispersion relations:
Fuchs-Kliewer:

$$(q_x^2 - q_0^2)^{1/2} + \frac{q_x^2}{[q_x^2 - (\beta_t/\beta_l\epsilon_0)q_+^2 q_-^2/q_0^2]^{1/2}} \; \frac{q_+^2 q_-^2 + \epsilon_0 q_0^2(q_0^2 - q_+^2 - q_-^2)}{\epsilon_0 q_+^2 q_-^2} - \frac{q_0^2(q_x^2 - q_-^2)^{1/2}}{q_-^2(q_+^2 - q_-^2)}\,(q_0^2\epsilon_0 - q_+^2) - i q_0^2 \, \frac{(q_+^2 - q_x^2)^{1/2}}{q_+^2(q_+^2 - q_-^2)}\,(q_0^2\epsilon_0 - q_-^2) = 0 \; ; \tag{3a}$$

Rimbey-Mahan:

$$(q_x^2 - q_0^2)^{-1/2} - \frac{1}{(q_+^2 - q_-^2)q_0^2}\left(\frac{q_-^2(q_0^2\epsilon_0 - q_+^2)}{(q_x^2 - q_-^2)^{1/2}} - i\,\frac{q_+^2(q_0^2\epsilon_0 - q_-^2)}{(q_+^2 - q_x^2)^{1/2}}\right) = 0 \; , \tag{3b}$$

where $q_0 = \omega/c$. q_+^2 and q_-^2 are the usual bulk transverse mode dispersion curves given from solutions to $\epsilon_t(q,\omega) = c^2q^2/\omega^2$.

In the limit that retardation can be neglected the two integrals reduce to the following:
Fuchs-Kliewer:

$$-1 = \frac{2q_x}{\pi}\int_0^\infty \frac{dq_z}{q^2\epsilon_l(q,\omega)} \; ; \tag{4a}$$

Rimbey-Mahan:

$$-1 = \frac{2q_x}{\pi}\int_0^\infty dq_z \, \frac{\epsilon_t(q,\omega)}{q^2} \; . \tag{4b}$$

The analytic expressions for these dispersion relations have been given elsewhere[8,9]; we briefly remark on the obvious differences. It is evident that the first dispersion enters the bulk longitudinal dispersion curve $\epsilon_l(q,\omega) = 0$ in the asymptotic limit. However, the second dispersion Eq. (3b) curve has a peculiar behavior in that it rises to a maximum, then in the $q \to \infty$ limit falls back to the local surface polariton dispersion $\epsilon(\omega) = -1$.[9] Parenthetically, we note that for a Lindhard transverse dielectric function $\epsilon_t^{\text{Lind}}(q,\omega) \to \epsilon(\omega)$ as $q \to \infty$, the local dielectric function.[19] Hence for large q_x Eq. (4b) yields $\epsilon(\omega) = -1$ identically, and the above statement is apparently not restricted to the simple hydrodynamic response. It is necessary to emphasize the origin of this behavior. Analysis of the fields for the two ABC's has shown that the RM ABC leads to a surface δ-function charge density exactly as in the local case.[18] However, the longitudinal fields of the FK formalism distributes this charge density totally into the solid and the surface charge density is zero. This fundamental difference in the two ABC's is dramatically illustrated in the above dispersion relations. It is the large-q behavior which determines the fields near the surface and the associated charge densities; therefore the fact that in the $q \to \infty$ limit the local and the RM dispersions are identical is a consequence of transversality of the ABC in that it does not allow coupling to longitudi-

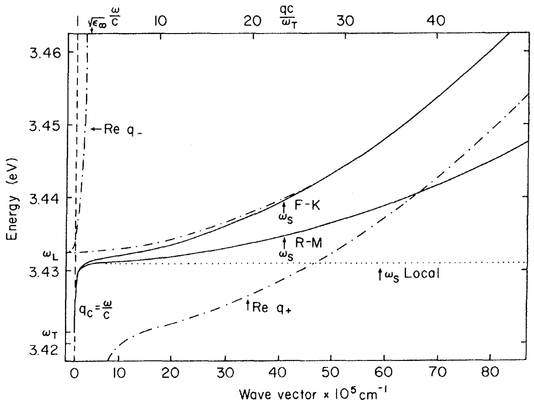

FIG. 1. Surface-exciton dispersion relations (solid lines) in ZnO (Ref. 20) for Fuchs-Kliewer (ω_s^{FK}) and Rimbey-Mahan (ω_s^{RM}) symmetry conditions; dotted line is the local (ω_s) surface dispersion, the dot-dash curves are the bulk polariton dispersions.

TABLE I. Complex-q solutions to surface-exciton dispersion with real ω for two ABC's and selected damping in ZnO($\omega_T = 3.4215$).

ω (eV)	FK $\frac{qc}{\omega_T}$	RM $\frac{qc}{\omega_T}$	τ^{-1} (meV)
3.4250	$1.035 + 0.96i \times 10^{-3}$	$1.036 + 0.26i \times 10^{-1}$	0
	$1.036 + 0.5i \times 10^{-2}$	$1.035 + 0.3i \times 10^{-1}$	0.5
	$1.032 + 0.2i \times 10^{-1}$	$1.025 + 0.43i \times 10^{-1}$	2.45

nal modes.[14,17,18]

The two dispersion curves are mapped over a limited range of wave vectors in Fig. 1. The parameters associated with the $C1$ exciton of ZnO have been utilized and the approximations $\beta_l = \beta_t$ and $\tau \to \infty$ have been made in the numerical evaluation. A much more drastic assumption is implicit in using ZnO (or any uniaxial crystal) in the above formalism. The fields yielding the respecitve surface impedances are rigorously true only for isotropic-homogeneous semi-infinite media. The dielectric functions for these uniaxial crystals are anisotropic; nevertheless, Lagois and Fischer[20] have demonstrated that the numerical errors are insignificant for calculations on ZnO and the theory need not be modified to include the anisotropy.

The explicit effect of spatial dispersion on the damping of the surface modes is given by the imaginary part of the complex wave vector or alternatively the complex frequency. This is also indicative of the longitudinal (FK) versus transverse (RM) nature of the coupling to the bulk modes. In Tables I and II, we list several values for complex q and ω, respectively, for various damping frequencies which are determined from attenuated-total-reflection spectra.[20] The first observation is that the value of τ does not substantially alter the real value of ω nor the splitting between the two dispersion curves. Damping determines the width and shape of the reflectivity curves and has a secondary effect on peak shifts. It must be kept in mind that a major problem in elucidating spatial dispersion effects in the past has been the ability to fit reflectivity spectra to numerous ABC's through a suitable choice of damping parameter.[13,14,21] To the contrary, surface exciton dispersion curves should be more definitive in this respect.

A second observation is that the $P_x(0^+) = 0$ ABC intrinsically yields a more strongly spatially and temporarily damped surface mode than does the $(\partial P_x/\partial z)(0^+) = 0$ ABC. This is immediately seen from the $\tau = \infty$ values for Imq or Imω, which indicates the strength of the coupling to the bulk mode and the associated attenuation (either spatial or temporal) do to spatial dispersion alone. The FK ABC is particularly sensitive to values of the damping parameter as is witnessed by the orders of magnitude increase in Imω^{FK} on incorporating a finite τ, whereas Imω^{RM} is not. Indeed, a finite τ brings the two imaginary parts (q or ω) to within comparable values corroborating the above com-

TABLE II. Complex-ω solutions to surface exciton dispersion with real q for two ABC's and selected damping in ZnO($\omega_T = 3.4215$).

qc/ω_T	FK ω_s (eV)	RM ω_s (eV)	$1/\tau$ (meV)
2.0	$3.4310 - 0.36i \times 10^{-6}$	$3.4307 - 0.9i \times 10^{-3}$	0
	$3.4310 - 0.25i \times 10^{-3}$	$3.4307 - 0.12i \times 10^{-2}$	0.5
	$3.4310 - 0.12i \times 10^{-2}$	$3.4307 - 0.21i \times 10^{-2}$	2.45
10.27	$3.4333 - 0.15i \times 10^{-7}$	$3.4318 - 0.36i \times 10^{-2}$	0
	$3.4333 - 0.25i \times 10^{-3}$	$3.43176 - 0.38i \times 10^{-2}$	0.5
	$3.4333 - 0.12i \times 10^{-2}$	$3.4317 - 0.48i \times 10^{-2}$	2.45

ments on the reflectivity.

Finally in a strict sense the Rimbey-Mahan formalism was originally constructed for Frenkel-exciton systems such as those found in molecular crystals.[14,22] The above dielectric function is not appropriate for such a discussion. A transverse dielectric function developed by Philpott[23] has yielded in our opinion a more realistic dispersion relation. These results will be reported elsewhere.

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