Local-field effects, x-ray diffraction, and the possibility of observing the optical Borrmann effect: Solutions to Maxwell's equations in perfect crystals

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The electromagnetic normal-mode solutions to Maxwell's equations in perfect crystals are investigated including local-field effects by means of the dielectric-response matrix. The dynamical theory of x-ray diffraction is seen to be a special case thereof. At optical frequencies, a perturbation-theory expansion in q, the reduced wave vector, is solved and used to investigate the possibility that a microscopically varying component of the normal mode, $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$ ($\vec{K}$ is a reciprocal-lattice vector), can transmit into the vacuum. The optimal effciency for this process is estimated to be 2.6×10^{-10} for $\hbar\omega = 1.5$ eV in diamond. However, this process may be affected by the intrinsic irregularities, on an atomic scale, of the crystal-vacuum interface.

I. INTRODUCTION

Traditionally, the electromagnetic response of solids under the action of applied fields of frequencies less than (say) 30 eV has been discussed in terms of the wave-vector- and frequency-dependent dielectric tensor $\overleftrightarrow{\epsilon}(\vec{q},\omega)$ under the assumption that the medium is homogeneous.[1] As a classical counter example, an electric field applied to a crystal of well-localized atoms induces a point dipole at each site; the resulting total electric field varies strongly on an atomic scale though the applied field does not. In order to retrieve the isotropic Clausius-Mossotti relation between the macroscopic dielectric constant and the (microscopic) atomic polarizability, one must explicitly include, in some fashion, the aforementioned small-scale fluctuations of the electric field.[2] It is experimentally known that the Clausius-Mossotti relation is satisfied in certain solids.[3]

Effects of this nature can be accounted for by means of the dielectric-response matrix $\epsilon(Q,Q')$. Generally, I consider any situation in which one takes into account the microscopic variation of the field and its response to be a "local-field effect." This article is devoted to normal-mode solutions to Maxwell's equations in crystals, explicitly taking into account the spatial inhomogeneity of the electronic charge. In Sec. II the problem is defined, the equation of motion derived, and a few general results presented. From this point of view, the dynamical theory of x-ray diffraction is seen to be a special case in Sec. III. I have presented a perturbation theory solution, valid at optical frequencies, in Sec. IV and have presented a possible (though difficult) experiment to directly observe the microscopically varying electric fields (those Fourier components of the normal mode whose wavelengths are on the order of an atomic diameter). Section V summarizes this paper.

II. MAXWELL'S EQUATIONS IN A NONMAGNETIC PERFECT CRYSTAL

A. Microscopic Maxwell's equations

Maxwell's equations can always be written as if in a vacuum,

$$\nabla\cdot\vec{\mathcal{E}} = 4\pi\rho_{\text{tot}}, \tag{2.1a}$$

$$\nabla\cdot\vec{\mathcal{B}} = 0, \tag{2.1b}$$

$$\nabla\times\vec{\mathcal{E}} = -\frac{\partial\vec{\mathcal{B}}}{\partial t}, \tag{2.1c}$$

$$c^2\nabla\times\vec{\mathcal{B}} = 4\pi\vec{J}_{\text{tot}} + \frac{\partial\vec{E}}{\partial t}, \tag{2.1d}$$

where ρ_{tot} and $\vec{J}_{\text{tot}}$ (in a crystal) include contributions from $\sim10^{24}$ particles and their spins. I wish to consider crystals externally perturbed, e.g., by monochromatic light, and so it is convenient to define $\vec{E} = \vec{\mathcal{E}}(\text{perturbed}) - \vec{\mathcal{E}}(\text{unperturbed})$ and similarly for $\vec{B}$;

$$\nabla\cdot\vec{E} = 4\pi(\rho_{\text{ex}}+\rho_{\text{ind}}), \tag{2.2a}$$

$$\nabla\cdot\vec{B} = 0, \tag{2.2b}$$

$$\nabla\times\vec{E} = -\frac{\partial\vec{B}}{\partial t}, \tag{2.2c}$$

$$c^2\nabla\times\vec{B} = 4\pi(\vec{J}_{\text{ex}}+\vec{J}_{\text{ind}}) + \frac{\partial\vec{\mathcal{E}}}{\partial t}. \tag{2.2d}$$

In these equations the conservation of external and induced charge densities can be assumed separately. It is convenient to define

$$\vec{P}(\vec{r},t) = \int^t \vec{J}_{\text{ind}}(\vec{r},t')\,dt', \tag{2.3a}$$

$$\vec{D}=\vec{E}+4\pi\vec{P}, \tag{2.3b}$$

so that Maxwell's equations reduce to their usual form

$$\nabla\cdot\vec{D}=4\pi\rho_{ex}, \tag{2.4a}$$

$$\nabla\cdot\vec{B}=0, \tag{2.4b}$$

$$\nabla\times\vec{E}=-\frac{\partial\vec{B}}{\partial t}, \tag{2.4c}$$

$$c^2\nabla\times\vec{B}=4\pi\vec{J}_{ex}+\frac{\partial\vec{D}}{\partial t}, \tag{2.4d}$$

with the significant difference that Eqs. (2.4) refer to difference fields which need not at all be smoothly varying on an atomic scale even if ρ_{ex} and $\vec{J}_{ex}$ are zero; the usual procedure is to consider the space-averaged fields (over a unit cell, for instance) in order to get equations involving smoothly varying (macroscopic) quantities, but this is not at all necessary and, from the point of view of microscopic response, undesirable for a patently inhomogeneous collection of atoms.

As I will not be considering contributions to $\vec{J}$ of the form $\nabla\times\vec{M}$, the boundary conditions at a mathematical plane separation between two different media are the continuity of $\vec{B}$, normal $\vec{D}$, and tangential $\vec{E}$, because all quantities on the right-hand sides of Eqs. (2.4) are finite. Boundary conditions will be discussed in more detail in Sec. IV. If one medium is the vacuum then $\vec{E}=\vec{\mathcal{E}}$(perturbed) unless the other is a ferroelectric.

B. Dielectric response

The most general form of linear dielectric response can be summarized[4] as

$$\vec{D}(\vec{r},t)=\int\int\vec{\epsilon}(\vec{r},\vec{r}\,';t-t')\cdot\vec{E}(\vec{r}\,',t')d^3r'\,dt'. \tag{2.5}$$

In a crystal, translational symmetry requires $\vec{\epsilon}(\vec{r}+\vec{R}_l,\vec{r}\,'+\vec{R}_l)=\vec{\epsilon}(\vec{r},\vec{r}\,')$ so that the Fourier transform $\vec{\epsilon}(\vec{Q},\vec{Q}';\omega)$ is nonzero only when $\vec{Q}-\vec{Q}'$ is a reciprocal-lattice vector. I will use the notation $\vec{\epsilon}(\vec{Q},\vec{Q}';\omega)=\vec{\epsilon}(\vec{q}+\vec{K},\vec{q}+\vec{G};\omega)=\vec{\epsilon}_{K,G}(\vec{q},\omega)$, where $\vec{q}$ can be taken in the first Brillouin zone and $\vec{K}$, $\vec{G}$ are reciprocal-lattice vectors, interchangeably. Fourier transforming Eq. (2.5) gives

$$\vec{D}(\vec{q}+\vec{K},\omega)=\sum_G\vec{\epsilon}_{K,G}(\vec{q},\omega)\cdot\vec{E}(\vec{q}+\vec{G},\omega). \tag{2.6}$$

I have defined $\vec{\epsilon}_{K,G}$ in terms of the fields rather than the potentials so that all elements are bounded for finite ω for all values of $\vec{q}$.[5]

The symmetry of the crystal is reflected in $\vec{\epsilon}_{K,G}$ as follows: If $\{\alpha|\tau\}$ is an element of the space group of the crystal, and if one chooses $\vec{E}(\alpha\vec{r}\,'+\vec{\tau})=\alpha\vec{E}(\vec{r}\,')$, then it automatically follows that $D(\alpha r+\tau)=\alpha D(r)$, which in turn implies [α and $\epsilon(Q,Q')$ are tensors]

$$\alpha^{-1}\cdot\epsilon(\alpha\vec{r}+\vec{\tau},\alpha\vec{r}\,'+\vec{\tau})\cdot\alpha=\epsilon(\vec{r},\vec{r}\,'), \tag{2.7a}$$

$$\alpha^{-1}\cdot\epsilon(\alpha(\vec{q}+\vec{K}),\alpha(\vec{q}+\vec{G}))\cdot\alpha e^{i\alpha(\vec{K}-\vec{G})\cdot\vec{\tau}}=\epsilon(\vec{q}+\vec{K},\vec{q}+\vec{G}). \tag{2.7b}$$

I am looking for normal-mode solutions to Maxwell's equations in a crystal, i.e., nontrivial solutions to Eqs. (2.4) when ρ_{ex} and $\vec{J}_{ex}$ are zero. Taking the Fourier transform of Eqs. (2.4) and using Eq. (2.6) I find[6]

$$\frac{\omega^2}{c^2}\vec{D}(\vec{r},\omega)=\frac{\omega^2}{c^2}\int\vec{\epsilon}(\vec{r},\vec{r}\,';\omega)\cdot\vec{E}(\vec{r}\,',\omega)\,d^3\vec{r}\,'=\nabla\times\nabla\times\vec{E}(\vec{r},\omega), \tag{2.8a}$$

$$\frac{\omega^2}{c^2}\vec{D}_K(\vec{q},\omega)=\frac{\omega^2}{c^2}\sum_G\vec{\epsilon}_{K,G}(\vec{q},\omega)\cdot\vec{E}_G(\vec{q},\omega)=-(\vec{q}+\vec{K})\times[(\vec{q}+\vec{K})\times\vec{E}_K(\vec{q},\omega)], \tag{2.8b}$$

a kind of eigenvector-$\{\vec{E}_G\}$–eigenvalue-$\{\omega_n(q)\}$ problem whose band structure can always be plotted in the first Brillouin zone in the absence of absorption. Note that Eq. (2.7b) implies $\omega_n(q)$ has the point symmetry of the crystal [$\omega_n(\alpha\vec{q})=\omega_n(\vec{q})$]. For any normal mode $|\vec{q},n\rangle$, the energy flow is normal to the surface of constant ω passing through $\omega_n(\vec{q})$.[7]

Ordinarily, one introduces the fiction that the crystal is homogeneous [i.e., $\epsilon(\vec{r},\vec{r}\,')=\epsilon(\vec{r}-\vec{r}\,')$] so that

$$\begin{aligned}\vec{\epsilon}_{K,G}(\vec{q},\omega)&=\vec{\epsilon}(\vec{q}+\vec{K},\omega)\delta_{\vec{K},\vec{G}}\\&=\{\epsilon_{\parallel}(\vec{q}+\vec{K},\omega)\hat{e}(\vec{q}+\vec{K})\hat{e}(\vec{q}+\vec{K})\\&\quad+\epsilon_{\perp}(\vec{q}+\vec{K},\omega)[\vec{I}-\hat{e}(\vec{q}+\vec{K})\hat{e}(\vec{q}+\vec{K})]\}\delta_{\vec{K},\vec{G}}\end{aligned} \tag{2.9}$$

for cubic crystals by Eqs. (2.7). [$\hat{e}(\vec{Q})$ is simply $\vec{Q}/|\vec{Q}|$.] Equation (2.8b) immediately decouples. The $\vec{K}=\vec{0}$ equation gives two kinds of solutions whose dispersion relations are as follows:

transverse (photon),

$$\vec{E}(\vec{q})\perp\vec{q}:\ \omega^2\epsilon_{\perp}(q,\omega)=c^2q^2; \tag{2.10a}$$

longitudinal (plasmon),

$$\vec{E}(\vec{q})\parallel\vec{q}:\ \epsilon_{\parallel}(q,\omega(q))=0. \tag{2.10b}$$

In a real crystal, the normal-mode solutions to Eqs. (2.8) are more complicated than a single plane wave but can be written in the Bloch form

$$\vec{E}_q(\vec{r}, t) = \sum_{\vec{K}} \vec{E}_{\vec{K}}(\vec{q}, \omega_n(\vec{q})) e^{i[(\vec{q}+\vec{K})\cdot\vec{r} - \omega_n(\vec{q})t]}, \qquad (2.11)$$

where n is a band index. The solutions can be classified group theoretically by observing that if $\{\alpha|\vec{\tau}\}$ is a member of the space group of the crystal and if $\vec{E}(\vec{r},\omega)$ is any solution to Eq. (2.8a), then $\alpha^{-1}\vec{E}(\alpha\vec{r}+\vec{\tau},\omega)$ is also a solution with the same frequency. The set of functions $\{\alpha^{-1}\vec{E}(\alpha\vec{r}+\vec{\tau},\omega)\}$ forms a basic for an irreducible representation[8] of the space group of the crystal. If the solutions are of the form (2.11), then the set $\{\alpha^{-1}\vec{E}_q(\alpha\vec{r}+\vec{\tau},\omega)\}$, where $\alpha\vec{q}=\vec{q}+\vec{K}$, forms a basic for an irreducible representation of the group of the wave vector, $\vec{q}$. Note that in this case

$$\alpha^{-1}\vec{E}_q(\alpha\vec{r}+\vec{\tau}) = \sum_{\vec{K}} [\alpha^{-1}\vec{E}_{\alpha\vec{K}}(\vec{q}) e^{i(\vec{q}+\alpha\vec{K})\cdot\vec{\tau}}] e^{i(\vec{q}+\vec{K})\cdot\vec{r}}, \qquad (2.12)$$

where the time dependence is $e^{-i\omega_n(\vec{q})t}$. In a cubic crystal there are solutions of Δ_1, Λ_1, and Σ_1 symmetry which are completely invariant under all the operations of the group of $\vec{q}$. This automatically implies that $\vec{E}_0(\vec{q})$ has no transverse component, i.e., $\vec{E}_0(\vec{q})\parallel\vec{q}$. A plasmon in a real crystal may therefore be rigorously defined as the lowest-frequency solution of Δ_1, Λ_1, or Σ_1 symmetry. Similarly, inspection of the character tables shows that the twofold-degenerate solutions Δ_5, Λ_3 have purely transverse $K=0$ components, $\vec{E}_0(\vec{q})\perp\vec{q}$, and correspond to photonlike solutions. The lowest-frequency solutions of Λ_3, Δ_5 symmetry will be discussed in detail in Sec. IV. Note that there is a double degeneracy only along Λ and Δ even for cubic crystals with an inversion center; the splitting between the Σ_3 and Σ_4 modes has been observed, in Si, by Pastrnak and Vedam.[9] Solutions of $\Lambda_2, \Delta_1', \Delta_2, \Delta_2', \Sigma_2$ symmetry are such that $\vec{E}_0(\vec{q})\equiv\vec{0}$ and these solutions have no "classical" analog; they arise from short-wavelength solutions, $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$, folded back into the first Brillouin zone. For $\vec{K}$ arbitrary, nothing in general can be said about the direction of $\vec{E}_K(\vec{q})$ for any solution of any symmetry. Note that in a triclinic crystal there is no distinction between photons and plasmons from this point of view.

One might think that the microscopically varying fields in Eq. (2.11) are unimportant (the off-diagonal $\{\overleftrightarrow{\epsilon}_{K,G}\}$ are small and only $\overleftrightarrow{\epsilon}_{0,0}$ need be retained) for optical properties of most crystals ($|q|\ll|K|$). This is not so; it has been established[10,11] that inclusion of off-diagonal response in calculating the macroscopic dielectric constant of diamond can change the calculated values of the static dielectric constant by 10% and can shift peaks in $\epsilon_2(\omega)$ by 1–2 eV. To make the approximation $D_0=\epsilon_{0,0}E_0$ is equivalent to the Drude approximation that the polarizing field (the local field) is in fact equal to the macroscopic average electric field.[12] The purpose of this paper is to investigate the true nature of the normal modes with an eye to the possible observation of the short-wavelength components $\vec{E}_{\vec{K}}e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$. Since the cumulative effect on the macroscopic dielectric constant is large (as will be discussed, $E_K\sim 0.1E_0$), one might expect these fields to be directly observable in some fashion.

III. DYNAMICAL THEORY OF X-RAY DIFFRACTION

The first quantum-mechanical formulas for $\epsilon_{K,G}$ were derived by Adler[12] and Wiser,[12] essentially by an extension of the random-phase approximation (ERPA), in an attempt to provide a quantum-mechanical extension of the classical Clausius-Mossotti (or Lorentz-Lorenz) relations at optical frequencies. (See Ref. 13 for a discussion of this point.) It was recently shown[13,14] that the limiting form of the dielectric-matrix tensor, within the ERPA of Adler and Wiser, is

$$\lim_{\omega\to\infty} \overleftrightarrow{\epsilon}_{K,G}(\vec{q},\omega) = \left[\delta_{K,G} - \left(\frac{\omega_p}{\omega}\right)^2 f(\vec{K}-\vec{G})\right]\overleftrightarrow{I},$$

$$\omega_p^2 = \frac{4\pi ne^2}{m}, \qquad (3.1)$$

where n is the average number density of electrons and $f(\vec{Q})$ is the Fourier transform of the density of electrons normalized to $f(0)=1$, although this result can be shown to be independent of the ERPA.[15] Equation (3.1) had also historically been derived[16] by classical arguments under the assumption that at high frequencies one is in the classical regime; not surprisingly, it is a quantum-mechanical result also.

Assuming this approximation is valid in the x-ray region ($\hbar\omega>1000$ eV, $\hbar\omega_p<30$ eV) one finds

$$\frac{\omega^2}{c^2}\sum_{\vec{G}}\left[\delta_{\vec{K},\vec{G}} - \left(\frac{\omega_p}{\omega}\right)^2 f(\vec{K}-\vec{G})\right]\vec{E}_G = -(\vec{q}+\vec{K})\times[(\vec{q}+\vec{K})\times\vec{E}_K], \qquad (3.2)$$

which is exactly the governing equation (neglecting absorption) for the dynamical, as opposed to kinematical, theory of x-ray diffraction, a theory previously derived from general classical-mechanics arguments.[16,17] Of course, all the results of that theory (Pendellösung, Borrmann effect) are derivable from Eq. (3.2). It is clear that at all frequencies for which $\overleftrightarrow{\epsilon}_{K,G}$ is nondiagonal, the normal modes contain fields which vary as $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$ in addition to $e^{i\vec{q}\cdot\vec{r}}$, although only if the Bragg condition ($|\vec{q}|\approx|\vec{q}+\vec{K}|$ at a zone boundary) is nearly satisfied will any two fields be of comparable size. [See, however, Eq. (4.20) and following.]

In short, Eq. (3.2) represents the first derivation of x-ray diffraction from an explicit quantum formula for dielectric response, a formula that had been derived with an eye to the classical local-field effect. X-ray diffraction is, therefore, seen to be a specific example of the more general problem of the "local-field effect," Eqs. (2.8); to neglect the off-diagonal response of the system in this frequency regime is equivalent to the neglect of x-ray diffraction.

IV. NORMAL MODES AT OPTICAL FREQUENCIES

A. Perturbation solution in the long-wavelength limit

Of particular interest is the solution to Eq. (2.8b) when ω is of the order of optical frequencies ($\hbar\omega < 30$ eV at the most) so that $|\vec{q}| \ll |\vec{K}|$. The macroscopic average of the fields in Eq. (2.10) over a unit cell is simply[12]

$$\langle \vec{E}(\vec{r}, t)\rangle = \vec{E}_0 e^{i(\vec{q}\cdot\vec{r}-\omega t)} \tag{4.1}$$

and the macroscopic dielectric constant is then given by D_0/E_0. Previous authors[12] have implicitly argued as follows, for cubic crystals: (i) All fields and responses are longitudinal, $\vec{E}_K = E_K \hat{e}(\vec{q}+\vec{K})$, $\vec{D}_K = D_K \hat{e}(\vec{q}+\vec{K})$, which implies

$$D_K = \sum_G (\epsilon_\parallel)_{K,G} E_G , \tag{4.2a}$$

where

$$(\epsilon_\parallel)_{K,G} = \hat{e}(\vec{q}+\vec{K})\cdot \vec{\epsilon}_{K,G}\cdot \hat{e}(\vec{q}+\vec{G}) . \tag{4.2b}$$

(ii) For a single plane-wave component of $\rho_{\text{ext}} = \nabla\cdot\vec{D} \sim e^{i\vec{q}\cdot\vec{r}}$, $D_K = D_0 \delta_{K,0}$. Substituting in Eq. (4.2a) one finds

$$\frac{D_0}{E_0} = \frac{1}{(\epsilon_\parallel{}^{-1})_{K=G=0}} = \epsilon_M(\omega) \tag{4.3}$$

for the macroscopic longitudinal dielectric constant in the limit $|\vec{q}| \to 0$. (iii) The macroscopic longitudinal dielectric constant, as determined by (4.3), is equal to the macroscopic transverse dielectric constant, as measured experimentally (e.g., reflectivity) for $|q| \to 0$ in cubic crystals.

It is clear that none of the above assumptions is obvious nor that they even make sense; $\{\vec{\epsilon}_{K,G}\}$ do not in general possess symmetry beyond Eq. (2.7b) so that longitudinal components of $\vec{E}(\vec{g}+\vec{G})$ will induce transverse components of $\vec{D}(\vec{q}+\vec{K})$ and *vice versa* even for $q \simeq 0$, so that each $\vec{E}_K$ has, in general, both longitudinal and transverse components with respect to $\vec{q}+\vec{K}$. Adler[12] explicitly showed this to be the case for $\vec{\epsilon}_{K,K}(0,\omega)$. Even in the homogeneous limit where $\vec{\epsilon}_{K,G} = \vec{\epsilon}(\vec{q}+\vec{K})\delta_{K,G}$, the transverse modes $\vec{E}_0(\vec{q}) \perp \vec{q}$ cannot, of course, be derived from a scalar potential. It is only because $\vec{\epsilon}(0,0;\omega) = \epsilon(\omega)\vec{I}$ [from (2.7b)] that $\epsilon_\perp(q=0,\omega) = \epsilon_\parallel(q=0,\omega)$, and so the dispersion relation for transverse modes is derivable from the longitudinal dielectric function in the long-wavelength limit for homogeneous, isotropic media. Nonetheless, Eq. (4.3) will be seen to be the correct result for cubic crystals, a result which reproduces the Clausius-Mossotti relation between the macroscopic dielectric constant and the atomic polarizability in the appropriate limit.[18]

Are there solutions to Eq. (2.8) of the form

$$\epsilon_M(\omega)\,\omega(q)^2 = c^2 q^2 \tag{4.4}$$

analogous to Eq. (2.10a)? It is necessary, first, to make two transformations. Equation (2.8b) can be written

$$\omega^2 \vec{D}_K = -c^2(\vec{q}+\vec{K})\times\left((\vec{q}+\vec{K})\times\sum_G \vec{\epsilon}^{\,-1}_{K,G}\cdot\vec{D}_G\right), \tag{4.5}$$

where $\sum_K \vec{\epsilon}^{\,-1}_{G,K}\cdot\vec{\epsilon}_{K,L} = \delta_{G,L}\vec{I}$. The nonexistence of $\vec{\epsilon}^{\,-1}_{K,G}$ presumably corresponds to longitudinal plasmons and will not be considered in this paper.[19] Since $\vec{D}_K$ is transverse, let $\hat{e}(K_\alpha)$, $\alpha = 1,2,3$, be mutually orthogonal unit vectors such that $\hat{e}(K_3) = (\vec{q}+\vec{K})/|\vec{q}+\vec{K}|$. Then

$$\vec{D}_K = \sum_{\alpha=1}^{2} |\vec{q}+\vec{K}|\, V_K^\alpha \hat{e}(K_\alpha) \tag{4.6}$$

and

$$\omega^2 V_K^\alpha = c^2 \sum_G \sum_{\alpha=1}^{2}{}' |\vec{q}+\vec{K}|\, T^{\alpha;\beta}_{K;G} |\vec{q}+\vec{G}|\, V_G^\beta , \tag{4.7a}$$

where

$$T^{\alpha;\beta}_{K;G}(q,\omega) = \hat{e}(K_\alpha)\cdot\vec{\epsilon}^{\,-1}_{K,G}\cdot\hat{e}(G_\beta) . \tag{4.7b}$$

The problem has been reduced from $3^\infty \times 3^\infty$ to $2^\infty \times 2^\infty$ simply by observing that $\vec{D}_K$ is transverse. (This transformation is also useful for treating homogeneous, but anisotropic, media.[20]) If $q=0$, there are solutions[21] $\omega = 0$, if $V_K^\alpha = \delta_{K,0}\chi_\alpha$. I wish to examine the long-wavelength ($|q| \ll |K|$) solution to (4.7a) by means of a perturbation expansion in $q = |\vec{q}|$, as is done in the case of phonon dispersion curves[22]:

$$V_K^\alpha = \delta_{K,0}\chi_\alpha + qA_K^\alpha + O(q^2) , \tag{4.8a}$$

$$\frac{\omega^2}{c^2} = vq + \frac{q^2}{\epsilon_M} + O(q^3) . \tag{4.8b}$$

The zeroth-order equation is automatically satisfied, the first-order equation gives $v = 0$ and

$$A_K^\alpha = -\sum_G{}' \sum_{\beta,\gamma=1}^{2} |G|^{-1}(F^{-1})^{\alpha;\beta}_{K;G}\, T^{\beta;\gamma}_{G;0}\chi_\gamma , \tag{4.9}$$

where $F=T$ restricted to $K\neq 0\neq G$ and the right-hand side of Eq. (4.9) is evaluated at $|\vec{q}|=0$. The second-order equation determines the proportionality constant $\epsilon_M(\omega)$,

$$\frac{1}{\epsilon_M(\omega)}\chi_\alpha=\sum_\beta\left((T)^{\alpha,\beta}_{0,0}-\sum_{\substack{G,K\\ \gamma,\xi}}(T)^{\alpha,\gamma}_{0,G}(F^{-1})^{\gamma,\xi}_{G,K}T^{\xi,\beta}_{K,0}\right)\chi_\beta\,, \tag{4.10}$$

which, after some manipulation with the partitioning theorem,[23] gives the dispersion relation in Eq. (4.4) or (4.8b) via the generalized Fresnel equation[20]

$$\sum_{\beta=1}^{2}[(T^{-1})^{\alpha,\beta}_{0,0}-\epsilon_M(\omega)\delta_{\alpha,\beta}]\chi_\beta=0; \tag{4.11}$$

i.e., given $\vec{\epsilon}_{K,G}(q=0,\omega)$, invert it, pick out the transverse components via Eq. (4.7b), and invert the (reduced) matrix. $(T^{-1})^{\alpha,\beta}_{0,0}$ is the 2×2 submatrix so obtained when $K=G=0$ (it depends on the direction of $\vec{q}$) and its eigenvalues are $\epsilon_M(\omega)$. In a cubic crystal, the only quadratic dispersion surface compatible with symmetry is spherical, so that $(T^{-1})^{\alpha,\beta}_{0,0}$ is diagonal and $(T^{-1})^{1,1}_{0,0}=(T^{-1})^{2,2}_{0,0}=\epsilon_M(\omega)$ independent of $\hat{e}(\vec{q})$. The dispersion curves in the limit $q\to 0$ are then

$$\omega^2\epsilon_M(\omega)=c^2q^2 \tag{4.12}$$

as in Eq. (2.10a). $\epsilon_M(\omega)$ so determined plays the role of the dielectric constant and, in fact, to lowest order, $\vec{E}_0\parallel\vec{D}_0$ (cubic only), so that by Eq. (2.8b)

$$D_0/E_0=\epsilon_M(\omega)\,. \tag{4.13}$$

That $\epsilon_M(\omega)$ [i.e., $(T^{-1})^{i,i}_{0,0}$] is the same quantity as given by Eq. (4.3), for cubic crystals, can be seen as follows. $\vec{D}_K(q)$ is perpendicular to $\vec{q}+\vec{K}$ for each K. Define

$$\vec{q}_\perp=|\vec{q}|\,\hat{e}(\vec{D}_0)\,. \tag{4.14}$$

Each D_K is first order or higher in $|q|$ [see (4.6) and (4.8a)]. For $K\neq 0$, the first-order component of $\vec{E}_K(q)$ is parallel to $\vec{K}$ because

$$(\omega^2/c^2)\,\vec{D}_K=(\vec{q}+\vec{K})^2\,\vec{E}^{\perp}_K\,, \tag{4.15}$$

and $E^{\perp}_K$ is at least third order in $|\vec{q}|$. Along Δ or Λ, $\vec{E}_0(\vec{q})\perp\vec{q}$ to all orders in $|\vec{q}|$ [paragraph following (2.12)] so that the $|\vec{q}|\to 0$ limit may be summarized as

$$\lim_{q\to 0}\{\vec{E}_K(q)=E_K\hat{e}(\vec{q}_\perp+\vec{K})\}\,. \tag{4.16}$$

Equation (2.6) becomes, in this limit,

$$\vec{D}_K=\sum_G\vec{\epsilon}_{K,G}(0,\omega)\cdot\hat{e}(\vec{q}_\perp+\vec{G})E_G\,. \tag{4.17}$$

Taking the dot product of (4.17) with $\hat{e}(\vec{q}_\perp+\vec{K})$, I obtain

$$D_0\delta_{K,0}=\sum_G\hat{e}(\vec{q}_\perp+\vec{K})\cdot\vec{\epsilon}_{K,G}(0,\omega)\cdot\hat{e}(\vec{q}_\perp+\vec{G})E_G\,, \tag{4.18}$$

which is exactly of the form (4.2) ff. Equation (4.3) (the Adler-Wiser result) automatically follows with $\vec{q}_\perp$ taking the place of $\vec{q}$, i.e.,

$$\epsilon_M(\omega)=\lim_{q\to 0}\frac{1}{[\epsilon_\parallel(q_\perp)]^{-1}_{0,0}}\,; \tag{4.19}$$

as mentioned above, $\epsilon_M(\omega)$ is independent of the direction of $\vec{q}$. Equation (4.19) reflects the fact that in the near zone[24] of an oscillating set of charges, the fields are given by their static values multiplied by $e^{-i\omega t}$.

The lowest-order components of $\vec{E}$ and $\vec{D}$ have all been determined. Each $\vec{D}_K(\vec{q})$ is orthogonal to $\vec{q}+\vec{K}$; the first-order terms are given by Eqs. (4.6), (4.8a), and (4.9) in terms of $\vec{D}_0$. The longitudinal component of $\vec{E}_K$ is first order in $|q|$ and can be obtained from Eq. (4.18) (for cubic crystals),

$$E^{\parallel}_K=(\epsilon^{-1}_\parallel)_{K,0}D_0=\frac{(\epsilon^{-1}_\parallel)_{K,0}}{(\epsilon^{-1}_\parallel)_{0,0}}\,E_0\,, \tag{4.20}$$

as has been reported[10] but not rigorously proven. In diamond, typical values[10,13] of $E^{\parallel}_K$ are (0.1–0.2)E_0, which are by no means negligible.

For a crystal with symmetry less than cubic, the eigenmodes must be determined by solving Eqs. (4.6), (4.8a), (4.9), and (4.11). Since the size of the off-diagonal response is, roughly speaking, related to the degree of localization of the valence charge,[13] it is desirable to have a Fresnel equation for anisotropic media, whose polarizable valence charge can be more highly localized than in cubic materials; e.g., trigonal selenium's "lone pair" valence band makes the dominant contribution to the polarization.[3]

In the presence of absorption (at optical frequencies) it is permissible to put $q=0$, ω real when calculating $(T^{-1})^{\alpha,\beta}_{0,0}$ and solve for the complex $\vec{q}$ in Eq. (4.12) (so that the mode decays spatially) rather than attribute a complex ω to a lifetime effect with $\vec{q}$ real (so that the mode decays temporally). In either case the fields in adjacent unit cells are nearly identical ($|q|\ll|K|$) and $\epsilon_{K,G}(0,\omega)$ can be assumed.

B. Boundary conditions

Consider an interface between a vacuum and a perfect crystal which, for convenience, I will take to be a perfect mathematical plane. Since all quantities on the right-hand sides of Eqs. (2.4) are finite (nonmagnetic crystal), the boundary conditions are the usual B, normal D, and tangential E, continuous. Consider an incident monochromatic beam from the vacuum impinging on the surface. The boundary conditions can be satisfied by matching onto the primary wave $e^{i\vec{q}\cdot\vec{r}}$ inside the crystal and a single reflected plane wave outside the crystal. The existence of boundary conditions independent of position and time means that the tangential components of the three wave vectors must be equal; the normal components are determined by requiring $c^2q^2=\omega^2\epsilon_M$. In this way Snell's law is rederived with $n=(\epsilon_M)^{1/2}$ playing the role of the complex index of refraction. Moreover, the intensities of the reflected and refracted beams are given by the usual formulas[24] in terms of the same $n(\omega)$. What happens to the microscopic fields $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$? At the interface the situation is schematized in Fig. 1; the direction of $\vec{q}+\vec{K}$ may be either into or out of the physical surface. The mere existence of boundary conditions at the surface, independent of position, implies that the plane-wave component $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$ couples to a single plane wave transmitted into the vacuum and a single plane-wave component (arbitrarily taken to be the primary wave of another normal mode) reflected back into the crystal, such that the tangential components of all three wave vectors are equal. The normal components are determined by the dispersion relations indicated in Fig. 1. Note that the mode $|q_x\rangle$ has secondary waves which induce, at the surface, yet more normal modes in the crystal and in the vacuum. In general, $\vec{q}+\vec{K}$ is not normal to the surface; since $|\vec{K}|\gg|\vec{q}|$ its tangential component is much larger than ω/c or $n\omega/c$ so that the normal components of the reflected and transmitted rays are pure imaginary, i.e., they are evanescent waves carrying no power.[24] Moreover, the normal components are of the order $\sim i|\vec{K}|$ so that the decay length is of the order of an atomic diameter, thus casting the assumption of a mathematical plane interface into serious jeopardy, even for a perfect crystal. Nonetheless, this approximation, the neglect of surface local fields, is made successfully for x-ray phenomena.[16] In the absence of a better theory I will continue to make this assumption as its consequences must surely have approximate validity.

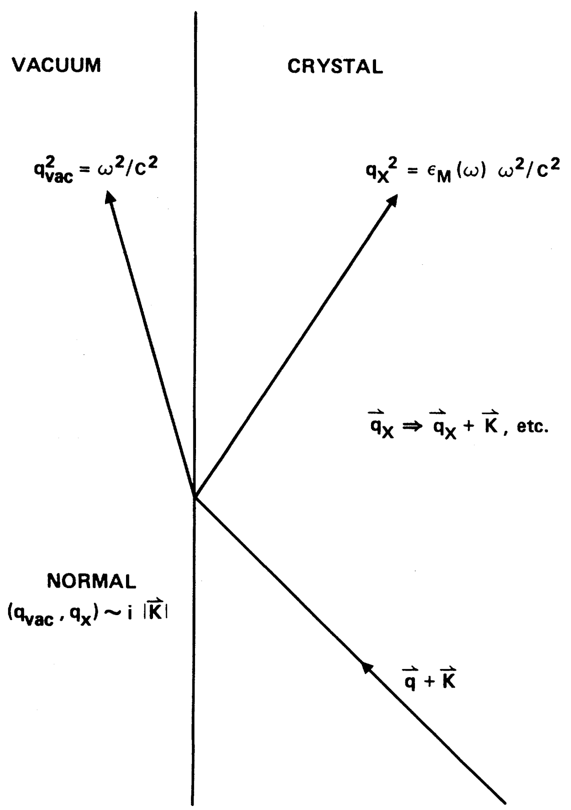

FIG. 1. Boundary conditions at a surface are satisfied if the secondary plane-wave components, $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$, of the electromagnetic normal mode in the crystal, each match onto a single plane wave in the vacuum plus the primary plane-wave component of another normal mode in the crystal. Since the tangential components of all three wave vectors must be equal, the normal components of the latter two are, in general, imaginary.

C. Optical Borrmann effect

If, however, there is an exit surface exactly perpendicular to some $\vec{q}+\vec{K}$ $(\vec{K}\neq\vec{0})$, all three wave vectors have zero tangential components, and the vacuum wave vector is purely real and should transmit power. A specific experimental arrangement is depicted in Fig. 2. This gedanken phenomenon is exactly equivalent in every respect to the x-ray Borrmann effect.[16] Using the boundary conditions it is not difficult to calculate the intensity of the transmitted Borrmann beam by observing that the tangential component of $\vec{E}_K$ is simply Eq. (4.15) and by using Eqs. (4.6), (4.8a), and (4.9). I find, for cubic crystals, that the intensity of the Borrmann beam relative to the incident intensity is $\sum_{\alpha=1}^{2}|\varphi_K^\alpha|^2$, where, to lowest order,

$$\varphi_K^\alpha=\frac{2\omega}{(n+1)^2c|K|}\sum_{\beta=1}^{2}(T^{-1})_{K,0}^{\alpha,\beta}\chi_\beta \qquad (4.21)$$

and $\{\chi_\beta\}$ is the unit polarization vector of $\vec{D}_0$ [see Eqs. (4.6) and (4.8a)].

In a previous paper,[13] I presented a simple model for the longitudinal response matrix which, slightly generalized, gives

$$\overleftrightarrow{\epsilon}_{K,G} = \left(\delta_{K,G} + \frac{(\epsilon_{\mathrm{RPA}} - 1) f_v(K-G)}{\{1 + \kappa[q + \frac{1}{2}(K+G)]^2\}^2} \right) \overleftrightarrow{I} \qquad (4.22)$$

for the low (optical)-frequency dielectric-response tensor, where $f_v(\vec{Q})$ is the Fourier transform of the valence charge density, κ, defined in Ref. 13, roughly describes the nonlocality of the response, and $\overleftrightarrow{\epsilon}_{0,0}(q=0) = \epsilon_{\mathrm{RPA}} \overleftrightarrow{I}$ defines ϵ_{RPA}. At the time, the only insulator for which a first-principles band-structure calculation of $\epsilon_{K,G}$ existed was diamond[10,25] and Eq. (4.22) was applied thereto with more or less good results. Equation (4.22) is based on a self-consistent field (SCF) theory which is never equivalent to the Clausius-Mossotti relation (a time-dependent Hartree theory); exchange is a necessary ingredient to retrieve the Clausius-Mossotti relation and this is known to be a large effect in diamond.[26] Nonetheless, for convenience sake I used Eq. (4.22) to calculate the optical Borrmann efficiency at 1.5 eV in diamond although this model or other models[18] could be applied to more suitably chosen insulators. I found the maximum efficiency[27] from Eq. (4.21) to be 2.6×10^{-10} for $\langle 111\rangle$ equivalent diffractions. That it is so small is due to $\omega/c|K|$ in (4.21), which is the ratio of the intercell spacing to the wavelength of light; the efficiency can be increased by more than a factor of 10 in diamond simply by increasing ω to just below the absorption edge. More profitably one might wish to consider large-unit-cell organo-metallic crystals. Note that the proposed effect is essentially a coherent scattering phenomenon, roughly proportional to ω^2 and highly directional, whereas incoherent Rayleigh scattering of small particles[7] is proportional to ω^4 and is omnidirectional.

The most serious drawback to such an experiment, aside from the obvious defects, oxide layers, etc., is the assumption of a perfect mathematical plane interface between the perfect crystal and the vacuum. One does not wish to consider $\vec{q} \parallel \vec{K}$ because then the emergent Borrmann beam and the main Snell beam are coincident. (The tangential components of $\vec{q}$ and of $\vec{q}+\vec{K}$ are each zero.) When $\vec{q} \perp \vec{K}$ the required interface is schematized in Fig. 3, where one can see that the interface consists roughly of a series of steps, perpendicular to $\vec{K}$, one unit cell high and $|K|/|q|$ approximately several thousand unit cells long (one wavelength long). The situation is somewhat like a series of surfaces orthogonal to $\vec{K}$, as indicated by the dashed lines; for a *single* planar exit surface normal to $\vec{K}$ (and not $\vec{q}+\vec{K}$), the Borrmann beam is again coincident with the Snell beam because the tangential components of $\vec{q}$ and of $\vec{q}+\vec{K}$ are then equal. If the exit surface of Fig. 3 is idealized by the indicated echelle grating (dashed lines) in which the properties of the crystal (i.e., $\overleftrightarrow{\epsilon}_{K,G}$) assume their bulk values right up to the surface of the sharp boundaries, then a simple short-wavelength Kirchoff integral calculation[24] $\int_s e^{-i(\vec{Q}-\vec{K})\cdot\vec{x}} ds$ indicates that the intensity of the Borrmann beam, in the Fraunhofer zone, is further reduced by $(n\omega/cK)^2 \sim 10^{-7}$ and, were this treatment valid, the optical Borrmann effect would probably not

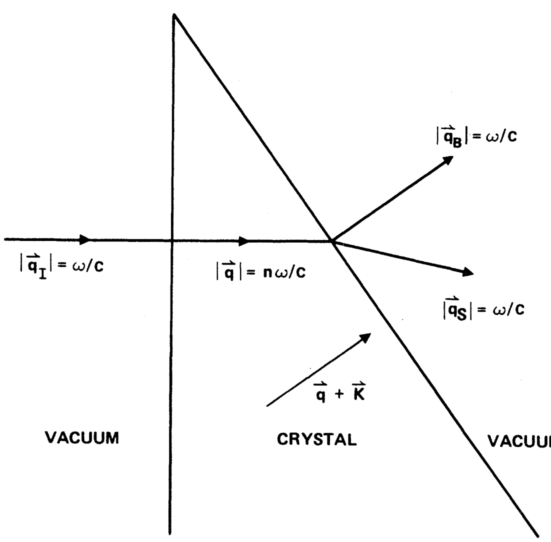

FIG. 2. Gedanken experimental arrangement to observe the optical Borrmann effect. A monochromatic beam is incident from the left on a nonabsorbing crystal (arbitrary angle of incidence) and the exit surface is normal to $\vec{q}+\vec{K}$. The Borrmann beam emerges normal to the surface whereas the main Snell beam is refracted away from the normal. No reflected rays have been included in the drawing.

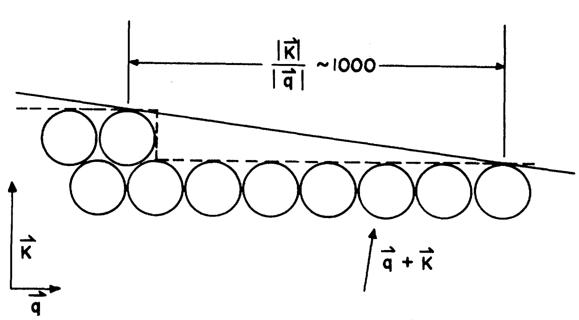

FIG. 3. Exit surface of Fig. 2 on an atomic scale (schematic). The solid line represents the average surface which is perpendicular to $\vec{q}+\vec{K}$; the dashed line represents the idealization of the true surface as an echelle grating. The length of a horizontal step is equal to a wavelength of light, which is several thousand unit cells long.

be observable. The attenuation by $(n\omega/cK)^2$ is directly traceable to the unphysical assumption that there is a component of the electric field which varies as $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$ at each point of the sharp dashed-line boundary of Fig. 3, i.e., over atomic dimensions. In reality, the polarizable valence charge of the outside-corner atoms diffuses into the region of the inner-corner atoms and also into the vacuum; the effective surface is much more nearly planar than indicated by the dashed lines of Fig. 3, and one may well expect that there is a component of the Borrmann beam given roughly by Eq. (4.21). If, for example, one assumes that the polarizability of the surface atoms decreases linearly from its bulk value at the inner corners of the steps to zero at the outer corners, then the same Kirchoff-integral calculation shows that the amplitude of the Borrmann beam is reduced by only $1/2\pi$ from Eq. (4.21) and still has a ω^2 dependence. A more thorough treatment of the effect of the surface local fields on the Borrmann beam in which one explicitly takes into account a realistic behavior of the surface atoms is beyond the scope of this paper.

In addition to its effect on the Borrmann beam, the surface grating partially diffracts the primary wave $e^{i\vec{q}\cdot\vec{r}}$ into the same direction as the Borrmann beam (see below). Although this effect is small, its intensity must be demonstrated to be smaller than that of the Borrmann beam or the latter will be obscured. One is now in the long-wavelength/small-aperature diffraction limit, however, and one is not justified in using standard Kirchoff-type diffraction theories.[28] I will, for the present purpose, assume that the medium is everywhere homogeneous and describable by the bulk index of refraction n within the echelle boundaries of Fig. 3. As before, this approximation will clearly overestimate the effect of the diffraction.

Let the periodic diffraction surface (dashed line of Fig. 3) be described by $y(x)=\sum_l A_l e^{iG_l x}$, where $G_l=2\pi l/a$ and a, the periodicity of the echelle grating, is

$$\left[\left(\frac{2\pi c}{n\omega}\right)^2+\left(\frac{2\pi}{|K|}\right)^2\right]^{1/2}.$$

The electric field inside the material is a Bloch function (in the x direction—parallel to the average surface) and is given by the sum of the incident wave plus the back diffracted waves, each of which is a solution to Maxwell's equations:

$$E_{\text{xtal}}=E_0 e^{i\vec{q}\cdot\vec{r}}+\sum_l E_l^r e^{i\vec{Q}_l\cdot\vec{r}}, \tag{4.23a}$$

$$\vec{Q}_l=(q_x+G_l, -[(n\omega/c)^2-(q_x+G_l)^2]^{1/2}, 0), \tag{4.23b}$$

and similarly for the fields in the vacuum:

$$E_{\text{vac}}=\sum_l E_l^t e^{i\vec{Q}_l'\cdot\vec{r}}, \tag{4.24a}$$

$$\vec{Q}_l'=(q_x+G_l, +[(\omega/c)^2-(q_x+G_l)^2]^{1/2}, 0). \tag{4.24b}$$

Note that the expansions are in terms of complete sets, including evanescent waves. Since $q_x=2\pi/a$, the diffracted wave with $l=-1$ in Eq. (4.24a) transmits in a direction exactly normal to the average surface; i.e., it is coincident with the emergent Borrmann beam. In fact, for any orientation of the average surface, or of $\vec{q}$, the Borrmann beam and the $l=-1$ surface diffracted primary wave are coincident because G_l is always equal to the tangential component of the pertinent bulk reciprocal-lattice vector. It is now a straightforward, if tedious, process to apply the continuity boundary conditions over the surface; in doing so it is permissible to expand $e^{iQ_{l,y}f(x)}=1+iQ_{l,y}f(x)$, since the step height is $\lesssim 10^{-3}$ times the step length. By equating the coefficients of the various $e^{iG_l x}$ that occur in the resultant equation, one can solve exactly (in the long-wavelength/small-aperature limit) for the coefficients E_l^t, E_l^r. The final result for the intensity of the $l=-1$ diffracted ray, relative to the incident beam, is

$$I_s=16\,\frac{n-1}{(n+1)^3}\left(\frac{n\omega}{cK}\right)^4=7.2\times10^{-14} \tag{4.25a}$$

for s-polarized light, and

$$I_p=16n^2\left(\frac{n-1}{n+1}\right)^2\left(\frac{\omega}{cK}\right)^4=6.0\times10^{-14} \tag{4.25b}$$

for p-polarized light. The numerical values correspond to $\hbar\omega=1.5$ eV in diamond. Equations (4.25) are valid whenever $|q|/|K|=n\omega/c|K|\ll 1$ and are to be compared with the square of Eq. (4.21) (2.6×10^{-10}) which, as discussed above, represents a reasonable upper bound for the intensity of the Borrmann beam. It is therefore probably reasonable to conclude that it is technically possible, if difficult, to observe and unambiguously identify (at least by its frequency dependence) the optical Borrmann effect, although other geometries and materials may be far more suitable for this purpose.

There is one other experiment which attempts to observe the microscopic fields directly but it has to date proven unsuccessful.[29] If one illuminates a crystal with monochromatic light, one induces charge densities which vary as $\rho_K(\vec{r},t)\sim e^{i[(\vec{q}+\vec{K})\cdot\vec{r}-\omega t]}$. In principle, one can Bragg scatter x-rays off the induced charge density according to $\Delta\vec{k}=\vec{q}+\vec{K}$, in addition to static Bragg scattering $\Delta\vec{k}=\vec{K}$; the former process is Doppler shifted by ω, the frequency of the pumping laser. There are two important differences between the present experiment and the Doppler-shifted Bragg-scattered one: (i) The former is strictly a linear response mechanism whereas the latter involves the interference between two external sources. (ii) The latter experiment involves the longitudinal component of $\vec{E}_K$ [$\rho_K \sim (\vec{q}+\vec{K})\cdot\vec{E}_K$] whereas the former involves the tangential component, a much smaller quantity [see Eqs. (4.15) ff.].

V. SUMMARY

Maxwell's equations in crystals have been examined explicitly including local-field effects by means of the nondiagonal dielectric-response matrix. The dynamical theory of x-ray diffraction is a special case thereof. At optical frequencies, the long-wavelength expansion has been used to solve exactly (in the long-wavelength limit, whenever $q/K \equiv n\omega/cK \ll 1$) modes and estimate the efficiency with which a microscopic component of the normal-mode electromagnetic field, $e^{i(\vec{q}+\vec{K})\cdot\vec{r}}$, transmits into the vacuum. This efficiency is, however, an upper limit due to the intrinsic irregularities of a crystalline-vacuum interface on an atomic scale. Unlike incoherent scattering, and unlike the diffraction effect on the main Snell beam, whose intensities vary as ω^4, the intensity of the undiffracted Borrmann beam is highly directional and its relative intensity varies as ω^2. The efficiency of the optical Borrmann effect (the coefficient of ω^2) is sensitive to the microscopic properties of the surface atoms and cannot, therefore, be used to directly deduce the values of the bulk fields; this effect, however, will not be present at all unless $E_K \neq 0$ in the bulk.

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