Grazing-incidence diffraction and the distorted-wave approximation for the study of surfaces

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A method is developed for calculating the scattering of a beam of x rays striking the plane surface of a crystal at an angle below the critical angle for total external reflection. The low penetration under this condition offers the possibility of determining the special structure of the surface layers, as has been pointed out by Marra, Eisenberger, and Cho. A distorted-wave approach is developed whereby the crystal is first taken to be a homogeneous dielectric slab for the purpose of calculating the distorted wave. The distorted wave is considered to illuminate the actual crystal, from which a scattering pattern can then be calculated. The effects of absorption can be taken into account; in some cases absorption may offer the possibility of observing near-surface structures at angles of incidence larger than the critical angle. Such illumination may also be useful for performing fluorescence analysis of the near-surface layers to determine their impurity content. Synchrotron sources offer new opportunities for measurements of these kinds. Thermal neutrons may also be used in place of x rays and offer unique opportunities for studying surface magnetization and, through inelastic scattering, surface phonons and, conceivably, surface magnons.

I. INTRODUCTION

Marra, Eisenberger, and Cho[1] have demonstrated that the surfaces of solids can be studied to advantage by using a highly collimated beam of x rays striking the surface at a grazing angle near or within the range for which total external reflection occurs. In this situation only the near-surface layer is illuminated and a diffraction pattern is produced which reveals the structure of the surface region in preference to that of the interior. Stated in other terms, the ratio of signal to noise for surface studies can be considerably improved by this arrangement. The idea could be extended to interfaces between different solids, and to other forms of radiation, particularly thermal neutrons. Although stringent requirements are placed on collimation of the beam and flatness of the surface, it appears that these could be met in many cases. Synchrotron sources are particularly well suited for providing the highly collimated radiation with necessary intensity.

To interpret the diffraction pattern produced in this arrangement the conventional theory of diffraction by small crystals[2] is inadequate because this theory is based on the Born approximation (i.e., single scattering), while it is the essence of the method that the illumination of the crystal is severely limited by total external reflection, a phenomenon inherently dependent upon multiple scattering. The dynamical theory of x-ray scattering overcomes the deficiency but its complexity weighs against easy application to the problem at hand. We are unaware of any dynamical treatment that gives a simple means of correcting for total reflection under conditions of grazing incidence while leaving parameters free to describe the imperfections that are to be determined by the scattering. Kishino et al. have applied dynamical theory to Bragg diffraction for glancing angles of incidence[3] and to Laue diffraction under conditions where a diffracted beam makes a glancing angle with the surface.[4] They have shown that the usual dynamical results for these arrangements are modified by effects of specular reflection and surface asymmetry. Four pairs of waves had to be considered inside the crystal to reach these results, which were for perfect crystals only.

It is the thesis of this paper that a distorted-wave approximation based on a homogeneous scatterer as a first approximation describes the essentials of the scattering, is simple to use, and allows the near-surface structures to be determined. In the following pages this approach is worked out.

II. THE DISTORTED-WAVE APPROXIMATION

A. General considerations

In the Born approximation a scattering sample is assumed to be illuminated by a single plane wave, calculated as if the scatterer were absent. Each element of the sample scatters this illuminating wave, and the resulting fields scattered to a distant point by all elements of the specimen are added up to find the total scattering. In the distorted-wave approximation[5] the scatterer is first replaced by a simpler distribution of material and the field produced at all points when a plane wave falls on this distribution is calculated exactly. This field, the distorted wave, in turn, is considered to illuminate each element of the real scatterer, and this interaction produces a scattered field which is summed over all elements of the scatterer. This scattered field is expected to resemble the true scattering better than the Born approximation. In the simplest distorted-wave approximation, which is employed here, the calculation ends at this point. Alternatively it is possible to construct an expansion of the exact solution, of which this is only the second term. Higher terms become very complicated and will normally be small because the scattering by an individual atom is exceedingly small, and even the scattering by a plane of atoms is small. In Apppendix B a model in which the crystal is replaced by regularly spaced homogeneous planes of scattering material is treated and it is shown that the distorted wave calculated by the simple model of this section is an excellent approximation. Because of the grazing angle of incidence, Bragg reflection from planes parallel to the crystal surface cannot occur. Bragg reflections from other sets of planes can occur but the extinction associated with these reflections must be small because the wave field is, so to say, continually renewed from outside the crystal. A formal development of the distorted-wave approximation for the electromagnetic field in a dielectric medium is given in Appendix A.

We shall start with the von Laue model[6] which assumes that the scatterer can be represented as a dielectric whose permittivity varies from point to point according to the instantaneous density of electrons at that point, $\rho(\vec{r})$. The permittivity at $\vec{r}$ is then (assuming that the frequency is not close to an absorption edge)

$$\epsilon(\vec{r}) = 1 - \frac{4\pi e^2}{m\omega^2}\rho(\vec{r}) , \qquad (1)$$

where the permittivity of free space is taken to be unity, e and m are the electronic charge and mass, and ω is the frequency of the radiation multiplied by 2π. Maxwell's equations for the case of spatially varying permittivity give the following conditions for the electric field $\vec{\mathscr{E}}$ and the magnetic field $\vec{\mathscr{H}}$:

$$\vec{\nabla} \times \vec{\nabla} \times \vec{\mathscr{E}} + \frac{\epsilon}{c^2}\ddot{\vec{\mathscr{E}}} = 0 , \qquad (2a)$$

$$\vec{\nabla} \times \vec{\mathscr{H}} = \frac{\epsilon}{c}\dot{\vec{\mathscr{E}}} , \qquad (2b)$$

$$\vec{\nabla} \cdot \epsilon\vec{\mathscr{E}} = 0 , \qquad (2c)$$

$$\vec{\nabla} \cdot \vec{\mathscr{H}} = 0 . \qquad (2d)$$

The general problem is to solve these with ϵ given by (1) and with a plane wave incident on the scatterer.

In the usual procedure of the distorted-wave approximation, the permittivity can be divided into two parts,

$$\epsilon(\vec{r}) = \epsilon_1(\vec{r}) + \epsilon_2(\vec{r}) , \qquad (3)$$

where $\epsilon_1(\vec{r})$ equals the average permittivity ϵ_1 within the scatterer and unity outside the scatterer, while $\epsilon_2(\vec{r})$ represents the atomic-scale structure in ϵ. The strategy then is to solve the scattering problem presented by using $\epsilon_1(r)$ for ϵ in Eqs. (2) with an incident plane wave, then to use the resulting wave as the incident wave for the scattering problem presented by $\epsilon_2(\vec{r})$.

B. Scattering by $\epsilon_1(\vec{r})$

For generality we start by considering two homogeneous dielectric slabs which have a plane interface at $z=0$. Let the medium above the interface have permittivity ϵ and let the medium below have permittivity ϵ'. In most cases ϵ will later be set equal to 1. Suppose a plane, linearly polarized electromagnetic wave

$$\vec{\mathscr{E}} = \vec{E}e^{i(\vec{k}\cdot\vec{r}-\omega t)}$$

falls upon the interface from above. There will be a reflected wave

$$\vec{\mathscr{E}}'' = \vec{E}''e^{i(\vec{k}''\cdot\vec{r}-\omega t)}$$

above the interface and a refracted wave

$$\vec{\mathscr{E}}' = \vec{E}'e^{i(\vec{k}'\cdot\vec{r}-\omega t)}$$

below the interface. The angle of incidence is α and the angle of refraction is α' (see Fig. 1).

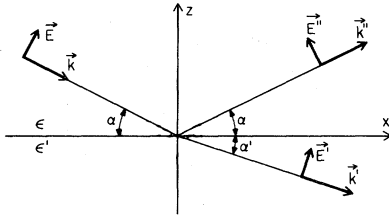Maxwell's equations and the boundary conditions

FIG. 1. Reflection and refraction of plane wave $\vec{k}$ incident upon an interface between two uniform dielectric media. Electric fields are illustrated for one polarization only.

at $z=0$ determine the refracted and reflected waves in terms of the parameters of the incident wave $\vec{k}$ and $\vec{E}$ (see, for example, Ref. 7, Chap. X). We collect the relevant formulas for our purposes, which are the following:

$$k' = \left[\frac{\epsilon'}{\epsilon} \right]^{1/2} k \ , \tag{5}$$

$$\sqrt{\epsilon}\cos\alpha = \sqrt{\epsilon'}\cos\alpha' \ . \tag{6}$$

Equation (5) is required by Maxwell's equations and (6) is Snell's law (since the indices of refraction equal the square roots of the respective permittivities). The amplitude of the refracted wave is linearly related to the amplitude of the incident wave, a relation which is conveniently written

$$\vec{E}' = \Phi \cdot \vec{E} \ , \tag{7}$$

where Φ is a second-rank tensor whose components can be shown to be the following:

$$\Phi_{xx} = \frac{2(\epsilon\epsilon' - \epsilon^2\cos^2\alpha)^{1/2}}{\epsilon'\sin\alpha + (\epsilon\epsilon' - \epsilon^2\cos^2\alpha)^{1/2}} \ , \tag{8a}$$

$$\Phi_{yy} = \frac{2\sqrt{\epsilon}\sin\alpha}{\sqrt{\epsilon}\sin\alpha + (\epsilon' - \epsilon\cos^2\alpha)^{1/2}} \ , \tag{8b}$$

$$\Phi_{zz} = \frac{2\epsilon\sin\alpha}{\epsilon'\sin\alpha + (\epsilon\epsilon' - \epsilon^2\cos^2\alpha)^{1/2}} \ , \tag{8c}$$

$$\Phi_{xy} = \Phi_{yx} = \Phi_{xz} = \Phi_{zx} = \Phi_{yz} = \Phi_{zy} = 0 \ . \tag{8d}$$

Equations (7) and (8), when expressed in more elementary terms for the separate cases of parallel and perpendicular polarization, are sometimes known as Fresnel's equations.

In the cases of interest here $\epsilon' < \epsilon$, and therefore when α is less than a critical angle α_c, given by

$$\alpha_c = \cos^{-1}\left[\frac{\epsilon'}{\epsilon} \right]^{1/2} , \tag{9}$$

total external reflection occurs. In this regime α' becomes imaginary and the refracted wave pro-

pagates parallel to the interface while being exponentially damped with distance below the interface.

When $\alpha \leq \alpha_c$ the components of $\vec{k}'$ become

$$k_x' = k\cos\alpha \ , \tag{10a}$$

$$k_y' = 0 \ , \tag{10b}$$

$$k_z' = -ik\left[\cos^2\alpha - \frac{\epsilon'}{\epsilon} \right]^{1/2} . \tag{10c}$$

The imaginary value of k_z', of course, provides the damping, which is an essential feature of the grazing incidence arrangement. The near-surface region is illuminated to a characteristic depth l at which the field has fallen by a factor e^{-1}. Using (10c) one finds

$$l \equiv \frac{1}{|\operatorname{Im}k_z'|} = \frac{1}{k(\cos^2\alpha - \epsilon'/\epsilon)^{1/2}}$$

$$\cong \frac{\lambda}{2\pi(\alpha_c^2 - \alpha^2)^{1/2}} \ , \tag{11}$$

where λ is the wavelength of the radiation in the upper medium, and the last form depends upon the smallness of α and α_c. Note that l is the e-folding depth for the fields; the e-folding depth for power is half of this. In typical cases, for x-rays of wavelength ~ 1Å and for $\alpha \ll \alpha_c$, l ranges from about 80 Å in materials of low density to about 25 Å in materials of high density. For $\alpha = \frac{1}{2}\alpha_c$ the values of l are about 15% larger, and become infinite at $\alpha = \alpha_c$. Although damped in the z direction the wave propagates in the x direction with a wavelength near to the free-space wavelength of the incident radiation. For this reason it is well suited to produce diffraction effects characteristic of the atomic structure, as was pointed out by Mara et al.[1] There is also a diffraction effect caused by atomic structure in the z direction, as will be shown below.

The electric field of the refracted wave has a magnitude given by Eqs. (7) and (8). It should also be noted that if the incident wave is polarized with its electric vector normal to the plane of incidence, (i.e., parallel to y) the refracted field $\vec{E}'$ is normal to this plane; if the incident wave is polarized in the plane of incidence the refracted wave is also polarized in the plane of incidence, and for small angles of incidence lies almost entirely in the z direction. In fact, the ratio of its x to its z component is $\tan\alpha'$. Also for $\alpha < \alpha_c$ there are phase shifts relative to the incident wave because α' becomes imaginary and because of the radicals in the denominators of Eqs. (8). The expressions can be simplified for the situa-

tions of interest here, where $\alpha \ll 1$ and ϵ and ϵ' are very close to 1. It is useful to define the small quantities δ and δ', where

$$\delta = 1 - \epsilon$$

and

$$\delta' = 1 - \epsilon' .$$

The critical angle, α_c, is then

$$\alpha_c \cong \sqrt{\delta' - \delta} . \tag{12}$$

One obtains δ' from Eq. (1) with $\bar{\rho}$ of the lower medium substituted for $\rho(\vec{r})$ on the right-hand side, and obtains δ by a similar relation for the upper medium. For x rays of about 1-Å wavelength, δ' is typically in the range 10^{-6} to 10^{-5}. Taking $\delta = 0$, $\alpha_c \cong 1$ to 10 mrad at 1 Å. Since δ and δ' are proportional to λ^2, α_c is proportional to λ. The penetration depth l on the other hand is more weakly dependent on λ and becomes independent of λ when $\alpha \ll \alpha_c$.

Simplifying the components of Φ by expanding to first order in the small quantities δ, δ', and α, one finds

$$\Phi_{xx} \simeq \frac{2[\alpha^2 - (\delta' - \delta)]^{1/2}}{\alpha + [\alpha^2 - (\delta' - \delta)]^{1/2}} , \tag{13a}$$

$$\Phi_{yy} \cong \frac{2\alpha}{\alpha + [\alpha^2 - (\delta' - \delta)]^{1/2}} , \tag{13b}$$

$$\Phi_{zz} = \frac{2\alpha}{\alpha + [\alpha^2 - (\delta' - \delta)]^{1/2}} . \tag{13c}$$

We apply Eq. (7) to these relations for the case where the incident polarization is perpendicular to the plane of incidence and find

$$E'_x = E'_z = 0 ,$$

$$E'_y \simeq E \frac{2\alpha}{\alpha + [\alpha^2 - (\delta' - \delta)]^{1/2}} . \tag{14}$$

If, instead, the incident polarization is parallel to the plane of incidence, then

$$E'_y = 0 ,$$

$$E'_x \cong E \frac{2\alpha[\alpha^2 - (\delta' - \delta)]^{1/2}}{\alpha + [\alpha^2 - (\delta' - \delta)]^{1/2}} \cong 0 ,$$

$$E'_z \cong E \frac{2\alpha}{\alpha + [\alpha^2 - (\delta' - \delta)]^{1/2}} .$$

Thus in both polarizations,

$$|E'| = E \frac{2x}{x + (x^2 - 1)^{1/2}} , \quad \alpha > \alpha_c$$

and

$$|E'| = 2xE, \quad \alpha \le \alpha_c$$

where $x \equiv \alpha / \alpha_c$ and $\alpha_c = \sqrt{\delta' - \delta}$. These relations are plotted in Fig. 2.

III. SCATTERING OF THE DISTORTED WAVE

Having developed the solution of Maxwell's equations for a plane wave falling upon a half-space filled with a homogeneous dielectric medium, we now consider this solution to be the distorted wave that is scattered by the distribution of dielectric material $\epsilon_2(\vec{r})$. A formal development of scattering theory for this purpose is given in Appendix A and the precise definition of the distorted-wave approximation being employed is given there. The result may also be reached intuitively by considering the distorted wave $\vec{\mathscr{E}}'(\vec{r})$ to excite the electrons at $\vec{r}$ which then radiate without further interactions with the medium according to the classical formula (Ref. 2, Chap. I). We proceed in the following manner: In the volume element dv at $\vec{r}$ there will be $\rho_2(\vec{r})dv$ electrons. Denote by $d\vec{\mathscr{E}}_s$ the electric field these electrons scatter to an arbitrary distant point $R\vec{s}$, where $\vec{s}$ is a unit vector. One then has

$$d\vec{\mathscr{E}}_s = \frac{e^2}{mc^2R}\rho_2(\vec{r})dv(I - \vec{s}\,\vec{s}) \cdot \vec{\mathscr{E}}'(\vec{r})e^{-2\pi i\vec{s}\cdot\vec{r}/\lambda} \tag{15}$$

where I is the unit tensor and $\vec{s}\,\vec{s}$ is the dyadic product. Writing

$$\vec{\mathscr{E}}'(\vec{r}) = \vec{E}'e^{i(\vec{k}'\cdot\vec{r} - \omega t)}$$

and setting

$$\vec{E}' = \Phi \cdot \vec{E} ,$$

we have

$$\vec{\mathscr{E}}_s = \frac{e^2}{mc^2R}e^{-i\omega t}(I - \vec{s}\,\vec{s}) \cdot \Phi \cdot \vec{E}$$

$$\times \int \rho_2(\vec{r})e^{i(\vec{k}' - 2\pi\vec{s}/\lambda)\cdot\vec{r}}dv , \tag{16}$$
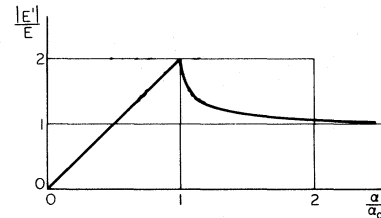

FIG. 2. Magnitude of the electric field inside the scatterer, compared with the incident field, as a function of the angle of incidence.

where the integration extends over all of the scatterer illuminated by the incident radiation. Note that the order of the two tensors in this formula must be preserved. This result is rederived more formally in Appendix A.

A further simplification may now be made: $\rho_2(\vec{r}) = \rho(\vec{r}) - \rho_1(\vec{r})$, where the electron density $\rho_1(\vec{r})$ is associated with the previously derived mean permittivity in the specimen $\epsilon_1(\vec{r})$ through a relation of the type of Eq. (1). This is a constant, $\bar{\rho}$, throughout the region of integration in Eq. (16). Thus, the integral in (16) can be written

$$\int \rho(\vec{r})e^{i[\vec{k}'-(2\pi/\lambda)\vec{s}]\cdot\vec{r}}dv$$

$$-\bar{\rho}\int e^{i[\vec{k}'-(2\pi/\lambda)\vec{s}]\cdot\vec{r}}dv . \qquad (17)$$

The second integral is small except when $2\pi\vec{s}/\lambda \cong \vec{k}'$, which is not in the region accessible to observations. Therefore this term may be dropped. Recognizing that $\rho(\vec{r})$ is the superposition of charge clouds centered on the instantaneous position of each atom in the specimen, we can set

$$\rho(\vec{r}) = \sum_n \sigma_n(\vec{r}-\vec{r}_n) , \qquad (18)$$

where $\sigma_n(\vec{\xi})$ is the charge density associated with the nth atom at distance $\vec{\xi}$ from its center and $\vec{r}_n$ is the instantaneous position of this atom. Equation (18) is inserted into (17), the second term of which has now been dropped, and in the usual way the formula becomes

$$\sum_n f_n(\vec{\kappa})e^{i\vec{\kappa}\cdot\vec{r}_n} , \qquad (19)$$

where $\vec{\kappa}$ has been written for the effective scattering vector,

$$\vec{\kappa} = \vec{k}' - \frac{2\pi}{\lambda}\vec{s} , \qquad (20)$$

and

$$f_n(\vec{\kappa}) = \int \sigma_n(\vec{\xi})e^{i\vec{\kappa}\cdot\vec{\xi}}dv . \qquad (21)$$

f_n is the structure factor of the nth atom for the scattering vector $\vec{\kappa}$. The basic equation [(15)] thus becomes

$$\vec{\mathscr{E}}_s = \vec{A}\sum_n f_n(\vec{\kappa})e^{i\vec{\kappa}\cdot\vec{r}_n} , \qquad (22)$$

where

$$\vec{A} = \frac{e^2}{mc^2 R}e^{-i\omega t}(I - \vec{s}\,\vec{s})\cdot\Phi\cdot\vec{E} ,$$

and if $|\vec{A}|$ is set equal to 1, Eq. (22) expresses the scattering amplitude relative to the scattering by a single electron. Equation (22) is the basic equation of our distorted-wave approximation.

For an incident angle below the critical angle for total external reflection, $\vec{k}'$, and thus $\vec{\kappa}$, have imaginary z components [see Eq. (10c)], and the magnitude of the imaginary component is given by Eq. (10).

Writing $(2\pi/\lambda)\vec{s} = \vec{S}$, so $\vec{\kappa} = \vec{k}' - \vec{S}$, we have the components of $\vec{\kappa}$ given by

$$\kappa_x = k_x' - S_x \simeq k - S_x , \qquad (23a)$$

$$\kappa_y = -S_y , \qquad (23b)$$

$$\kappa_z = -i\tilde{k} - S_z , \qquad (23c)$$

where

$$\tilde{k} \equiv k(\cos^2\alpha - \epsilon')^{1/2} \cong k(\delta' - \alpha^2)^{1/2} . \qquad (24)$$

Later it will be convenient to allow the incident radiation to have arbitrary orientation around the z axis—that is to let $\vec{k} = (k_x, k_y, k_z)$, in which case (23a) and 23(b) are generalized to

$$\kappa_x \cong k_x - S_x , \qquad (25a)$$

$$\kappa_y \cong k_y - S_y , \qquad (25b)$$

with (23c) unchanged. Note that the components of Φ will also be altered.

The atomic structure factor for a complex scattering vector is a generalization of the usual structure factor of x-ray diffraction, where the scattering vector is considered to be real. Rewriting (21) with the use of Eqs. (22), one has

$$f_n(\vec{\kappa}) = \int \sigma_n(\vec{\xi})e^{i[(k-s_x)\xi - s_y\eta - s_z\zeta]}e^{\tilde{k}\zeta}dv_\xi , \qquad (26)$$

when ξ, η, ζ are the components of $\vec{\xi}$. The last factor in the integrand of (26) can be approximated by $1 + \tilde{k}\zeta$. In the region of integration this factor differs from unity at most by $\tilde{k}a$, where a is the atom's radius. Because $\tilde{k}$ is smaller than 0.04 Å^{-1} in all realistic cases and a is not larger than about 1 Å (in fact, the bulk of the charge density in atoms lies at smaller distances yet) neglect of this term will produce errors of the order of 1% or less. In all that follows, we will make this approximation, thus assuming that $f_n(\vec{\kappa})$ can be replaced by the ordinary atomic structure factor with

$$\vec{\kappa} = (k_x - S_x, k_y - S_y, -S_z) .$$

Since the atoms will have thermal motions, $\vec{r}_n$ is an instantaneous position of an atom and fluctuates many times during a scattering measurement. This

may be taken into account in the usual way by averaging over the temperature motions. Let

$$\vec{r}_n = \vec{R}_n + \vec{u}_n ,$$ (27)

where $\vec{R}_n$ is the mean position of the nth atom and $\vec{u}_n$ is its instantaneous displacement. The usual arguments can be applied by substituting (27) into Eq. (22) and averaging the $\vec{u}_n$ terms over time, remembering that $\vec{\kappa}$ is complex. Assuming a harmonic approximation for the atomic vibrations, the elastic component of the scattered intensity becomes the square of the absolute value of the right-hand side of (22) with $\vec{r}_n$ replaced by $\vec{R}_n$ and with a Debye-Waller factor multiplying the whole expression. This factor depends on the scattering vector $\vec{\kappa}$ and is customarily written in a form which incorporates the structure factors in a sum over a unit cell of the crystal lattice (see Warren[2], Sec. 3.4). In our case the thermal motions will, in general, be different for atoms near the surface and in the bulk. To proceed it will usually be necessary to assume a uniform temperature factor appropriate to the atoms in the illuminated region of the sample. For the case of one atom per unit cell a single temperature factor will then suffice. The factor multiplying the scattered intensity will be

$$e^{-(M+M^*)}$$ (28)

instead of the familiar e^{-2M}, where, on the harmon-

ic approximation, $M = \frac{1}{2} \langle (\vec{\kappa} \cdot \vec{u})^2 \rangle$. M^* appears in (28) because $\vec{\kappa}$ is complex. The general expression for an arbitrary number of atoms per unit cell is readily written down in analogy with (28). Hereafter we will assume that an appropriate temperature factor will be employed to correct the observed intensities before comparing them with calculations based on Eq. (22).

IV. SCATTERING BY A PERFECT CRYSTAL IN THE DISTORTED-WAVE APPROXIMATION

As an illustration of the distorted-wave method we calculate the scattering from a monatomic perfect crystal bounded by a planar surface. The incident beam will strike this surface at a grazing angle α which is below the critical angle for total external reflection. Let the basis vectors of the lattice be $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, so that $\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, with n_1, n_2, and n_3 integers, gives the mean position of an arbitrary atom. We further simplify by assuming that $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are mutually perpendicular and take $\vec{a}_3$ parallel to the z axis. Let the illuminated face of the crystal be at $n_3 = 0$, so $n_3 \leq 0$, and let the face contain $N_1 N_2$ atoms, so that the lateral boundaries are given by $0 \leq n_1 \leq N_1 - 1$, and $0 \leq n_2 \leq N_2 - 1$. Then employing Eq. (22) with $\vec{r}_n$ replaced by $\vec{R}_n$, we have

$$\vec{\mathscr{E}}_s = \vec{A} f \sum_n e^{i\vec{\kappa} \cdot \vec{R}_n} = \vec{A} f \sum_{n_1=0}^{N_1-1} e^{i\kappa_x a_1 n_1} \sum_{n_2=0}^{N_2-1} e^{i\kappa_y a_2 n_2} \sum_{n_3=0}^{-\infty} e^{i\kappa_z a_3 n_3} .$$ (29)

Summing the three geometrical series, one finds

$$\vec{\mathscr{E}}_s = \vec{A} f \left[\frac{1 - e^{i\kappa_x a_1 N_1}}{1 - e^{i\kappa_x a_1}} \right] \left[\frac{1 - e^{i\kappa_y a_2 N_2}}{1 - e^{i\kappa_y a_2}} \right] \left[\frac{1}{1 - e^{-i\kappa_z a_3}} \right]$$

$$= \vec{A} f e^{i\psi} \left[\frac{\sin \dfrac{\kappa_x a_1 N_1}{2}}{\sin \dfrac{\kappa_x a_1}{2}} \right] \left[\frac{\sin \dfrac{\kappa_y a_2 N_2}{2}}{\sin \dfrac{\kappa_y a_2}{2}} \right] \left[\frac{1}{1 - e^{(iS_z - \tilde{k})a_3}} \right] ,$$ (30)

where $\psi = \frac{1}{2} [\kappa_x a_1 (N_1 - 1) + \kappa_y a_2 (N_2 - 1)]$, which is simply a phase angle and of no physical consequence. The square of the absolute value of this can be written

$$| \vec{\mathscr{E}}_s |^2 = | \vec{A} |^2 f^2 \left[\frac{\sin^2 \dfrac{\kappa_x a_1 N_1}{2}}{\sin^2 \dfrac{\kappa_x a_1}{2}} \right] \left[\frac{\sin^2 \dfrac{\kappa_y a_2 N_2}{2}}{\sin^2 \dfrac{\kappa_y a_2}{2}} \right] \left[\frac{1}{1 + e^{-2\tilde{k}a_3} - 2e^{-\tilde{k}a_3} \cos S_z a_3} \right] .$$ (31)

In the last factor of (31) the term $\tilde{k}a_3$ is the reciprocal of the effective number of lattice planes penetrated by the x-rays. Calling this N_3 [where also $N_3a_3 = l$ with l defined in Eq. (11)] we have

$$N_3 = \frac{1}{\tilde{k}a_3} \; . \tag{32}$$

From the arguments given earlier, N_3 will be of the order of 10 to about 40. It is thus convenient to expand the denominator of the last factor in (31) in powers of N_3^{-1}, carrying this through to second order. Then, recalling Eqs. (23) and generalizing by removing the restriction that the y axis be perpendicular to the incident beam [see Eqs. (25a) and (25b)], we have

$$|\vec{\mathscr{E}}_s|^2 = |\vec{A}|^2 f^2 \frac{\sin^2\frac{1}{2}(k_x - S_x)a_1 N_1}{\sin^2\frac{1}{2}(k_x - S_x)a_1} \frac{\sin^2\frac{1}{2}(k_y - S_y)a_2 N_2}{\sin^2\frac{1}{2}(k_y - S_y)a_2} \frac{N_3^3(N_3-1)^{-1}}{1+4N_3^2\sin^2\frac{S_z a_3}{2}} \; . \tag{33}$$

Equation (33) shows that the scattered intensity is peaked when $(k_x - S_x)$, $(k_y - S_y)$, and S_z are at any reciprocal-lattice point. The profiles in $k_x - S_x$ and $k_y - S_y$ are each of the familiar form,[2] peaked at reciprocal-lattice points with altitudes proportional to N_1^2 and N_2^2 and widths inversely proportional to N_1 and N_2, respectively. The profile in S_z is a little different but also is peaked at reciprocal-lattice points, has altitude proportional to N_3^2, and width inversely proportional to N_3. Since N_3 is much smaller than N_1 and N_2 this profile is lower and broader, but nevertheless is significantly structured.

It is interesting to compare areas under the two kinds of peaks. Letting φ stand for $\frac{1}{2}(k_x - S_x)a$, or for $\frac{1}{2}S_z a_3$, as appropriate, and approximating $N_3(N_3-1)^{-1}$ by 1, we deal with two typical functions,

$$\theta_1(\varphi) = \frac{\sin^2 N\varphi}{\sin^2\varphi}$$

and

$$\theta_3(\varphi) = \frac{N^2}{1+4N^2\sin^2\varphi} \; .$$

These have peaks of identical height, N^2. θ_1 has a halfwidth at half-maximum of $\varphi_1 \cong 1.39/N$ and θ_3 has a halfwidth at half-maximum of $\varphi_3 \cong 1/2N$. One can also show that

$$\int_{-\pi/2}^{\pi/2} \theta_1(\varphi)d\varphi = \pi N$$

and

$$\int_{-\pi/2}^{\pi/2} \theta_3(\varphi)d\varphi = \left[\frac{\pi}{2}\right]N \; .$$

Thus, for a given N, the θ_3 distribution is a little narrower than the θ_1 distribution.

Finally, we record the generalization of Eq. (30) for a triclinic lattice with m atoms per unit cell,

subject only to the condition that the surface of the crystal be a plane of the lattice.

Let the lattice be defined by the basis vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$, where $\vec{a}_1$ and $\vec{a}_2$ lie in the surface of the crystal. Let the jth atom of the unit cell have structure factor f_j and location $q_j^1\vec{a}_1 + q_j^2\vec{a}_2 + q_j^3\vec{a}_3$ with respect to the origin of the cell. The one finds

$$\vec{\mathscr{E}}_s = \vec{A}e^{i\psi}F\frac{\sin(\frac{1}{2}\kappa_1 N_1)}{\sin(\frac{1}{2}\kappa_1)} \frac{\sin(\frac{1}{2}\kappa_2 N_2)}{\sin(\frac{1}{2}\kappa_2)} \frac{1}{1-e^{-i\kappa_3}} \; , \tag{34}$$

where

$$F = \sum_{j=1}^{m} f_j e^{i(\kappa_1 q_j^1 + \kappa_2 q_j^2 + \kappa_3 q_j^3)} \tag{35}$$

and

$$\kappa_1 = \vec{i}_1 \cdot \vec{a}_1 \kappa_x + \vec{i}_2 \cdot \vec{a}_1 \kappa_y \; ,$$

$$\kappa_2 = \vec{i}_1 \cdot \vec{a}_2 \kappa_x + \vec{i}_2 \cdot \vec{a}_2 \kappa_y \; ,$$

$$\kappa_3 = \vec{i}_1 \cdot \vec{a}_3 \kappa_x + \vec{i}_2 \cdot \vec{a}_3 \kappa_y + \vec{i}_3 \cdot \vec{a}_3 \kappa_z \; .$$

Here $\vec{i}_1$, $\vec{i}_2$, and $\vec{i}_3$ are the cartesian unit vectors, and $\vec{i}_3$ is normal to the surface of the crystal. Note that κ_1 and κ_2 are purely real, while κ_3 has an imaginary component because of the term in κ_z.

V. THE DETERMINATION OF SURFACE STRUCTURES

The foregoing formulas can be used to calculate the scattering pattern produced by surface layers whose structure or composition differs from that of the bulk material. Because of experimental errors and lack of symmetry it may not be feasible to perform Fourier inversions of the observed scattering to determine atomic positions directly, although the

formalism for this could be worked out. More practical is the comparison with experiment of predicted scattering based on various plausible models of surface structure. We present here some simple examples of how such calculations can be made.

Equation (33), which was calculated on the assumption of a perfect crystal, can be modified readily to allow for imperfections. Suppose we choose the unit cell so that the basis vector $\vec{a}_1$ and $\vec{a}_2$ correspond to the horizontal periodicities in the surface layer (this period may be larger than in the bulk—see, e.g., Eisenberger and Marra[1]). Distortions near the surface do not repeat in the direction normal to the surface and therefore the unit cell will be chosen to be indefinitely elongated in this direction (the basis vector $\vec{a}_3$ will be suitably increased). Its actual dimension will be immaterial as long as it is somewhat greater than the penetration depth l, given by Eq. (11). With these conventions, there is only one term in the summation over n_3 leading to Eq. (33), and the cellular structure factor, F, contains all the effects of the surface distortions through the intracellular coordinates $\vec{q}_j$. If the penetration depth is small and there are not many atoms in the unit cell, trial values of $\vec{q}_j$ may be inserted into (35) directly and comparison made with

experiment. An alternative is to write

$$\vec{q}_j = \vec{Q}_j + \vec{v}_j \ ,$$

where $\vec{Q}_j$ is the position of the jth atom in the elongated unit cell for the perfect crystal and $\vec{v}_j$ is the displacement from perfection caused by the surface. Normally the $\vec{v}_j$ will approach zero rapidly as one goes away from the surface, usually in a distance short compared with l. In this situation it is convenient to rewrite F as

$$F = \sum_{j=1}^{\infty} f_j (e^{i\vec{\kappa}\cdot(\vec{Q}_j+\vec{v}_j)} - e^{i\vec{\kappa}\cdot\vec{Q}_j}) + \sum_{j=1}^{\infty} f_j e^{i\vec{\kappa}\cdot\vec{Q}_j} \ .$$

(36)

The second term in (36) can be calculated by summing over one original unit cell and then over a column of unit cells in the direction of $\vec{a}_3$, to become $F(1-e^{-i\kappa_3}).^{-1}$ This multiplied by the rest of the expression for $\vec{\mathcal{E}}$ gives Eq. (34) again. The first term in (36) gives the alteration in scattering caused by the atomic displacements. It may be calculated by summing over one or only a small number of layers near the surface, or, in the case where all displacements are small, by expanding $e^{i\vec{\kappa}\cdot\vec{v}_j}$ to first order in $\vec{\kappa}\cdot\vec{v}_j$. To recapitulate, with this procedure, one finds

$$\vec{\mathcal{E}}_s = \vec{A}e^{i\psi}F\frac{\sin(\frac{1}{2}\kappa_1 N_1)}{\sin(\frac{1}{2}\kappa_1)}\frac{\sin(\frac{1}{2}\kappa_2 N_2)}{\sin(\frac{1}{2}\kappa_2)}\frac{1}{1-e^{-i\kappa_3}} + \vec{A}e^{i\psi}\frac{\sin(\frac{1}{2}\kappa_1 N_1)}{\sin(\frac{1}{2}\kappa_1)}\frac{\sin(\frac{1}{2}\kappa_2 N_2)}{\sin(\frac{1}{2}\kappa_2)}\sum_{j=1}^{\bar{j}} f_j e^{i\vec{\kappa}\cdot\vec{Q}_j}(e^{i\vec{\kappa}\cdot\vec{v}_j}-1) \ .$$

(37)

In the last term the summation over j has been cut off at a limit $\bar{j}$ at which the summand becomes negligible. As has been shown, the first term in (37) is large only in the vicinity of points of the perfect reciprocal lattice. The second term is broader and may be determined by measurements of scattered intensity away from the reciprocal-lattice points. If the surface layer has a larger period the term will include contributions from the superlattice points.

Another possibility is a surface layer that is crystalline but not in registry with the underlying lattice, or a surface layer that is amorphous. All of these are embraced by the general formula (22) where it is to be remembered that, because of the imaginary component of κ_z, the summation need extend only over the surface layer to a depth somewhat greater than l. Because of the variety of possible arrangements a variety of formulas can be developed in a straightforward manner; they will not be elaborated upon here.

VI. INTRODUCTION OF ABSORPTION

So far the specimen has been assumed to be nonabsorbing. In practice some absorption is always present, and at a low angle of incidence the penetration will be limited on this account, even if the incidence angle is larger than the critical angle for total external reflection. The distorted-wave approach can be generalized to allow for this. One only needs to assume that the permittivity of the distorting medium is complex. It is not necessary to allow for absorption in the second stage of the calculation because the scattered waves travel through only small distances in the medium. Previously the distorting medium was characterized by a uniform permittivity $\epsilon' = 1 - \delta'$, where δ' was real and was given by the second term on the right-hand side of Eq. (1). If the medium has a linear absorption coefficient for x-ray power μ this is equivalent to adding an imaginary part δ_i' to δ' which is given

by[8]

$$\delta_i' = \frac{-\mu}{k} = \frac{-\lambda\mu}{2\pi} . \quad (38)$$

Then

$$\epsilon' = 1 - \delta' - i\delta_i' , \quad (39)$$

and both δ' and δ_i' are much smaller than 1. The solution to Maxwell's equations exhibited in Sec. II remain valid with this modification. In Eqs. (13) and elsewhere δ' is replaced by $\delta' + i\delta_i'$. External reflection below α_c is no longer total, but for δ_i' small compared with δ', which is usually the case, it is nearly total.

However, the characteristic depth of propagation into the specimen now is limited at all angles of incidence. The relevant wave vector k_z' is given by

$$k_z' = -k(\sin^2\alpha - \delta' - i\delta_i')^{1/2}$$
$$\cong -k(\alpha^2 - \delta' - i\delta_i')^{1/2} . \quad (40)$$

Note that k_x' and k_y' remain real and are not changed by the introduction of δ_i'.

If α is appreciably larger than α_c, but still small, we have

$$k_z' \cong -k\alpha \left[1 - \frac{\delta'}{2\alpha^2} \right] + ik\frac{\delta_i'}{2\alpha} . \quad (41)$$

The characteristic depth l for fields now becomes

$$l = \frac{1}{|\mathrm{Im}k_z|} \cong \frac{2\alpha}{k|\delta_i'|} = \frac{2\alpha}{\mu} . \quad (42)$$

The factor 2 on the right-hand side of (42) must be removed if we want the characteristic depth for energy.

For light elements and for x rays in the vicinity of 1 or 2 Å, μ ranges from about 1 to 1000 cm^{-1}, depending sensitively on wavelength. For heavy elements it ranges up to 10^4 cm^{-1} (e.g., Pb at 2.74 Å). Thus for $\alpha = 0.01$ rad, l can be as small as 1000 Å for light elements and 100 Å for heavy elements. Thus in some cases absorption may provide attenuation in the specimen at angles somewhat above the critical angle qualitatively similar to that provided by total external reflection below the critical angle, and which may allow diffraction measurements of surface structure to be made in the manner discussed above. A technical modification of the formulas arises because k_z' now has a real component, but this merely changes the real component of κ_z [Eq. (23c)] by a small amount. Below the critical angle, absorption will not ordinarily produce a large effect compared with the real part of $1 - \epsilon$ but it

can easily be taken into account by the formulas given.

VII. FURTHER CONSIDERATIONS AND CONCLUSIONS

Slow neutrons could be used for surface studies instead of x rays, since most substances have an index of refraction for thermal neutrons which is less than unity and therefore cause total external reflection of neutrons at low angles of incidence.[9] Typical critical angles for neutrons are comparable with those for x rays. However, a further degree of control arises in the case of magnetic materials because the magnetization of a substance produces an additional birefringent component of the index of refraction for neutrons. This suggests the interesting possibility of observing in a new way the near-surface part of the magnetization. There is experimental evidence of a "dead layer" on the surfaces of several magnetic substances,[10] and suggestions have also been made that the surface layer of some nonmagnetic materials could possess a net magnetic moment. There would also be inelastic scattering processes in which the neutron energy is altered by a relatively large factor and which conceivably could be observed. Although the low intensities available will cause problems, the observations would have special interest because they could reveal preferentially the frequencies and momenta of surface phonons. A theory for this effect can be written down using the distorted-wave approach of this paper, but will not be given here. A final possibility of such inelastic experiments would be the observation of surface magnons. Mazur and Mills[11] have recently calculated the cross section for such a scattering process, employing a distorted-wave approach similar to that used here.

One further opportunity for useful experiments suggests itself: X-ray fluorescence analysis of the surface layers alone could be carried out by illuminating the specimen at grazing incidence so that only atoms in or very near the surface would be excited. Equations (7) and (13) allow the calculation of the pattern of exciting electric field which would be present. Since the affected atoms would be very near the surface, x-ray photoemission might also be measured.[12]

The accuracy of the distorted-wave method employed here deserves to be investigated further. Relatively little is known on this general subject (a recent study for a compact scatterer, as opposed to the distributed scatterer dealt with in this paper, has

been reported by MacMillan and Redish[13]). If the scattering specimen has a surface layer of substantially different properties than the bulk, the dielectric slab could be allowed to have a smooth z dependence of its permittivity. The illuminating wave would then have a profile in z different from exponential damping and interesting variations on the basic problem treated here might be found. More work is indicated.

ACKNOWLEDGMENTS

APPENDIX A: FORMAL DEVELOPMENT OF THE DISTORTED-WAVE APPROXIMATION FOR THE ELECTROMAGNETIC FIELD

We start with Maxwell's equations (2), allowing ϵ to be an arbitrary function of position and setting $\epsilon = 1 - \delta$. We separate out the time dependence through the factor $e^{-i\omega t}$ and set $k = \omega/c$. Then the equations satisfied by $\vec{\mathscr{E}}$ become

$$-\vec{\nabla} \times \vec{\nabla} \times \vec{\mathscr{E}} + k^2 \vec{\mathscr{E}} = k^2 \delta \vec{\mathscr{E}} , \qquad (A1)$$

$$\vec{\nabla} \cdot (1 - \delta) \vec{\mathscr{E}} = 0 . \qquad (A2)$$

Note that, because of (A2) the right-hand side of (A1) is not divergence free. However, if $\vec{\mathscr{E}}$ satisfies (A1), it also satisfies (A2), which follows from the identity $\vec{\nabla} \cdot \vec{\nabla} \times \vec{\nabla} \times \vec{\mathscr{E}} = 0$.

Tensor Green's functions for the vector Helmholtz Eq. (A1) are known and are discussed in some detail in Ref. 14 (pp. 1777—1783.) The necessary function, $\mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k)$, allows (A1) to be transformed into an integral equation,

$$\vec{\mathscr{E}}(\vec{r}) = \vec{\mathscr{E}}_0(\vec{r}) - \frac{k^2}{4\pi} \int \mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k) \cdot \delta(\vec{r}')$$
$$\times \vec{\mathscr{E}}(\vec{r}'') dv' , \qquad (A3)$$

where $\vec{\mathscr{E}}_0(\vec{r})$ satisfies the homogeneous equation

$$-\vec{\nabla} \times \vec{\nabla} \times \vec{\mathscr{E}}_0 + k^2 \vec{\mathscr{E}}_0 = 0$$

and

$$\vec{\nabla} \cdot \vec{\mathscr{E}}_0 = 0 .$$

If $\vec{\mathscr{E}}(r')$ on the right-hand side of (A3) is replaced by $\vec{\mathscr{E}}_0(r')$ this gives just the Born approximation.

To arrive at the distorted-wave approximation as used in this paper, write, as before

$$\delta(\vec{r}) = \delta_1(\vec{r}) + \delta_2(\vec{r}) ,$$

where $\delta_1(\vec{r})$ is the distorting component of the permittivity, and insert into (A3), giving

$$\vec{\mathscr{E}}(\vec{r}) = \vec{\mathscr{E}}_0(\vec{r}) - \frac{k^2}{4\pi} \int \mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k) \cdot \delta_1(\vec{r}') \vec{\mathscr{E}}(\vec{r}'') dv' - \frac{k^2}{4\pi} \int \mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k) \cdot \delta_2(\vec{r}') \vec{\mathscr{E}}(\vec{r}'') dv' . \qquad (A4)$$

The approximation now consists in replacing $\vec{\mathscr{E}}$ in both integrals on the right-hand side of (A4) by $\vec{\mathscr{E}}_1$, where $\vec{\mathscr{E}}_1$ is the distorted wave, which satisfies

$$\vec{\mathscr{E}}_1(\vec{r}) = \vec{\mathscr{E}}_0(\vec{r}) - \frac{k^2}{4\pi} \int \mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k) \cdot \delta_1(\vec{r}') \vec{\mathscr{E}}_1(\vec{r}'') dv' . \qquad (A5)$$

As a result,

$$\vec{\mathscr{E}}(\vec{r}) \cong \vec{\mathscr{E}}_1(\vec{r}) - \frac{k^2}{4\pi} \int \mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k) \cdot \delta_2(\vec{r}') \vec{\mathscr{E}}_1(\vec{r}'') dv' . \qquad (A6)$$

The Green's function $\mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k)$ differs from the purely transverse Green's function by subtraction of a longitudinal δ function of $(\vec{r} - \vec{r}')$ (see Ref. 14). For application to our problem it is necessary to know $\mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k)$ only when $|\vec{r} - \vec{r}'| = R$ is large. The limiting form is

$$\mathscr{G}_c(\vec{r} \mid \vec{r}' \mid k) = - \left[I - \frac{\vec{R}\vec{R}}{R^2} \right] \frac{e^{ikR}}{R} . \qquad (A7)$$

Inserting (A7) in (A6), employing (1) to determine $\delta_2(\vec{r})$, setting $\vec{R}/R = \vec{s}$, and $kR = k\vec{s} \cdot (\vec{r} - \vec{r}')$ in the exponent of (A7), one arrives at Eq. (16).

APPENDIX B: THE STRATIFIED LATTICE: A MODEL THAT CAN BE SOLVED EXACTLY

We consider here a model in which the three-dimensional lattice is replaced by a layered lattice with the dielectric material distributed uniformly in the lattice planes parallel to the surface of the specimen. The planes are also assumed to be very thin compared with the lattice spacing. Maxwell's equations in this stratified structure can be reduced to a one-dimensional scalar-wave equation with a periodic distribution of scattering matter.[15] For technical reasons the transverse magnetic polarization is somewhat intricate and we first limit the discussion to the case of transverse electric polarization. For the latter case the distribution of dielectric material can be considered to be a sum of equally spaced δ functions, and this problem is mathematically equivalent to the well-known Kronig-Penney model of electrons in a crystal lattice.[16] The virtue of this model is that it is solvable in simple analytic form (see particularly Saxon and Hutner[17]).

We let M be the number of atoms per unit area in each atomic plane, with f_0 electrons per atom. Let the interplanar spacing be d, and take the z axis perpendicular to the planes, pointing into the specimen, with the plane $z=0$ bounding the specimen (note the reversal of z from Fig. 1). Then the permittivity can be written as

$$\epsilon(\vec{r})=1, \quad z<0$$

and

$$\epsilon(\vec{r})=1-\frac{r_e\lambda^2 Mf_0}{\pi}\sum_{n=0}^{\infty}\delta_D(z-nd), \quad z\geq 0 \tag{B1}$$

where δ_D is the Dirac δ function and r_e is the classical electron radius, e^2/mc^2. Maxwell's equations, as given in Appendix A, are to be solved using this permittivity as a coefficient.

In the case of transverse electric polarization the electric field has only a y component, $\mathscr{E}_y$, and $\mathscr{E}_y$ depends only on x and z. Maxwell's equations require

$$\frac{\partial^2\mathscr{E}_y}{\partial x^2}+\frac{\partial^2\mathscr{E}_y}{\partial z^2}+k^2\epsilon\mathscr{E}_y=0 . \tag{B2}$$

Setting $\mathscr{E}_y=X(x)U(z)$ this becomes

$$\frac{d^2U}{dz^2}+k^2(\epsilon-\beta^2)U=0 \tag{B3}$$

and

$$\frac{d^2X}{dx^2}+k^2\beta^2 X=0 . \tag{B4}$$

β is a separation constant which will later be set equal to $\cos\alpha$, where α is the (glancing) angle of incidence. Equation (B4) gives $X=e^{ik\mu x}$. For $z<0$ the solution of (B3) is

$$U(z)=e^{ik(1-\beta^2)^{1/2}z}+Re^{-ik(1-\beta^2)^{1/2}z} , \tag{B5}$$

where R is a constant, the reflection coefficient. For $z\geq 0$ (B3) with (B1) becomes the Schrödinger equation of the Kronig-Penney model. Its solutions have the form $e^{i\mu z}\phi(z)$ where $\phi(z)$ has the period of the lattice and μ, the Bloch parameter, is determined by the relation

$$\cos\mu d=\cos Kd+\frac{C}{2K}\sin Kd . \tag{B6}$$

Here $K=k(1-\beta^2)^{1/2}$ and $C=4\pi r_e Mf_0$. As shown by Saxon and Hutner,[17] the solution of (B3) can be written

$$U(z)=\frac{C}{2K}U(0)e^{i\mu nd}\left[\frac{e^{i\mu d}\sin K(z-d)-\sin K(z-nd-d)}{\cos\mu d-\cos Kd}\right] , \quad nd\leq z\leq nd+d , \quad n=0,1,2,\ldots . \tag{B7}$$

Despite the singularities in ϵ at the lattice points $U(z)$ is continuous everywhere. However, the derivative $U'(z)$ has a discontinuity at each lattice point such that

$$\lim_{\sigma\to 0}[U'(nd+\sigma)-U'(nd-\sigma)]=CU(nd) . \tag{B8}$$

Between each pair of lattice points $U(z)$ is a simple harmonic wave with wave number K, as seen from (B7). The boundary conditions at $z=0$ and ∞, the discontinuities of U' at each lattice point, and the harmonic behavior between, serve to determine $U(z)$ completely.

We take the surface of the crystal at $z=-\sigma$, where σ is an arbitrarily small positive number, and match the fields on this surface. The tangential components of electric and magnetic fields must be continuous, which requires continuity of $\mathscr{E}_y$ and $\partial\mathscr{E}_y/\partial z$. From these conditions one finds

$$U(0)=1+R=\frac{2\sin Kd}{\sin Kd-i\cos Kd+ie^{-i\mu d}} \tag{B9}$$

and

$$R = \frac{\sin Kd + i\cos Kd - ie^{-i\mu d}}{\sin Kd - i\cos Kd + ie^{-i\mu d}} \ . \tag{B10}$$

Equation (B6) shows that for $C > 0$, μ is purely imaginary for sufficiently small K and becomes real at a critical value, K_c. For $0 \leq K < K_c$ we set $\mu = +i\,|\mu|$ (the positive sign is required for the solution to be bounded as $z \to \infty$). In the range where μ is imaginary $|R| = 1$, as is evident from (B10). For $C < 0$ note that $K_c = 0$, so that there is no stop band at low K and total external reflection does not occur except near the Bragg angles. Negative C corresponds to an index of refraction of the medium that is larger than one. In the range where μ is imaginary the wave is damped exponentially in z, and the depth in the crystal at which fields are attenuated by e^{-1} is

$$l = \frac{1}{|\mu|} \ . \tag{B11}$$

Since $Kd = kd\sin\alpha \ll 1$ in examples of interest here the right-hand side of (B6) may be expanded in powers of KD, recognizing that also $Cd \ll 1$, to give

$$\cos\mu d \cong 1 + \frac{Cd}{2} - \frac{1}{2}(Kd)^2 \ , \tag{B12}$$

from which, with (B7), it follows that

$$K_c^2 = \frac{\dfrac{C}{d}}{1 + \dfrac{C}{6d}} \cong \frac{C}{d} = \frac{4\pi r_e M f_0}{d}$$

or

$$\alpha_c = \left[\frac{r_e\lambda^2 M f_0}{\pi d}\right]^{1/2} \ .$$

Since $M f_0/d$ is the average number of electrons per unit volume in the crystal, this agrees with the optical formula for total external reflection from a homogeneous slab, as given in Eqs. (1) and (12).

Finally (B11) and (B12) give

$$l = \frac{d}{\cosh^{-1}\left[1 + \dfrac{CD}{2} - \dfrac{K^2 d^2}{2}\right]} \ .$$

With the approximation, valid for small x, $\cosh^{-1}(1 + x) \cong \sqrt{2x}$, this becomes

$$l = \frac{1}{\left[\dfrac{C}{d} - K^2\right]^{1/2}} = \frac{\lambda}{2\pi(\alpha_c^2 - \alpha^2)^{1/2}} \ , \tag{B13}$$

which is identical with Eq. (11) for the homogeneous slab.

Employing (B7) and (B6) and the expression given earlier for X, the electric field in the crystal for angles less than the critical angle can now be written

$$\mathcal{E}_y(z) = U(0)\left[\frac{e^{-|\mu|d}\sin K(z - nd) - \sin K(z - nd - d)}{\sin Kd}\right]e^{-|\mu|nd + ik\beta x} \ , \quad nd \leq z \leq nd + d, \quad n = 0,1,2,\dots \ . \tag{B14}$$

One can eliminate $U(0)$ with the aid of (B9) and (B10). If one then expands the trigonometric and exponential functions to first order in the small quantities $Kd = kd\alpha$ and $|\mu|d = kd(\alpha_c^2 - \alpha^2)^{1/2}$ [the latter expression comes from (B11) and (B13)] one finds

$$\mathcal{E}_y(nd) = \frac{2\alpha}{\alpha + i(\alpha_c^2 - \alpha^2)^{1/2}}e^{-|\mu|nd + i(k\cos\alpha)x} \ . \tag{B15}$$

This agrees precisely at $z = nd$ with the field found in Sec. II B for the homogeneous slab [refer to Eq. (14), recognizing that $E = 1$ and $\delta = 0$ in this appendix, and $\delta' = \alpha_c^2$].

Thus, for transverse polarization and for small

angles of incidence we have demonstrated that the value of the field at each lattice plane agrees with that calculated for the homogeneous dielectric slab. There remains to be considered the fluctuating factor in large parentheses in (B14), which causes the field to differ from that in the homogeneous slab. As z increases from nd to $nd + d$ this factor goes from 1 to $e^{-|\mu|d}$ and represents an interpolation between these values. In exaggerated form, the expression (B14) is shown as a function of z in Fig. 3, along with the simple damped exponential for the field in the homogeneous slab. The fractional differences are maximal near the midpoints $(n + \frac{1}{2})d$ and are denoted by Δ.

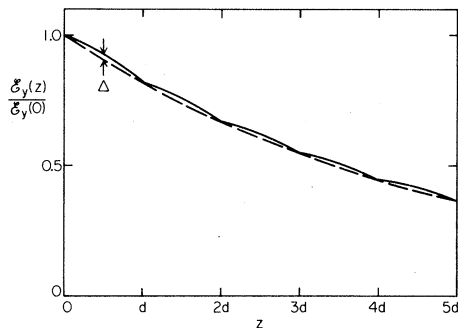Consideration of the factor in large parentheses in Eq. (B14) gives the following estimate for Δ,

FIG. 3. $\mathscr{E}_y(z)$ from Eq. (B14), solid line, compared with the field in the homogeneous dielectric slab, dashed line. Fractional difference in the fields at the midpoints of the intervals is indicated as $\triangle$. Difference is greatly exaggerated in the figure.

which is valid to second order in small quantities:

$$\triangle \cong \frac{(Kd)^2}{12} + \frac{(\,|\mu\,|\,d)^2}{8} \, . \tag{B16}$$

An illustrative calculation can be made for the case of copper $K\alpha$ radiation ($\lambda = 1.54$ Å) incident on the (100) face of germanium at one-half the critical angle. In this example, $d = 1.41$ Å, $l = 52$ Å, and the critical angle, α_c, is 5.4 mrad. It is found that $\triangle \cong 10^{-4}$. Thus the difference between the two curves in Fig. 3 should actually be less than the width of the line in the drawing.

In a crystal the electron density in each lattice plane is spread out over a considerable part of the interplanar distance and thus the δ-function distribution differs more severely from the homogeneous model than does a real substance. It would thus be expected that the field in a real crystal would depart from the field in a homogeneous slab by less than that calculated above, as long as the effects of the lattice are primarily confined to the z dependence of $\epsilon(\vec{r})$.

For transverse magnetic polarization, nonphysical behavior occurs if the lattice planes are assumed infinitely thin (essentially because $\vec{\mathscr{E}}$ now has a z component and this responds anomalously to the negative dielectric constant in the planes). Instead, the planes can be assumed to be layers that are thin compared with the interplanar separation, d, but thick enough that the dielectric constant within them departs from unity by only a small amount. The parameters of real crystals at x-ray wavelengths permit these conditions to be met and the results are insensitive to the exact choice of layer thickness. The magnitude of the field within the crystal model now becomes the same, to first order in α, as that for the transverse electric polarization, and is again very closely the same as in the equivalent homogeneous slab. From these considerations we conclude that the homogeneous slab is an excellent basis for calculating the distorted wave and determining the scattering from surface distortions in conditions of grazing incidence.

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