Expanded Distorted-Wave Theory for Phase-Sensitive X-Ray Diffraction in Single Crystals

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(Received 15 June 1999)

We present an expanded distorted-wave theory for x-ray diffraction from a crystal. By adding a single sinusoidal component to the distorting susceptibility, the new theory provides a simple first-principle approach to the phase-sensitive scattering phenomenon in reference-beam diffraction experiments.

PACS numbers: 61.10.Dp, 78.70.Ck

Diffraction of x rays is a widely used technique for studying structural information in condensed matter. One of the main advantages of this structural technique is that the diffracted intensities measured in experiments can be easily interpreted by a simple *kinematic* theory [1–3] that is based on the first-order Born approximation where single scattering events are the predominant mechanism. The kinematic theory, however, is intrinsically limited by the phase problem of diffraction, i.e., its result is generally insensitive to the phases of scattering amplitudes even though both the phases and the magnitudes are needed for solving a complex structure. The only existing diffraction theory to date that can be phase sensitive is the so-called *dynamical* theory [4,5], which includes all possible interactions among multiply excited Bragg reflection waves inside a crystal. Unfortunately, this theory is rather complicated in its mathematical formulation, especially in the case of multiple Bragg waves [5], and it is generally viewed as a specialist's theory and is rarely used in everyday x-ray diffraction and crystallography analyses.

The practical need for a simple, phase-sensitive, first-principle x-ray diffraction theory is greatly exemplified by the recent experimental innovation of *reference-beam* diffraction [6,7], which in principle allows a phase-sensitive intensity data collection of a large number of Bragg reflections using a routine crystallography setup. With this new technique, it is conceivable that every Bragg diffracted beam from a crystalline specimen contains a multiple-beam interference component that can be analyzed by a phase-sensitive diffraction theory to provide the desired information for solving the crystallographic phase problem. It is thus the purpose of this Letter to furnish such a simple phase-sensitive theory that is easy to use, and at the same time provides an intuitive physical picture of the reference-beam diffraction process.

Previous efforts to develop an approximate phase-sensitive theory have been based mainly on a perturbational approach [8,9]. In this approach, one calculates the diffracted intensity of a single main Bragg reflection, and treats the additional Bragg waves as perturbations to the main reflection. The results in general provide good descriptions on the tails of a multiple reflection interference peak, but diverge at the center of the peak where the multiple reflection is fully excited. The failure at the peak center is intrinsic within the perturbational framework, and a much different approach is needed in order to solve this problem.

The new phase-sensitive approach that we present in this Letter is based on a distorted-wave Born approximation (DWA) in quantum mechanical scattering theory [10] used in calculations of nuclear collisions [11]. For x rays, the only existing application of the DWA theory, to our knowledge, is in the area of grazing-angle diffraction and scattering from surface structures [12–14], in which the scattering medium is first approximated by its zeroth-order Fourier component representing the average homogeneous substance. The scattering problem for this averaged scatter, termed the distorting component, is solved by the standard optical theory and a distorted wave, i.e., the Fresnel wave, is obtained. This distorted wave is then rescattered by surface roughness or other inhomogeneous surface structures, and this part of the problem is solved using the Born approximation.

Our new theoretical approach, which we will refer to as an expanded distorted-wave approximation (EDWA), follows closely to the algorithm of the conventional DWA for x rays outlined above, with an important revision that a *sinusoidal* Fourier component $\mathbf{G}$ is added to the distorting component of the electric dielectric function. This sinusoidal component represents a perturbing reference $\mathbf{G}$ charge density component used to excite a reference beam, and the resulting distorted wave is in fact composed of two waves, $\mathbf{O}$ and $\mathbf{G}$ waves. Instead of the Fresnel theory, a two-beam dynamical theory is employed to evaluate these distorted waves, while the subsequent scattering of these waves is again handled by the Born approximation. The final result is a simple analytical expression of a phase-sensitive diffracted intensity that is valid for all measured Bragg reflections and for the entire excitation range of the reference reflection $\mathbf{G}$ in a reference-beam diffraction experiment.

The fundamental equation that governs the scattering of an x-ray plane wave, $\mathbf{D}_0(\mathbf{r}) = \mathbf{D}_0^{(0)} \exp(-i\mathbf{k}_0 \cdot \mathbf{r})$, by a crystal with an electric susceptibility $\chi(\mathbf{r}) =$

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$-(r_e\lambda^2/\pi)\rho(\mathbf{r})$ is given by

$$(\nabla^2 + k_0^2)\mathbf{D} = -\nabla \times \nabla \times (\chi \mathbf{D}), \qquad (1)$$

where $\mathbf{D}$ is the electric displacement vector, $r_e = 2.818 \times 10^{-5}$ Å is the classical radius of an electron, λ is the x-ray wavelength, and $k_0 = 2\pi/\lambda$. The electron density $\rho(\mathbf{r})$ is a periodic function of the crystal lattice and can be expanded into a Fourier series: $\rho(\mathbf{r}) = (1/V_c)\sum_H F_H \exp(-i\mathbf{H}\cdot\mathbf{r})$, where V_c is the unit-cell volume and F_H are the structure factors. The differential equation (1) is equivalent to the following integral equation [2,9]:

$$\mathbf{D}(\mathbf{r}) = \mathbf{D}_0(\mathbf{r}) + \frac{1}{4\pi}\int d\mathbf{r}' \frac{\exp(-ik_0|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\nabla' \times \nabla' \times [\chi(\mathbf{r}')\mathbf{D}(\mathbf{r}')]. \qquad (2)$$

Following the formal description of the distorted-wave approximation given in Ref. [12], we separate $\chi(\mathbf{r})$ into a distorting component $\chi_1(\mathbf{r})$ and the remaining part $\chi_2(\mathbf{r})$:

$$\chi(\mathbf{r}) = \chi_1(\mathbf{r}) + \chi_2(\mathbf{r}).$$

In the conventional distorted-wave description, $\chi_1(\mathbf{r})$ contains only the homogeneous average susceptibility $\chi_0 = -\Gamma F_0$ inside the crystal, where $\Gamma = r_e\lambda^2/(\pi V_c)$. In our new expanded distorted-wave approximation, we add a single predominant Fourier component $\mathbf{G}$ to $\chi_1(\mathbf{r})$ so that the total distorting component is given by

$$\chi_1(\mathbf{r}) = -\Gamma(F_0 + F_G e^{-i\mathbf{G}\cdot\mathbf{r}} + F_{-G}e^{i\mathbf{G}\cdot\mathbf{r}}), \qquad (3)$$

and the remaining $\chi_2(\mathbf{r})$ is thus

$$\chi_2(\mathbf{r}) = -\Gamma \sum_{L\neq 0,\pm G} F_L e^{-i\mathbf{L}\cdot\mathbf{r}}. \qquad (4)$$

Writing out explicitly that $F_G = |F_G|\exp(i\alpha_G)$ and $F_{-G} = F_G^* = |F_G|\exp(-i\alpha_G)$ when anomalous dispersion corrections are negligible, it can be seen that the additional component in Eq. (3) represents simply a sinusoidal distortion, $-2\Gamma|F_G|\cos(\alpha_G - \mathbf{G}\cdot\mathbf{r})$, as illustrated schematically in Fig. 1.

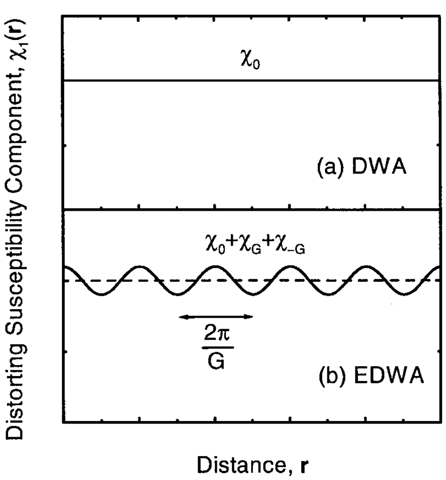

FIG. 1. Schematic illustration of the distorting susceptibility in (a) distorted-wave approximation (DWA) and (b) expanded distorted-wave approximation (EDWA).

The distorted-wave solution of Eq. (2) is a two-step process. First, we solve for the distorted wave $\mathbf{D}_1(\mathbf{r})$ due only to $\chi_1(\mathbf{r})$, which satisfies Eq. (2) with $\chi(\mathbf{r})$ substituted by $\chi_1(\mathbf{r})$. However, since Eq. (2) is equivalent to Eq. (1), this part of the solution can be obtained by solving

$$(\nabla^2 + k_0^2)\mathbf{D}_1 = -\nabla \times \nabla \times (\chi_1 \mathbf{D}_1). \qquad (5)$$

Since only $\mathbf{O}$ and $\mathbf{G}$ Fourier components are involved in $\chi_1(\mathbf{r})$, Eq. (5) represents a simple two-beam case and can therefore be solved by the standard dynamical theory [4]. For clarity, we assume a parallel plate sample geometry with b being the ratio of the normal component of the incident wave vector $\mathbf{k}_0$ to that of the reflected $\mathbf{k}_G = \mathbf{k}_0 + \mathbf{G}$. In addition, we assume that the incident beam polarization direction $\mathbf{D}_0$ is perpendicular to the scattering plane formed by $\mathbf{k}_0$ and $\mathbf{k}_G$. Using a normalized angular parameter

$$\eta_G = \frac{b(\theta - \theta_G)\sin 2\theta_G + \Gamma F_0(1-b)/2}{\Gamma(|b|F_G F_{-G})^{1/2}},$$

the field ratio r_G between the $\mathbf{G}$ and the $\mathbf{O}$ waves inside the crystal is given by [4]:

$$\mathbf{D}_G = r_G \mathbf{D}_0 = -(|b|F_G/F_{-G})^{1/2}[\eta_G \pm (\eta_G + b/|b|)^{1/2}]\mathbf{D}_0, \qquad (6)$$

where the choice of $\pm$ is such that a smaller $|r_G|$ is retained. An example of r_G is shown in Fig. 2(a) for GaAs (004).

The total distorted wave is given by the sum of the $\mathbf{G}$ and the $\mathbf{O}$ waves:

$$\mathbf{D}_1(\mathbf{r}) = \mathbf{D}_0 e^{-i\mathbf{K}_0\cdot\mathbf{r}} + \mathbf{D}_G e^{-i\mathbf{K}_G\cdot\mathbf{r}}. \qquad (7)$$

Here we use capital $\mathbf{K}$'s to indicate that these are *internal* waves inside the crystal, $\mathbf{K}_G = \mathbf{K}_0 + \mathbf{G}$. To obtain the absolute field strengths, we would apply the boundary conditions that are used in standard dynamical theory [4,5] to express $\mathbf{D}_0$ and $\mathbf{D}_G$ in terms of $\mathbf{D}_0^{(0)}$ of the incident wave. It is important to note that these fields include such dynamical effects as primary extinction in Bragg reflection geometry and the Pendellosung effect in Laue transmission geometry. For convenience, we separate out the slow-varying exponentials of the imaginary parts of $\mathbf{K}_0$ and $\mathbf{K}_G$ and include them in $\mathbf{D}_0$ and $\mathbf{D}_G$, so that $\mathbf{K}_0$ and $\mathbf{K}_G$ in Eq. (7) are only referring to their real parts.

The second step of the expanded distorted-wave solution is to evaluate the scattering of the total distorted wave, Eq. (7), by the remaining susceptibility component $\chi_2(\mathbf{r})$, as is done in the conventional distorted-wave Born approximation [12]:

$$\mathbf{D}(\mathbf{r}) = \mathbf{D}_1(\mathbf{r}) + \frac{1}{4\pi}\int d\mathbf{r}' \frac{\exp(-ik_0|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\nabla' \times \nabla' \times [\chi_2(\mathbf{r}')\mathbf{D}_1(\mathbf{r}')]. \qquad (8)$$

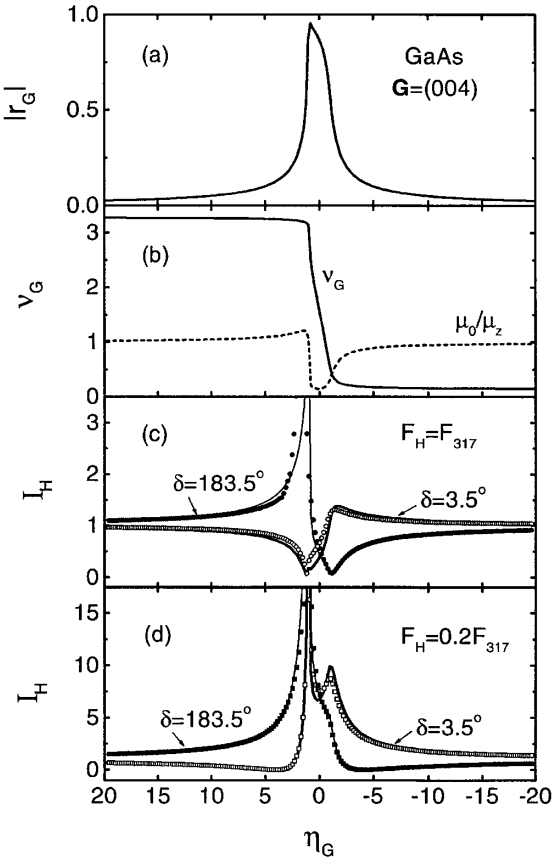

FIG. 2. Calculated results of expanded distorted-wave approximation for $\mathbf{G} = (004)$ and $\mathbf{H} = (317)$ of GaAs in reference-beam geometry. (a) Field ratio $|r_G|$ for $\mathbf{G} = (004)$. (b) Dynamical phase shift ν_G and exctinction correction μ_0/μ_z for the (004). (c) Normalized intensity of $\mathbf{H} = (317)$ with the correct triplet phase $\delta = 3.5°$ (thick line) and an artificial phase $\delta = 183.5°$ (thin line), using the EDWA theory. The open and filled circles are the corresponding full dynamical N-beam calculations. (d) Same as (c) except that the (317) structure factor is reduced by a factor of 5 to illustrate the *Umweganregung* effect.

The first term in Eq. (7), $\mathbf{D}_0 \exp(-i\mathbf{K}_0 \cdot \mathbf{r})$, gives rise to a scattered wave field $\mathbf{D}_0'$. The mathematics is similar to that used in the first-order Born approximation [9], except that the primary extinction effect due to $\mathbf{G}$ reflection has been accounted for in $\mathbf{D}_0$ which is now a function of $\mathbf{r}'$. However, since a typical extinction length is on the order of many micrometers, $\mathbf{D}_0$ is a slow-varying function, and thus can be replaced by its average value $\overline{\mathbf{D}}_0$ over the extinction depth and taken out of the volume integral. For a thick parallel plate Bragg geometry, it can be shown that the averaged field intensity $|\overline{\mathbf{D}}_0|^2$, normalized to the conventional absorption coefficient μ_0 along the surface normal, is given by $|\overline{\mathbf{D}}_0|^2 = |\mathbf{D}_0^{(0)}|^2 \mu_0/\mu_z$, where μ_z is the effective absorption coefficient including extinction [15]: $\mu_z = \mu_0[1 + \mathrm{Im}(F_{-G} r_G)/F_0'']$, with F_0'' being the imaginary part of the zeroth-order structure factor F_0. An example of μ_0/μ_z is shown in Fig. 2(b) for GaAs (004) reflection. With the above approximation and using the algebra detailed in Ref. [9], we obtain

$$\mathbf{D}_0'(\mathbf{r}) = N r_e F_H \mathbf{u} \times (\mathbf{u} \times \overline{\mathbf{D}}_0) \frac{e^{-ik_0 r}}{r}, \quad (9)$$

where N is the number of unit cells in the crystal participating in the scattering process, and we have assumed that the crystal is oriented in such a way that another set of atomic planes, $\mathbf{H}$, satisfies the Bragg's law, $k_0\mathbf{u} = \mathbf{K}_0 + \mathbf{H} \equiv \mathbf{K}_H$, with $\mathbf{u}$ being a unit vector.

The scattering of the second term in Eq. (7), $\mathbf{D}_G \exp(-i\mathbf{K}_G \cdot \mathbf{r})$, gives rise to a scattered wave field $\mathbf{D}_G'$. Using the same approach outlined above and approximating $\mathbf{D}_G$ by its extinction-averaged value $\overline{\mathbf{D}}_G \equiv r_G \overline{\mathbf{D}}_0$, we obtain that

$$\mathbf{D}_G'(\mathbf{r}) = N r_e F_{H-G} \mathbf{u} \times (\mathbf{u} \times \overline{\mathbf{D}}_G) \frac{e^{-ik_0 r}}{r}, \quad (10)$$

where the mathematical details again follow closely to that in Ref. [9]. Combining Eqs. (9) and (10), we arrive at the total scattered wave in $\mathbf{u}$ direction:

$$\begin{aligned} \mathbf{D}'(\mathbf{r}) &= \mathbf{D}_0'(\mathbf{r}) + \mathbf{D}_G'(\mathbf{r}) \\ &= N r_e \mathbf{u} \times (\mathbf{u} \times \overline{\mathbf{D}}_0) \frac{e^{-ik_0 r}}{r} (F_H + F_{H-G} r_G). \end{aligned} \quad (11)$$

Equation (11) constitutes the key result of our expanded distorted-wave theory. The two terms in parentheses represent the rescattering of the forward-diffracted incident $\mathbf{O}$ beam by reflection $\mathbf{H}$ and of the Bragg-diffracted reference $\mathbf{G}$ beam by reflection $\mathbf{H} - \mathbf{G}$, respectively. These two waves travel along the same direction $\mathbf{u}$, and interfere with each other, producing a phase-sensitive diffracted intensity. To see its phase dependence explicitly, we recall that according to the dynamical theory, the phase of r_G is equal to the $\mathbf{G}$ structure-factor phase, α_G, plus the dynamical phase shift, ν_G, which changes by π across the $\mathbf{G}$ rocking curve (Fig. 2b). Thus the phase difference between the two waves is the sum of α_{H-G} and $\alpha_G + \nu_G$ minus α_H, or, $\delta + \nu_G$, where $\delta = \alpha_{H-G} + \alpha_G - \alpha_H$ is the *invariant triplet phase* used in crystallography. The diffracted intensity along $\mathbf{u}$ is obtained by squaring Eq. (11). For simplicity, this intensity is normalized to that in the first-order Born approximation [9] given by a formula identical to Eq. (9), except that $\overline{\mathbf{D}}_0$ is replaced by $\mathbf{D}_0^{(0)}$. Thus the final normalized intensity, I_H, is given by

$$I_H = \left[1 + 2\left|\frac{F_{H-G} r_G}{F_H}\right| \cos(\delta + \nu_G) + \left|\frac{F_{H-G} r_G}{F_H}\right|^2\right] \frac{\mu_0}{\mu_z}. \quad (12)$$

Equation (12) provides a simple compact expression for calculating three-beam interference profiles as a function of $\mathbf{G}$ reflection rocking angle in the reference-beam diffraction geometry. A numerical example for a GaAs $\mathbf{G} = (004)$ symmetric Bragg case ($b = -1$) is shown in Fig. 2. The main characteristics of the $\mathbf{G}$ reference reflection, internal field ratio r_G, dynamical phase shift ν_G, and primary extinction correction factor μ_0/μ_z, are plotted in (a) and (b) as a function of the normalized angular parameter η_G. The x-ray wavelength used in the calculation is $\lambda = 0.918$ Å. In Fig. 2(c) we show the calculated diffracted intensity profiles, using Eq. (12), of the GaAs $\mathbf{H} = (317)$ reflection, for both the true triplet phase $\delta = 3.5°$ (thick line) and for an artificial case with $\delta = 183.5°$ (thin line). The apparent reversal of the asymmetric patterns demonstrates the phase sensitivity of the intensity profiles as expected from Eq. (12). For comparison, we plot the results calculated using a rigorous N-beam dynamical theory originally developed by Colella [5] and modified for the reference-beam geometry. These results are shown as open and filled circles in Fig. 2(c) for $\delta = 3.5°$ and for $\delta = 183.5°$, respectively. The agreements between the two theories in both cases are excellent over the entire range of η_G.

In addition to its validity over the entire excitation range of the reference detour reflection, our expanded distorted-wave theory also automatically takes into account the energy flow balance that depends on the strengths of the structure factors involved, the so-called *Aufhellung* and *Umweganregung* effects. To illustrate these effects, we artificially adjust the ratio of $|F_H|/|F_G|$ from 0.425 (strong **H**) to 0.085 (weak **H**) by reducing the structure factor of the $\mathbf{H} = (317)$ reflection by a factor of 5 while keeping the same triplet phase, and repeat the same calculations performed for Fig. 2(c). These results are shown in Fig. 2(d) with a much greater vertical scale, where considerable peak intensities appear as *Umweganregung*. Nonetheless, the agreements between the N-beam results (open and filled squares) and the EDWA (thick and thin solid lines) are again excellent, even in the central region of the **G** reflection where the profiles are very complex.

Even though some mathematical similarities exist between the second-order Born approximation [9] and our present EDWA theory in arriving at Eqs. (9) and (10), the physical concepts involved in the two approaches are very different. In the former perturbational approach, a main reflection **H** is considered as a first-order approximation and a detour perturbing reflection **G** is introduced later in the second order, which prevent the accurate evaluation of the **G** wave field close to its full peak excitation. In the EDWA, the perturbing **G** wave field is treated on equal bases as the incident **O** beam, and the subsequent rescattering of the two waves is again evaluated equally, both in first-order Born approximation.

It is also interesting to note that Eq. (12) resembles an expression for an x-ray standing-wave yield [4,15]. This suggests that the multiple-beam interference effect is closely related to the intrinsic standing-wave fields inside the crystal. The EDWA theory presented here has indeed provided a theoretical basis that the multibeam effects can be viewed as an extension of the conventional incoherent standing-wave yield to the regime of coherent scattering processes of Bragg reflections.

In summary, by adding a sinusoidal component to the distorting susceptibility, we have expanded the distorted-wave theory to account for the phase-sensitive multiple-Bragg-wave interference in x-ray diffraction. The combination of the dynamical treatment in evaluation of the distorted-waves and the kinematic approach in subsequent scattering of the distorted waves leads to a simple analytical intensity expression that can be routinely used to extract a large number of Bragg reflection phases in the recently developed reference-beam diffraction crystallographic technique. The theoretical approach presented here may also stimulate other developments with the basic distorted-wave scattering theory for a variety of diffraction physics applications.

This work is supported by the NSF through CHESS under Grant No. DMR-9713424.

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