

atoms in the asymmetric unit, is almost a factor of five larger than any structure that has previously been determined without the use of isomorphous or molecular replacement or anomalous dispersion.

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The Reflected and Refracted Fundamental Modes of Dynamical X-ray Diffraction

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Abstract

An energy-conservation relation is derived between the power absorption, energy flux and absorption coefficient of an arbitrary fundamental mode in the n -beam dynamical theory of X-ray diffraction. From this relation, it is proven that the $4n$ fundamental modes selected by arbitrary incidence conditions are evenly divided into two types. The types are distinguished by the sign of their absorption coefficient and by the sign of their energy flux through a plane of constant absorption. In a bounded crystal, they represent reflected and refracted beams. It is noteworthy that these results apply for arbitrary n , even though the solution of the n -beam equations only satisfies Maxwell's equations in the limit of infinite n . In this

limit, the energy-conservation relation is equivalent to Poynting's theorem.

Introduction

It is known that the fundamental modes in the dynamical theory of X-ray diffraction may represent reflected as well as refracted beams. However, because the index of refraction for X-rays is nearly 1, reflected beams are usually negligible. An exception is two-beam Bragg diffraction from a thin-crystal plate (Zachariasen, 1945). For each state of polarization, a reflected and a refracted mode are excited. If the plate is sufficiently thin, interference between the two beams strongly modulates the rocking curve. As the thickness increases, the modulation rapidly disappears because the refracted beam is strongly damped by extinction and absorption before it is reflected from the exit surface. The absorption coefficients of

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the reflected and refracted modes, defined as the imaginary part of the normal component of their wave vectors, have opposite signs, ensuring that all modes are damped as they propagate.

The purpose of this paper is to prove that the fundamental modes of n -beam dynamical diffraction are evenly divided between reflected and refracted modes. Mathematically, the two types of modes are distinguished by the sign of their absorption coefficient and the sign of their energy flux through a plane of constant absorption. Since absorption and energy flux are related by energy conservation, it is not surprising that the proof which follows is based on an energy-conservation relation. This relation has not appeared previously in the dynamical-diffraction literature, even though properties of the Poynting vector have been studied extensively [see review articles by James (1963) and Batterman & Cole (1964)]. Collela (1972, 1974) has offered an explanation why the absorption coefficients should be evenly divided positive and negative, but a rigorous proof is missing.

The standard treatment of two-beam Laue diffraction apparently contradicts the above thesis, since it predicts two refracted modes and no reflected modes for each state of polarization. However, a rigorous analysis predicts four fundamental modes (Ashkin & Kuriyama, 1966; Farwig & Schurmann, 1967; Kishino & Kohra, 1971). The standard treatment simply ignores the two reflected modes because normally they are very weakly excited. Aleksandrov, Afanas'ev & Stepanov (1984) have proven that the absorption coefficients of these four modes are evenly divided positive and negative. However, their method cannot be applied to n -beam diffraction, because it would require an algebraic solution of a greater than fourth-degree polynomial equation.

If the above thesis were false, the n -beam boundary-value problem for a semi-infinite crystal would not have a unique solution. As discussed by Collela (1974), the boundary conditions at the incidence surface are $4n$ inhomogeneous linear equations whose unknowns are the amplitudes and polarizations of n external reflected beams and the amplitudes of the $4n$ fundamental modes selected by the incidence conditions. For a semi-infinite crystal, the reflected fundamental modes must be excluded. Then the $4n$ equations contain $m + 2n$ unknowns, where m is the number of refracted fundamental modes, so a unique solution exists only if $m = 2n$. Thus, the number of reflected and refracted modes must be equal.

An energy-conservation relation

In the theory of dynamical diffraction (James, 1963; Batterman & Cole, 1964), the complex representation of the displacement field inside the crystal is

$$\mathbf{D}(\mathbf{r}, t) = \sum_{\mathbf{G}} \mathbf{D}_{\mathbf{G}} \exp [i(\mathbf{k}_{\mathbf{G}} \cdot \mathbf{r} - \omega t)], \quad (1)$$

where the summation is over all reciprocal-lattice points \mathbf{G} of the crystal. The angular frequency ω is given, while the complex field amplitudes $\mathbf{D}_{\mathbf{G}}$ and the complex wave vectors $\mathbf{k}_{\mathbf{G}}$ are to be determined. The wave vectors are related by $\mathbf{k}_{\mathbf{G}} = \mathbf{k}_{\mathbf{O}} + \mathbf{G}$, where the point \mathbf{O} is the origin of the reciprocal lattice. The boundary conditions on the incidence surface require that $\mathbf{n} \times \mathbf{k}_{\mathbf{O}} = \mathbf{n} \times \mathbf{k}_i$, where \mathbf{n} is a unit vector normal to the crystal surface and \mathbf{k}_i is the wave vector of the incident beam. Replacement of \mathbf{D} in (1) by \mathbf{E} , \mathbf{B} and \mathbf{H} gives the complex representations of the other electromagnetic fields. Substituting these representations into Maxwell's equations and equating Fourier coefficients, one gets

$$\mathbf{k}_{\mathbf{G}} \times \mathbf{E}_{\mathbf{G}} = (\omega/c) \mathbf{B}_{\mathbf{G}} \quad (2a)$$

$$\mathbf{k}_{\mathbf{G}} \times \mathbf{H}_{\mathbf{G}} = -(\omega/c) \mathbf{D}_{\mathbf{G}}. \quad (2b)$$

The fields also satisfy the constitutive relations $\mathbf{B}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r}, t)$, assuming the crystal is non-magnetic, and $\mathbf{E}(\mathbf{r}, t) = \epsilon^{-1}(\mathbf{r}) \mathbf{D}(\mathbf{r}, t)$, where $\epsilon(\mathbf{r})$ is the complex periodic dielectric function. Equating Fourier coefficients in these relations, one gets

$$\mathbf{B}_{\mathbf{G}} = \mathbf{H}_{\mathbf{G}} \quad (3a)$$

$$\mathbf{E}_{\mathbf{G}} = \sum_{\mathbf{G}'} \epsilon_{\mathbf{G}-\mathbf{G}'}^{-1} \mathbf{D}_{\mathbf{G}'}, \quad (3b)$$

where $\epsilon_{\mathbf{G}-\mathbf{G}'}^{-1}$ is a Fourier coefficient of $\epsilon^{-1}(\mathbf{r})$. With the n -beam approximation, $\mathbf{D}_{\mathbf{G}}$ and $\mathbf{E}_{\mathbf{G}}$ are assumed to be non-zero at only n reciprocal-lattice points, including the origin. Thus, the summation in (3b), and all subsequent equations, may be restricted to these n points. Standard practice is to expand the inverse of the dielectric function in powers of the polarizability, neglecting second- and higher-order terms since the polarizability is small. Because the results herein do not require the polarizability to be small, this practice is avoided.

The energy conservation relation is derived as follows. Adding the scalar product of $\mathbf{H}_{\mathbf{G}}^*$ with (2a) to the scalar product of $\mathbf{E}_{\mathbf{G}}$ with the complex conjugate of (2b) and eliminating $\mathbf{B}_{\mathbf{G}}$ by (3a), one gets

$$(\omega/c)(|\mathbf{H}_{\mathbf{G}}|^2 - \mathbf{E}_{\mathbf{G}} \cdot \mathbf{D}_{\mathbf{G}}^*) = 2i \operatorname{Im}(\mathbf{k}_{\mathbf{O}}) \cdot \mathbf{E}_{\mathbf{G}} \times \mathbf{H}_{\mathbf{G}}^*,$$

where the function Im yields the imaginary part of its argument. Eliminating $\mathbf{E}_{\mathbf{G}}$ from the left side of this equation by (3b), summing both sides over the n \mathbf{G} , multiplying by $c/8\pi$, and taking the imaginary part, one gets

$$-(\omega/8\pi) \sum_{\mathbf{G}, \mathbf{G}'} (\operatorname{Im} \epsilon^{-1})_{\mathbf{G}-\mathbf{G}'} \mathbf{D}_{\mathbf{G}'}^* \cdot \mathbf{D}_{\mathbf{G}} \\ = 2 \operatorname{Im}(\mathbf{k}_{\mathbf{O}}) \cdot \operatorname{Re} \left[(c/8\pi) \sum_{\mathbf{G}} \mathbf{E}_{\mathbf{G}} \times \mathbf{H}_{\mathbf{G}}^* \right], \quad (4)$$

where $(\operatorname{Im} \epsilon^{-1})_{\mathbf{G}-\mathbf{G}'}$ is a Fourier coefficient of $\operatorname{Im} \epsilon^{-1}(\mathbf{r})$ and the function Re yields the real part of its argument. When \mathbf{n} is not parallel to any \mathbf{G} , as can

always be arranged by an infinitesimal rotation of \mathbf{n} , this equation is an energy-conservation relation. Indeed, it is equivalent to Poynting's theorem (Jackson, 1962), except that the fields in Poynting's theorem solve Maxwell's equations, while the fields in (4) solve the n -beam approximation. Only in the limit of infinite n , when all \mathbf{G} are included, are the fields identical.

The interpretation of (4) as an energy-conservation relation proceeds as follows. The time-averaged Poynting vector $\mathbf{S}(\mathbf{r})$, defined as $(c/8\pi) \text{Re} [\mathbf{E}(\mathbf{r}, t) \times \mathbf{H}^*(\mathbf{r}, t)]$, is the product of an exponential factor which depends on $\mathbf{n} \cdot \mathbf{r}$ alone and a periodic factor. Likewise, the average value of $\mathbf{S}(\mathbf{r})$ on the plane of constant absorption $\mathbf{n} \cdot \mathbf{r} = d$, denoted by $\mathbf{S}_n(d)$, is generally the product of an exponential and periodic factor, both functions of d . (Note that this spatial averaging procedure differs from the standard one, in which the Poynting vector is averaged in one unit cell by ignoring absorption.) However, if \mathbf{n} is not parallel to any \mathbf{G} , then the periodic factor becomes a constant, because the plane uniformly samples all points of the unit cell. In this case,

$$\mathbf{S}_n(d) = \exp(-2d\mathbf{n} \cdot \text{Im } \mathbf{k}_0) \text{Re} \left[(c/8\pi) \sum_{\mathbf{G}} \mathbf{E}_{\mathbf{G}} \times \mathbf{H}_{\mathbf{G}}^* \right].$$

Thus, the net power density flowing into the slab bounded by the planes $\mathbf{n} \cdot \mathbf{r} = 0$ and $\mathbf{n} \cdot \mathbf{r} = \delta$, where δ is an infinitesimal, is

$$\begin{aligned} & \mathbf{n} \cdot [\mathbf{S}_n(0) - \mathbf{S}_n(\delta)] / \delta \\ & = 2 \text{Im}(\mathbf{k}_0) \cdot \text{Re} \left[(c/8\pi) \sum_{\mathbf{G}} \mathbf{E}_{\mathbf{G}} \times \mathbf{H}_{\mathbf{G}}^* \right]. \end{aligned}$$

But this equals the right side of (4), so by conservation of energy the left side must be the power density absorbed by the slab and must be positive. Since the left side equals the average value of

$$-(\omega/8\pi) \text{Im } \varepsilon^{-1}(\mathbf{r}) \left| \sum_{\mathbf{G}} \mathbf{D}_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \right|^2$$

over the unit cell, it is indeed positive for arbitrary $\mathbf{D}_{\mathbf{G}}$, as long as $\omega \text{Im } \varepsilon^{-1}(\mathbf{r})$ is everywhere negative. Physically, this condition simply demands that absorption occur throughout the unit cell. The sign of ω is a matter of convention, but that of $\text{Im } \varepsilon^{-1}(\mathbf{r})$ must be opposite.

Before (4) is used below, it is necessary to solve the dispersion equation in the special case of a constant dielectric function. Elimination of $\mathbf{E}_{\mathbf{G}}$, $\mathbf{B}_{\mathbf{G}}$ and $\mathbf{H}_{\mathbf{G}}$ from the system of equations (2) and (3) gives the fundamental equation of dynamical diffraction:

$$(\omega/c)^2 \mathbf{D}_{\mathbf{G}} = -\mathbf{k}_{\mathbf{G}} \times \mathbf{k}_{\mathbf{G}} \times \sum_{\mathbf{G}'} \varepsilon_{\mathbf{G}-\mathbf{G}'}^{-1} \mathbf{D}_{\mathbf{G}'}. \quad (5)$$

This system of homogeneous linear equations in $\mathbf{D}_{\mathbf{G}}$ has non-trivial solutions only when $\mathbf{n} \cdot \mathbf{k}_0$ satisfies the

associated dispersion equation, which generally does not have an algebraic solution. A trivial exception occurs when $\varepsilon(\mathbf{r}) = \varepsilon_0$. Then, from (5), the roots of the dispersion equation are

$$\mathbf{n} \cdot \mathbf{k}_0 = -\mathbf{n} \cdot \mathbf{G} \pm [(\omega/c)^2 \varepsilon_0 - |\mathbf{n} \times \mathbf{k}_i + \mathbf{n} \times \mathbf{G}|^2]^{1/2}.$$

In this case, the absorption coefficients $\text{Im}(\mathbf{n} \cdot \mathbf{k}_0)$ come in pairs of opposite sign, as long as $\text{Im } \varepsilon_0$ is non-zero.

Now (4) may be applied to prove the thesis of the paper. Suppose that the dielectric function evolves continuously from a constant to an arbitrary function, with its imaginary part never vanishing. For example, the evolving function could be $(1-p)\varepsilon_0 + p\varepsilon(\mathbf{r})$, where p varies from 0 to 1. Since the coefficients of the dispersion equation are then continuous functions of p , so are the absorption coefficients. When $p=0$, the absorption coefficients are evenly divided positive and negative. If the absorption coefficients were not likewise divided when $p=1$, then at least one of them would have to vanish for some value of p . But this is forbidden by (4), because the left side is always positive. Finally, when \mathbf{n} is not parallel to any \mathbf{G} , (4) shows that the absorption coefficient ($\mathbf{n} \cdot \text{Im } \mathbf{k}_0$) and the energy flux through a plane of constant absorption [$\mathbf{n} \cdot \mathbf{S}_n(d)$] have the same sign. Since the sign of $\mathbf{n} \cdot \mathbf{S}_n$ distinguishes the reflected modes from the refracted, the number of each must be the same.

As a fine point, when \mathbf{n} is parallel to some \mathbf{G} , (4) does not fully represent energy conservation, because then $\mathbf{S}_n(d)$ has a factor which depends periodically on d . Consequently, the conservation relation must also depend periodically on d . Each side of (4) is the average value over d of the corresponding side of the complete conservation relation. However, the left side of the complete relation is not positive for arbitrary $\mathbf{D}_{\mathbf{G}}$, even though $\omega \text{Im } \varepsilon^{-1}(\mathbf{r})$ is everywhere negative, except in the limit of infinite n when all \mathbf{G} are included. Thus, it is possible that, for some d , the computed absorption coefficient and energy flux through a plane of constant absorption have opposite signs.

Summary

Conservation of energy prevents an absorption coefficient from ever vanishing. Since the absorption coefficients are evenly distributed positive and negative when the dielectric function is constant, they must remain so for any physically admissible dielectric function. Conservation of energy also requires a definite relation between the signs of an absorption coefficient and the energy flux through a plane of constant absorption. These results rigorously establish that the fundamental modes of n -beam dynamical diffraction are evenly divided between reflected and refracted modes. While these results are physically intuitive, it is important to recognize that they have

been obtained for fields which only approximately satisfy Maxwell's equations, and have been obtained without requiring the polarizability to be small.

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General Connections for the Form of Property Tensors in the 122 Shubnikov Point Groups

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Abstract

The 122 Shubnikov point groups (SPGs) are obtained from the 32 ordinary crystallographic point groups (OPGs) by taking time inversion into account. Like the OPGs, the SPGs can be grouped into 11 Laue classes. Tensors can be invariant under space inversion (s tensors), time inversion (t tensors), space-time inversion (u tensors) or all three inversions (i tensors). The restrictions imposed on the form of a property tensor by the SPG of the material under consideration depend, for i tensors, only on the Laue class of the SPG. If these restrictions are known for an i tensor, the corresponding restrictions for s , t and u tensors of the same rank and internal symmetry can be written down immediately for all the 122 SPGs and for all orientations in which the SPG under consideration appears in the corresponding holohedry. These connections provide tests for the forms of tensors given in the literature. A number of corrections and of possible simplifications are pointed out. The results are illustrated by showing how the form of the i tensor describing linear electrogyration determines the form of the piezoelectric t tensor and the piezomagnetic s tensor for all 122 SPGs. Similarly, the form of the t tensor describing quadratic electrogyration is derived explicitly from the i tensor describing the piezooptic effect.

1. Introduction

The 32 ordinary point groups (OPGs) and the 122 Shubnikov point groups (SPGs) that are compatible with a periodic structure in all three space dimensions

are often arranged in a two-dimensional table. Its six columns essentially correspond to the crystal systems. The monoclinic point groups (PGs) appear either in the first column together with the anorthic PGs or in the second together with the orthorhombic PGs or in both in different orientations. PGs having certain features in common are placed in the same row. One such arrangement is given in *International Tables for X-ray Crystallography* (1952); another, which differs in important details (e.g. $\bar{4}3m$ in the same row as $4mm$ not as $\bar{4}2m$), has been proposed by Grimmer (1980), who called it the periodic arrangement. It has three long columns with PGs in every row and three short columns for which PGs are lacking in the same rows. He showed that, in his arrangement, each long column has the same subgroup structure if subgroups appearing several times in different orientations are distinguished. The same holds for the subgroup structure in the short columns. Groups in a given row have certain structural features in common, e.g. having space inversion $\bar{1}$, time inversion $1'$ or space-time inversion $\bar{1}'$ among their elements or containing such inversions only in combination with rotations. In this paper it is shown that the restrictions demanded by the PG of a material for the form of the tensors describing its properties also have features in common for all PGs in a given row. These restrictions are expressed as usual for the components of the tensor in a right-handed orthogonal coordinate system with the same length unit on the three axes. Care is taken to define completely the orientation of these axes with respect to the orientations of the symmetry elements, which are expressed by the order of the entries in the Hermann–Mauguin symbol.