Anisotropic dynamic model of forbidden reflections in x-ray diffraction

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A dynamic model of anisotropic x-ray diffraction is developed using two-wave approximation. A dispersion surface equation is derived for the screw-axis and glide-plane forbidden reflections. Propagation and polarization phenomena of waves are discussed. The deductions show that all these forbidden reflections may be excited except the $00l$ $(l=2n+1)$ reflections for a 6_3 screw axis and the $00l$ $(l=6n+3)$ reflections for 6_1 and 6_5 screw axes. The general methods are illustrated by their application to the rutile structure.
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I. INTRODUCTION

It is well known that the conditions limiting possible x-ray reflections are only satisfied when the equivalent positions in a crystal are assumed to be occupied by atoms with the same scattering amplitude. The interatomic interaction leads to small asphericity of atoms so that the scattering amplitudes of the crystallographically equivalent atoms are not the same. Hence, forbidden reflections can occur.[1] It has been known that one cause of forbidden reflections is the anisotropy of x-ray susceptibility of atoms in crystals.[2] This anisotropy is very small in the x-ray regime. In conventional x-ray diffraction theories susceptibility is supposed to be isotropic.[3–5] But near x-ray absorption edges the absorption of x-ray beams depends on their polarization. In this case the anisotropy of susceptibility is essential.[6–8] It is this small anisotropy of susceptibility that gives rise to a series of anisotropic anomalous-scattering phenomena, such as the energy-dependent dichroism, birefringence, and forbidden-reflection diffraction.[2,7,9] Kinematical theory of diffractions has been developed to explain the intensity of the waves and the polarization phenomena in forbidden reflections.[1] But a characteristic feature of the kinematical theory is that it ignores multiwave scattering and, what is especially important, the interaction of the diffracted waves with the refracted one. It cannot provide information concerning the wave phase and propagation, which indicates the intrinsic mechanism of x-ray polarization.[3,10,11]

In our previous work, a ''one-beam'' equation was developed for cases where only refracted waves are considered.[12] We found the two refracted waves in crystals are elliptic polarized with their major (minor) axes perpendicular to each other. In the present paper our purpose is to show the general principles governing the anisotropic x-ray diffraction by taking into account the interaction between the refracted and diffracted waves in crystals. As anisotropic scattering occurs, the x-ray susceptibility is a second-order tensor. Starting from Maxwell equations, dynamic model is established. It is found that, in a forbidden reflection, the isotropy of the susceptibility is insignificant, which leads to very unusual propagation and polarization phenomena. The possible conditions for the experimental observation of the anisotropy of susceptibility and application of this dynamic model are also discussed.

II. TWO-WAVE APPROXIMATION OF ANISOTROPY DIFFRACTION

It is well known that in nonmagnetic crystals with zero electric conductivity, the reduced Maxwell's equation can be written as

$$\nabla^2\mathbf{D}-\frac{1}{c^2}\frac{\partial^2\mathbf{D}}{\partial t^2}=-\boldsymbol{\nabla}\times\boldsymbol{\nabla}\times\mathbf{P},\tag{1}$$

where $\mathbf{D}$ is electric displacement and $\mathbf{P}$ is induced polarization. For anisotropic x-ray optics, the electric susceptibility is a second-order tensor $\hat{\chi}$. Then the electric field $\mathbf{E}$ is related to the electric displacement $\mathbf{D}$ by $\mathbf{D}=(\hat{\mathbf{I}}+\hat{\chi})\mathbf{E}$, where $\hat{\mathbf{I}}$ is the unit matrix. Since the susceptibility components χ_{ij} are small in the x-ray regime, the induced polarization $\mathbf{P}$ can be written as

$$\mathbf{P}=\mathbf{D}-\mathbf{E}=[\hat{\mathbf{I}}-(\hat{\mathbf{I}}+\hat{\chi})^{-1}]\mathbf{D}\simeq\hat{\chi}\mathbf{D}.\tag{2}$$

Based on this relation, the Maxwell equation has the general solutions

$$\mathbf{D}_j=\frac{1}{K^2-\mathbf{K}_j\cdot\mathbf{K}_j}\sum_n \mathbf{K}_j\times[\mathbf{K}_j\times(\hat{\chi}_{j-n}\mathbf{D}_n)],\tag{3}$$

where $\mathbf{K}$ is the vacuum vector, $\hat{\chi}_n$ is the Fourier component of the tensor susceptibility $\hat{\chi}$, $\mathbf{D}_j$ and $\mathbf{K}_j$ are the amplitude and wave vector of the jth Bloch wave, respectively.[3]

In the case only the refracted and diffracted waves are taken into account, the dynamic theory of two-wave approximation has been well developed,[1] where the electric susceptibility of crystals is defined as a scalar. For anisotropic x-ray optics in crystals, considering the tensor susceptibility, the wave equation of two-wave approximation has the form

$$2\eta_0\mathbf{D}_0-(\hat{\chi}_0\mathbf{D}_0)_{[\mathbf{K}_0]}-(\hat{\chi}_{\bar{g}}\mathbf{D}_g)_{[\mathbf{K}_0]}=0,\tag{4}$$

$$2\eta_g\mathbf{D}_g-(\hat{\chi}_g\mathbf{D}_0)_{[\mathbf{K}_g]}-(\hat{\chi}_0\mathbf{D}_g)_{[\mathbf{K}_g]}=0,\tag{5}$$

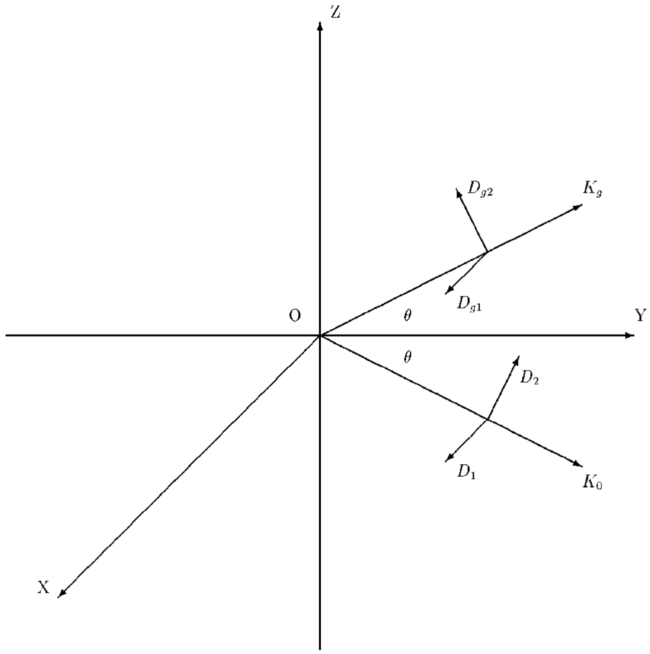

FIG. 1. The mutual positions of D_0 and D_g.

where

$$\eta_j = \frac{K_j^2 - K^2}{2K_j^2} \tag{6}$$

is a small wave-vector correction associated with x-ray refraction. $(\hat{\chi}_0 \mathbf{D}_0)_{[\mathbf{K}_0]}$ is the perpendicular component of $\hat{\chi}_0 \mathbf{D}_0$ with respect to the wave-propagating direction $\mathbf{K}_0$. The other vectors in Eqs. (4) and (5) have similar meanings. For convenience, we define that

$$\mathbf{D}_0 = \begin{pmatrix} D_1 \\ D_2 \cos\theta \\ D_2 \sin\theta \end{pmatrix}, \quad \mathbf{D}_g = \begin{pmatrix} D_{g1} \\ -D_{g2}\cos\theta \\ D_{g2}\sin\theta \end{pmatrix}, \tag{7}$$

where $\mathbf{D}_0$ and $\mathbf{D}_g$ are the electric displacements of refracted beam and reflected beam. D_2, D_{g2} are the components parallel to the incident plane and D_1, D_{g1} the vertical components. The mutual positions of these vectors are shown in Fig. 1.

III. DISPERSION SURFACE AND POLARIZATION

Starting from Eqs. (4) and (5), we can get the dispersion surface equation of any specific reflection. In present paper we mainly discuss ''forbidden'' reflections as defined by kinematical theory.[1]

Usually the anisotropy of $\hat{\chi}$ is very small in most cases. Perfect results can be obtained by conventional dynamic theory if we consider $\hat{\chi}$ as a scalar. So it is convenient to write

$$\hat{\chi} = \chi^i \hat{\mathbf{I}} + \hat{\chi}^a, \tag{8}$$

TABLE I. The components of the tensor susceptibility $\hat{\chi}_g$ and indices l for anisotropic x-ray reflections ($n=0, \pm 1, \pm 2, \ldots$; other components of $\hat{\chi}_g$: $\chi_{22}=-\chi_{11}$; $\chi_{33}=0$; $\chi_{12}=\chi_{21}$; $\chi_{13}=\chi_{31}$; $\chi_{23}=\chi_{32}$).

Screw axis or glide plane	χ_{11}	χ_{12}	χ_{13}	χ_{23}	l
2_1	0	0	F_1	F_2	$2n+1$
3_1	F_1	$\mp iF_1$	F_2	$\pm iF_2$	$3n\pm 1$
3_2	F_1	$\pm iF_1$	F_2	$\mp iF_2$	$3n\pm 1$
4_1	0	0	F_1	$\pm iF_1$	$4n\pm 1$
4_1	F_1	F_2	0	0	$4n+2$
4_2	F_1	F_2	0	0	$2n+1$
4_3	0	0	F_1	$\mp iF_1$	$4n\pm 1$
4_3	F_1	F_2	0	0	$4n+2$
6_1	0	0	F_1	$\pm iF_1$	$6n\pm 1$
6_1	F_1	$\pm iF_1$	0	0	$6n\pm 2$
6_1	0	0	0	0	$6n+3$
6_2	F_1	$\pm iF_1$	0	0	$3n\pm 1$
6_3	0	0	0	0	$2n+1$
6_4	F_1	$\mp iF_1$	0	0	$3n\pm 1$
6_5	0	0	F_1	$\mp iF_1$	$6n\pm 1$
6_5	F_1	$\mp iF_1$	0	0	$6n\pm 2$
6_5	0	0	0	0	$6n+3$
c	0	F_1	F_2	0	$2n+1$

where $\hat{\mathbf{I}}$ is the unit matrix, χ^i represents the large isotropic part of the susceptibility, and $\hat{\chi}^a$ is a small correction related to anisotropic diffraction.

Let us turn to Eqs. (4) and (5); the Fourier components $\hat{\chi}_0$ and $\hat{\chi}_g$ are defined as

$$\hat{\chi}_j = \frac{1}{V}\int_V \hat{\chi} \exp(2\pi i \mathbf{g}_j \cdot \mathbf{r}) dV \tag{9}$$

when $j=0$, $\hat{\chi}_0 = (1/V)\int_V \hat{\chi} dV$. $\hat{\chi}_0$ has the same symmetry as $\hat{\chi}$. Similar to that in the conventional theory, we take $\hat{\chi}_0$ as a scalar χ_0. When $j \neq 0$, especially in a screw-axis or glide-plane forbidden reflection, the symmetry properties of the tensor susceptibility are very unusual. In these reflections, the isotropic part of the tensor $\hat{\chi}_g$ disappears because of the symmetry of the space group. The effect of the anisotropic part of susceptibility that still remains in such a forbidden reflection becomes significant. And all components of the tensor $\hat{\chi}_g$ are determined by at most two independent parameters.[1] The results have been given by Dmitrienko (see Table I).

The tensors listed in Table I have a common form

$$\hat{\chi}_g = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & -\chi_{11} & \chi_{23} \\ \chi_{13} & \chi_{23} & 0 \end{pmatrix}. \tag{10}$$

Hereafter the two-waves approximation will be investigated using this common form. Inserting into Eqs. (4) and (5), omitting the tedious calculation, we can get the following equations:

$$(2\eta_0-\chi_0)D_1-\chi_{11}^*D_{g1}+(\chi_{12}^*\cos\theta-\chi_{13}^*\sin\theta)D_{g2}=0, \tag{11}$$

$$(2\eta_0-\chi_0)D_2-(\chi_{12}^*\cos\theta+\chi_{13}^*\sin\theta)D_{g1}-\chi_{11}^*\cos^2\theta D_{g2}=0, \tag{12}$$

$$-\chi_{11}D_1-(\chi_{12}\cos\theta+\chi_{13}\sin\theta)D_2+(2\eta_g-\chi_0)D_{g1}=0, \tag{13}$$

$$(\chi_{12}\cos\theta-\chi_{13}\sin\theta)D_1-\chi_{11}\cos^2\theta D_2+(2\eta_g-\chi_0)D_{g2}=0. \tag{14}$$

The determinant of this system, being zero,

$$\Delta=\begin{vmatrix} 2\eta_0-\chi_0 & 0 & -\chi_{11}^* & \chi_{12}^*\cos\theta-\chi_{13}^*\sin\theta \\ 0 & 2\eta_0-\chi_0 & -\chi_{12}^*\cos\theta-\chi_{13}^*\sin\theta & -\chi_{11}^*\cos^2\theta \\ -\chi_{11} & -\chi_{12}\cos\theta-\chi_{13}\sin\theta & 2\eta_g-\chi_0 & 0 \\ \chi_{12}\cos\theta-\chi_{13}\sin\theta & -\chi_{11}\cos^2\theta & 0 & 2\eta_g-\chi_0 \end{vmatrix}=0, \tag{15}$$

gives the equation of dispersion surfaces in reciprocal space that has the form

$$X^2-BX+C=0, \tag{16}$$

where

$$X=(2\eta_0-\chi_0)(2\eta_g-\chi_0), \tag{17}$$

$$B=|\chi_{11}|^2(\cos^4\theta+1)+|\chi_{12}\cos\theta-\chi_{13}\sin\theta|^2+|\chi_{12}\cos\theta+\chi_{13}\sin\theta|^2, \tag{18}$$

$$C=|\chi_{11}^{*2}\cos^2\theta+(\chi_{12}^2\cos^2\theta-\chi_{13}^2\sin^2\theta)|^2. \tag{19}$$

From Eq. (16), we have the solutions

$$X=\frac{B\pm\sqrt{B^2-4C}}{2} \tag{20}$$

and rewriting Eq. (20), we get the dispersion surface equations

$$(2\eta_0-\chi_0)(2\eta_g-\chi_0)=\frac{B\pm\sqrt{B^2-4C}}{2}. \tag{21}$$

It is clear that in Eq. (20), $B\geqslant 0$, $C\geqslant 0$, and $B^2-4C\geqslant 0$. For different forbidden reflections B and C have different values. The surfaces described by Eq. (21) are two-sheet surfaces of revolution (a hyperbolic cylinder). This equation tells us that two types of waves exist that are excited on the different dispersion surfaces when a beam is incident into a crystal. Here, we call them ''ordinary'' (o) and ''extraordinary'' (e) waves. In such cases the reflected wave owes to the anisotropy of susceptibility, though the form of the dispersion surface equation is very similar to the conventional dynamic theory that considers the susceptibility as a scalar. Since the dispersion surface is known, following the steps in the well-developed conventional theory, we can get the solutions of $\mathbf{K}_0$ and $\mathbf{K}_g$ which fully determine the refracted and reflected waves.[3]

Other than in the conventional theory, where the incident beam splits into two plane polarized waves known as π polarization and σ polarization, two elliptic polarized waves are generated by the incident beam. This is the basic property of an anisotropic reflection. It is known that, in fact, in the conventional theory the two types of polarized waves are investigated separately. Here we can find the relation of them. The ''ordinary'' (o) and ''extraordinary'' (e) waves can be determined by a single equation and these two waves propagate separately in the crystal.

Usually the isotropic part of susceptibility is much larger than the anisotropic part. For simplicity, waves in the crystal could be treated as plane polarized waves. The conventional dynamic theory is based on this approximation.[3] And it could also be supposed that in a common reflection it is difficult to observe the anisotropy of $\hat{\chi}$. But in a forbidden reflection, the additional symmetry of the space group let the isotropic part of the susceptibility become insignificant. Many new properties appear due to the anisotropy of susceptibility.

Now we can discuss the properties of the reflection in details for some special cases. When $\chi_{11}=\chi_{12}=0$, such as in 2_1, $4_1(l=4n\pm 1)$, $4_3(l=4n\pm 1)$, $6_1(l=6n\pm 1)$ or $6_5(l=6n\pm 1)$ reflection, B and C are very simple as given by definitions (18) and (19), we get

$$B=2|\chi_{13}|^2\sin^2\theta, \tag{22}$$

$$C=|\chi_{13}|^4\sin^4\theta. \tag{23}$$

Furthermore, due to $B^2-4C=0$, Eq. (16) has one solution. It is interesting to find that in such a forbidden reflection there is only one dispersion surface existing in reciprocal space. Usually two separate waves, known as ''ordinary'' (o) and ''extraordinary'' (e) waves, exist in crystals, which is described above as well as in conventional theory. The refractive indices of these two waves are generally not equal to each other, which gives rise to the birefringence of the crystal. But here, inserting the B and C given above into Eq. (21), we get

$$(2\eta_0-\chi_0)(2\eta_g-\chi_0)=|\chi_{13}|^2\sin^2\theta. \tag{24}$$

It is an extreme case when two elliptic waves excited in the crystal equal to each other. It is the unique phenomenon appearing in the anisotropic reflection. Only one ordinary wave exists in the crystal and the polarization of this wave is very unusual.

Because what we are interested in is the direction and phase of $\mathbf{D}_0$ and $\mathbf{D}_g$, hereafter we omit the factor $(2\eta_g-\chi_0)$ in Eqs. (12) and (13), which is a constant for a respective reflection, and rewrite these equations as

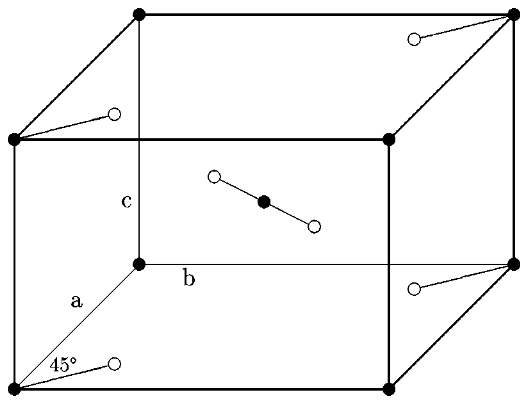

FIG. 2. The rutile structure (○, oxygen; ●, titanium).

$$D_{g1}=\chi_{11}D_1+(\chi_{12}\cos\theta+\chi_{13}\sin\theta)D_2, \tag{25}$$

$$D_{g2}=-(\chi_{12}\cos\theta-\chi_{13}\sin\theta)D_1+\chi_{11}\cos^2\theta D_2. \tag{26}$$

For $\chi_{11}=\chi_{12}=0$, Eqs. (25) and (26) turn to

$$D_{g1}=\chi_{13}\sin\theta D_2, \tag{27}$$

$$D_{g2}=\chi_{13}\sin\theta D_1. \tag{28}$$

When the incident wave is plane polarized, the reflected one is also plane polarized. And the amplitude of the reflected wave has the same order as incident one. Especially when the incident wave is π polarized or σ polarized, the polarization state of the reflected wave will be changed. A π-polarized incident wave will give a σ-polarized reflected one and vice versa. This conclusion is consistent with the kinematical model developed by Dmitrienko.[1]

If only a screw axis (or glide plan) is taken into account, the nonzero items of $\hat{\chi}_g$ are listed in Table I. Other symmetry operations can lead to additional relationships between F_1 and F_2 or even make them vanish. It should be noted that for a 6_3 screw axis with $l=2n+1$ and 6_1, 6_5 screw axes with $l=6n+3$, the reflections remain forbidden because only the dipole interaction of x rays is taken into account in the developing theory.[1]

To illustrate the developed model carefully, let us consider the $00l$ ($l=2n+1$) reflections in crystals with TiO_2 (rutile) structure (the space group is D^4_{4h}, $P4_2/mnm$). The structure is shown in Fig. 2. From Table I one can obtain the tensor susceptibility taking into account both the screw axis 4_2 and the glide plane n [for $00l$ ($l=2n+1$) reflections there is no difference between c and n glide planes]. It can be found from Table I that due to the combined action of the screw axis and the glide plane only $\chi_{12}\neq 0$. Thus we get

$$B=2|\chi_{12}|^2\cos^2\theta, \tag{29}$$

$$C=|\chi_{12}|^4\cos^4\theta. \tag{30}$$

Similar to the case above, the dispersion surface equation has the form

$$(2\eta_0-\chi_0)(2\eta_g-\chi_0)=|\chi_{12}|^2\cos^2\theta. \tag{31}$$

Only one dispersion surface has been obtained and no birefringence will be observed when only an ordinary dispersion exists in the crystal. We rewrite Eqs. (25) and (26) as

$$D_{g1}=\chi_{12}\cos\theta D_2, \tag{32}$$

$$D_{g2}=-\chi_{12}\cos\theta D_1. \tag{33}$$

From Eqs. (32) and (33), it is very interesting to find that the reflected one is also a plane polarized wave with the vector perpendicular to that of the incident wave if the incident wave is plane polarized. It is as though the incident wave is rotated by 90°.

Usually the anisotropy of susceptibility is hard to observe because the anisotropic part of $\hat{\chi}$ is very small compared to the isotropic part. It has been shown above in forbidden reflection that the reflected wave is only related to the anisotropic part of $\hat{\chi}$. If the environment of crystals is changed, for example, by putting samples in an electric field, then the $\hat{\chi}_{\text{eff}}$ will also change. Thus it may be possible by such a method to make the anisotropic part of $\hat{\chi}$ significant, thereby enable diffractions owing to the anisotropy of $\hat{\chi}$ to be observed.

IV. CONCLUSION

Starting from the Maxwell equations, dynamic model of forbidden reflections is established, where the susceptibility of crystals is considered as a second-order tensor. The main properties of forbidden reflections are obtained.

(1) Similar to the conventional dynamic theory, two dispersion surfaces exist in the reciprocal space on which ordinary (o) and extraordinary (e) waves are excited. Usually the o and e waves propagate separately in the crystals and are totally elliptic polarized. But owing to the anisotropy of $\hat{\chi}$, in some special case, we can only get one dispersion surface.

(2) Considering the tensor susceptibility, all the screw-axis and glide-plane forbidden reflections may be excited except the $00l$ ($l=2n+1$) reflections for a 6_3 screw axis and the $00l$ ($l=6n+3$) reflections for 6_1 and 6_5 screw axes.

(3) The polarization properties of forbidden reflections are very unusual due to the different symmetry of $\hat{\chi}$. The transformation of π polarization into σ polarization and vice versa are possible.

From this dynamic theory, we can suppose that crystals can act as efficient x-ray polarizers to change linearly polarized radiation into an elliptical polarized one or vice versa.[12] In fact, highly polarized x rays have many applications in materials science, crystallography, chemistry, biology, etc. The availability of highly polarized and tunable synchrotron radiation has made anisotropic refraction and diffraction an attractive tool for a broad range of studies of these fields in both transmission and diffraction cases.[11,13,14]

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