Width of the Darwin Table for Forbidden Reflections

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(Received 6 June 1996)

It is shown that reflections with structure factor equal to zero are not absent, but have very small Darwin table width, which is determined by a shift of the Bragg point and by structure factors of another type. It is pointed out that this effect cannot be obtained within the Ewald theory of dynamical diffraction on single crystals. [S0031-9007(96)01593-1]

PACS numbers: 61.12.Bt

In neutron, x-ray, and electron diffraction on single crystals the reflections, for which structure factor $F(\mathbf{q}) = 0$, are called forbidden because the kinematical theory and the Ewald theory of dynamical diffraction predict zero intensity for these q. Here $\mathbf{q} = \mathbf{k}_d - \mathbf{k}_0$ is the momentum transfer, $\mathbf{k}_0$ is the wave vector of the incident, and $\mathbf{k}_d$ of the diffracted beam. We want to show here that these reflections, strictly speaking, are not forbidden. They are the same as nonforbidden ones with the only difference being that the Darwin table width (DTW) for them is very narrow, and only for that reason is their intensity much smaller than the intensity of nonforbidden reflections.

It is well known that the forbidden reflections were experimentally observed in x-ray [1], neutron [2], and electron [3–6] diffraction. However, they are imitated by two successive nonforbidden ones (so-called "umweg" effect). To see this effect in the case of x-ray and neutron diffraction, it is necessary to have a special orientation of crystals, while in the case of electrons the umweg effect exhibits itself very easily because the diffraction, especially at high energies, proceeds via many different waves. Moreover, since the interaction between electron and matter is strong, some forbidden reflections can be observed when few atomic layers have an incomplete elementary cell, as may happen on surfaces or in stacking faults [7].

We shall show that nothing of that is required to observe forbidden reflections. An ideal crystal without incomplete cells, without stacking faults, and without an umweg effect of any kind totally reflects in the directions for which the structure factor is zero.

To prove this assertion, and to make the ideas of the proof as simple as possible, we consider here only neutron diffraction from a semi-infinite single crystal in Bragg geometry. For even more simplification we shall use a very artificial model of a single crystal with two identical motionless nonabsorbing atoms in an elementary cell, with very short crystalline parameters α in a, b plane, which coincides with the crystal surface, and a long period s in the c direction along the normal to the surface. This model permits us to reduce the problem of diffraction to one-dimensional scattering and to make an estimation of the magnitude of the effect, which is also valid for real crystals. In some respect, this model can be visualized as some kind of multilayer mirror.

Our main theoretical tool is the dynamical diffraction theory based on the multiple wave Darwin (MWD) approach [8,9]. We use the artificial model because, in that case, our approach is reduced to the single wave Darwin one. It means that the crystal is imagined to be cut in slices [10] parallel to the entrance surface, the width of a slice being that of a single period [such a slicing is very common in electron diffraction], and the scattering on a slice is described by direct transmission and specular reflection. If we know reflection ρ and transmission τ of a single period, we can find an equation for reflection R from a semi-infinite set of such slices:

$$R = \rho + \tau R \tau + \tau R \rho R \tau + \cdots + \tau R (\rho R)^n \tau + \cdots , \tag{1}$$

where the nth term in this sum means transmission through the first slice, n times multiple reflection between the first slice and remaining set, and finally transmission back to the vacuum through the first slice. The terms in the right hand side represent a geometrical progression, which can be easily summed, and as a result we get the equation

$$R = \rho + \tau^2 R/(1 - \rho R) , \tag{2}$$

whose solution can be represented [10] in the form

$$R = \frac{\sqrt{(1+\rho)^2 - \tau^2} - \sqrt{(1-\rho)^2 - \tau^2}}{\sqrt{(1+\rho)^2 - \tau^2} + \sqrt{(1-\rho)^2 - \tau^2}} . \tag{3}$$

The amplitudes ρ and τ depend on neutron energy k^2, and, for some $k = k_B$, the expression (3) becomes of the form $R = (a - ib)/(a + ib)$ with real a and b. It means

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that for these k we have total (Bragg) reflection because $|R| = 1$. Reflection remains total in some range, called the "Darwin table," which width Δk^2 is called the "Darwin table width" (DTW).

Our approach helps to predict the effect discussed here, and we shall show why, in the Ewald theory of dynamical diffraction, this effect was missed.

Our main result is that the ratio of intensities of forbidden I_f and nonforbidden I_n reflections, which is equal to the ratio of the widths of the Darwin tables, is of the order

$$I_f/I_n = u/k_B^2, \tag{4}$$

where u is the optical potential of the crystal $u = 4\pi N_0 b$, N_0 is the atomic density, b is the coherent scattering amplitude, $k_B = \pi n/s$ is the Bragg wave number, and n is an integer. For a majority of crystals in the case of neutron scattering, the ratio (4) is of the order $\approx 10^{-5}$.

Now let us return to our model of a semi-infinite crystal consisting of crystalline planes parallel to the entrance surface. The elementary cell of a plane is a square with the lattice parameter α being considerably smaller than the period s in the direction of the normal to the surface. The period consists of two identical planes separated by distance a along the normal. All the atoms of the crystal are motionless, nonabsorbing, and have the same scattering amplitude b_s, which, for a single atom isolated from the crystal and placed into vacuum, is represented in the form

$$b_s = b_0/(1 + ikb_0), \tag{5}$$

where b_0 is a real magnitude, called the "scattering length," and k is the wave number of the incident neutron. Such a representation of the amplitude automatically satisfies the requirements of optical theorem: Im $b_s = k|b_s|^2$.

We consider the reflection of neutrons from this crystal when neutrons have the wave number $k \ll 2\pi/\alpha$. For such neutrons we can neglect diffraction on a single crystalline plane and describe the scattering on a plane with the help of only two scalar parameters, reflection r and transmission $t = 1 + r$ amplitudes.

Our goal is to calculate ρ and τ for a single period, to substitute them into (3), to show that there is a total reflection at the position of the forbidden reflection, and to calculate its DTW.

To calculate ρ and τ we must first calculate reflection r and transmission t amplitudes of the single atomic plane, and then calculate reflection r_{12} and transmission t_{12} of two planes constituting a single period.

Reflection amplitude r from a plane is equal to

$$r = -ip/(k_\perp + ip), \qquad p = 2\pi N_2 b, \tag{6}$$

where N_2 is the two-dimensional density of atoms $N_2 = 1/\alpha^2$, and b is a somewhat renormalized amplitude b_0 [see (5)], which was calculated in [8]. The expression (6) can be obtained with the help of the multiple wave scattering theory [8] or with the one-dimensional Schrödinger equation in which the crystalline plane is represented by a potential of the form $2p\delta(x)$ such as in the Kronnig-Penney potential. In the following we shall omit the subscript $\perp$.

Now we consider reflection r_{12} and transmission t_{12} amplitudes for the system of two planes separated by a distance a. Using the same method as in (1) with R in the right hand side replaced by $r\exp(2ika)$, we get

$$\begin{aligned} r_{12} &= r + t^2 e^{2ika} r/(1 - r^2 e^{2ika}) \\ &= r\frac{1 + (t^2 - r^2)\exp(2ika)}{1 - r^2\exp(2ika)}, \end{aligned} \tag{7}$$

and, similarly,

$$t_{12} = t^2\exp(ika)/[1 - r^2\exp(2ika)].$$

Substitution of $t = 1 + r$ and r from (6) in these relations gives

$$r_{12} = -2ipe^{ika} \times \frac{k\cos(ka) + p\sin(ka)}{k^2 + 2ipk + 2ip^2\sin(ka)\cos(ka) - 2p^2\sin^2(ka)}, \tag{8}$$

$$t_{12} = e^{ika} \times \frac{k^2}{k^2 + 2ipk + 2ip^2\sin(ka)\cos(ka) - 2p^2\sin^2(ka)}. \tag{9}$$

Now we must define reflection from a period. To do that, it is necessary to choose the form of the period. We choose it to be symmetrical, as is shown in Fig. 1.

The reflection amplitude from the period ρ is $\rho = \exp[ik(s - a)]r_{12}$, where the first factor appears because before and after reflection from two planes the wave propagates through the vacuum gap of the width $(s - a)/2$. Substitution of (8) in this formula leads to

$$\rho = -2ipe^{iks} \times \frac{k\cos(ka) + p\sin(ka)}{k^2 + 2ikp + 2ip^2\sin(ka)\cos(ka) - 2p^2\sin^2(ka)}. \tag{10}$$

In the same way, we get the transmission amplitude τ of the period

$$\tau = e^{ik(s-a)}t_{12} = e^{iks} \times \frac{k^2}{k^2 + 2ipk + 2ip^2\sin(ka)\cos(ka) - 2p^2\sin^2(ka)}. \tag{11}$$

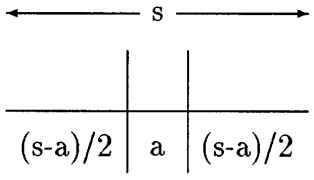

FIG. 1. The single period of the model. It contains two planes at distance a and two vacuum gaps on both sides of them. The total width s is the length of the period.

Now we substitute (10) and (11) into (3). Before doing that, it is helpful to modify (3) by dividing the numerator and denominator by $\sqrt{(1+\rho+\tau)(1-\rho+\tau)}$. As a result we get

$$R = \frac{\sqrt{(1-\tau+\rho)/(1+\tau-\rho)} - \sqrt{(1-\tau-\rho)/(1+\tau+\rho)}}{\sqrt{(1-\tau+\rho)/(1+\tau-\rho)} + \sqrt{(1-\tau-\rho)/(1+\tau+\rho)}}. \tag{12}$$

From (10) and (11) it follows that $\tau \pm \rho$ can be represented in the form

$$\begin{aligned}\tau \pm \rho &= e^{iks}\frac{k^2 \mp 2ip[k\cos(ka) + p\sin(ka)]}{k^2 + 2ikp + 2p^2\sin^2(ka) + 2ip^2\sin(ka)\cos(ka)} \\ &= \exp(iks - i\delta_\pm),\end{aligned}$$

with $\delta_\pm = \mp\phi_1 - \phi_2$, and

$$\phi_1 = \arctan\left(\frac{2p[k\cos(ka) + p\sin(ka)]}{k^2}\right), \tag{13}$$

$$\phi_2 = \arctan\left(\frac{2pk + 2p^2\sin(ka)\cos(ka)}{k^2 - 2p^2\sin^2(ka)}\right). \tag{14}$$

After substitution into (12), we get

$$R = \frac{\sqrt{\tan(ks/2 + \phi_1/2 - \phi_2/2)} - \sqrt{\tan(ks/2 - \phi_1/2 - \phi_2/2)}}{\sqrt{\tan(ks/2 + \phi_1/2 - \phi_2/2)} + \sqrt{\tan(ks/2 - \phi_1/2 - \phi_2/2)}}. \tag{15}$$

If two tan have a different sign, this expression becomes of the form $R = (a - ib)/(a + ib)$ with real a and b. In that case $|R| = 1$, and we have the total or Bragg reflection. It happens when

$$ks - \phi_1 - \phi_2 \le n\pi \le ks + \phi_1 - \phi_2, \tag{16}$$

where n is the integer. The inequalities (16) can be reduced to the form

$$|k_B - k - \phi_2/s| \le \phi_1/s, \qquad k_B = \pi n/s,$$

from which it follows that ϕ_2 determines the position of the Bragg peak center k_c, and $2\phi_1$ determines DTW.

Now, let us remember how the structure factor of the elementary cell is defined. Usually it is defined as

$$F(q) = \sum_j b_j \exp(iqr_j),$$

where b_j is the scattering amplitude of an atom at point r_j, and q is the momentum transfer. We use a slightly modified definition:

$$F(q) = \sum_j \beta_j \exp(iqr_j), \qquad \beta_j = b_j \Big/ \sum_l b_l.$$

In our model we have two atoms, so the structure factor is equal to

$$F(q) = \cos(qa/2),$$

if the origin is chosen in the middle between the planes. For specular reflection we have $q = 2k$, so, in our case, $F(q) = \cos(ka)$.

In expressions (13) and (14), $F(q)$ enters with another structure factor, which is represented by $\sin(ka)$, and which we shall denote by $G(q)$. Thus expressions (13) and (14) can be represented in the form

$$\phi_1 = \arctan\left(\frac{2pkF(2k) + 2p^2F(0)G(2k)}{k^2}\right), \tag{17}$$

$$\phi_2 = \arctan\left(\frac{2pkF(0) + 2p^2F(k)G(2k)}{k^2 - 2p^2G^2(2k)}\right). \tag{18}$$

where $F(0) = 1$ is introduced to get a structure factor for every entry of p.

It may be supposed that it is $G(q)$ which is important for the determination of the DTW for forbidden reflections, but it is not the full truth.

To get the width of the Darwin table it is necessary to find $2|\phi_1(k_c)|$, where k_c is the solution of the equation $(k_c - k_B)s = \phi_2(k_c)$. Let us suppose that $a = s/4$. The forbidden reflection should be at $k_B = 2\pi/s$, but, because of the small shift, the center of the reflection is not at k_B. It is shifted to $k_c = k_B + 2p/sk_B$. Substitution of this value into (13) gives

$$\phi_1(k_c) = \frac{2p}{k_B}\left(-\frac{p}{2k_B} + \frac{p}{k_B}\right) = \frac{p^2}{k_B^2}. \tag{19}$$

If we take into account that $p = 2\pi N_2 b \equiv us/4$, where $u = 4\pi N_0 b$ is the optical potential of the medium (we can also represent it in the form $u = uF(0)$, since $F(0) = 1$) and N_0 is the number of atoms in a unit volume, we find that the DTW in the considered case is equal to

$$\Delta k = 2\frac{\phi_1}{s} = \frac{\pi}{4}\frac{u^2}{k_B^3} \quad \text{or} \quad \Delta k^2 = 2k_B\Delta k = \frac{\pi}{2}\frac{u}{k_B^2}u. \tag{20}$$

For nonforbidden reflection (for instance, for $k \approx \pi/s$), we have $\Delta k^2 = 2uF(k_B) = \sqrt{2}\,u$, and from (20) immediately follows the ratio of intensities pointed out in (4).

It follows from (19) that the DTW is determined not only by the additional structure factor but also by the main structure factor which is zero only precisely at the Bragg point, and is not zero at the shifted position. For instance, let us suppose that there are no additional structure factors, i.e., we calculate ϕ_1 and ϕ_2 by perturbation theory and get

$$\phi_1 = \arctan[2pF(2k)/k], \qquad \phi_2 = \arctan(2p/k).$$

Since for $p > 0$ the reflection takes place for $k > k_B$, and the phase $\phi_1 < 0$ for these k, the inequality (16) must be

represented in the form

$$ks + \phi_1 - \phi_2 \leq n\pi \leq ks - \phi_1 - \phi_2$$

or $$|k_B s - ks + 2p/k| \leq |(2p/k)\cos(ka)|, \quad (21)$$

which determines the DTW of the reflection. Usually this DTW is of the same order of magnitude as (20), but does not necessarily coincide with it, as happened purely accidentally in our model.

The physical nature of the obtained result can be explained as follows. To have a total reflection it is necessary to have, first, the nonzero reflection ρ of a single period and, second, the phase difference $2\pi n$ of waves reflecting on two consecutive periods. The last condition can be satisfied only for $k = k_B$.

Forbidden reflections are those for which $\rho = 0$. It is zero because reflections from consecutive planes inside one period cancel each other.

However, first, it is easy to show that ρ can never be zero. Indeed, the first plane screens the second one, so amplitudes A_1 and A_2 of the waves reflected by two planes are different and cannot completely cancel each other. It follows from (7) that $A_1 = r$ and $A_2 = rt^2 \exp(2ika)/[1 - r^2 \exp(2ika)]$. Thus even if $\exp(2ika) = -1$, we get $|A_1 + A_2| > 0$.

Such a screening was observed in numerical calculations of many beam diffractions of electrons on an Au crystal [3], but from these calculations it was not clear whether the screening is a physical effect or the result of insufficient approximation, i.e., of an insufficient number of diffracting waves taken into account. However, the magnitude of that screening permitted good agreement of the calculations with experimental results. In our approach the screening is marked by the additional structure factor $G(q)$. It follows immediately that the greater the scattering the greater the effect, and that absorption and inelastic scattering enhance the effect. In Ewald theory the screening is not taken into account.

Second, if k is slightly increased by Δk, the phase difference of the waves reflected on consecutive periods becomes $2\pi n + \delta$. This mismatch violates the condition of total reflection, but at the same time it decreases the negative interference on the planes inside a single period, which leads to the increase of ρ. The magnitude of ρ is complex. It contains a phase ϕ which is negative (for positive p) and compensates the mismatch δ. It is this compensation which gives a finite width to the Darwin table. This compensation provides the finite DTW to forbidden reflections also. In Ewald theory, ρ contains $F(k_B) = 0$, which is a number and does not change with the change of k, thus no compensation can be obtained.

In conclusion, we proved that forbidden reflections differ from nonforbidden ones only by the width of the Darwin table. This width is provided by an additional structure factor and by the shift of the central point in the main structure factor. The forbidden reflections observed in polycrystals or deformed and vibrating crystals (see, for example, [11–14]) are usually ascribed to double nonforbidden ones. In our opinion they can be due to the discussed effect. The bends and vibrations create some quasimosaicity which increases the intensity of forbidden reflections in the same way as it increases nonforbidden ones. Of course, these considerations do not exclude the possibility of double reflection and umweg effect.

The considerations presented here are also applicable to x-ray diffraction. We hope that the predicted effects can be easily observed with intense synchrotron radiation. In electron diffraction the forbidden reflections must be especially well seen because of the strong scattering of electrons on atoms, thus, in the case when the observation of forbidden reflections is interpreted in terms of stacking faults and incomplete cells, the results should be modified. For high energy electrons the umweg effect is very strong, and the fine features following from our approach might be important only in some special cases. We hope, nevertheless, that our approach will give better agreement of numerical calculations with experiment even with fewer numbers of waves in n-beam approximation.

Two authors (V. K. I. and M. U.) want to express their gratitude to the Ministry of Education, Science, Sport and Culture of the Japanese Government for the opportunity it gave to them to work together, to M. Ono for useful discussions, and to our referees who, with their constructive criticism, helped to improve our paper considerably. One of the authors (V. K. I.) also thanks I. Carron for his gracious assistance. D. P. expresses gratitude to his coordinator E. Borca and to W. Furman for the invitation to work in JINR and for hospitality in Dubna.

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