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Kinematical Structure Factors from Dynamical Electron Diffraction?

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Abstract

Electron diffraction intensities are not simply related to the corresponding structure factors except in the case of 'dynamical extinctions'. These extinctions, explained by Gjønnes & Moodie [*Acta Cryst.* (1965), **19**, 65-67], occur for reflections that are kinematically forbidden - thus the resulting intensity is zero. If it was possible to find conditions when 'dynamical extinction' occurs for reflections that are not forbidden, it would be possible to use electron diffraction intensities for the determination of structure factors in a simple way. Unfortunately, it can be shown that this is not possible.

Introduction

A student asked me the following question: 'If *G-M* lines can be understood as the result of pair-wise cancellation of multiple-diffraction routes in the case of reflections that are kinematically forbidden, can this same cancellation occur for a reflection that is not kinematically forbidden?'

This is a good question because, if such cancellation did occur, the intensity in such a reflection would depend only on the structure factor for that reflection. Then, we could use those intensities in a very direct way to contribute to structure determination.

The answer, unfortunately, is no.

Background

In electron diffraction, reflections that have structure factor zero (kinematically forbidden reflections), because of the presence of screw axes or glide planes in the crystal, often appear with intensities that are as high as those of allowed reflections. This is because of the importance of dynamical diffraction or multiple-diffraction routes. However, there are certain conditions under which the intensity of diffraction into these kinematically forbidden reflections is identically zero. These are known as dynamical extinctions.

The conditions under which dynamical extinctions occur refer to both particular symmetry elements and particular orientations. The development of these ideas occurred in three papers (Cowley & Moodie, 1959; Miyake, Takagi & Fujimoto, 1960; Cowley, Moodie, Miyake, Takagi & Fujimoto, 1961); Gjønnes & Moodie (1965) then provided the definitive description in a paper that is clear, concise and correct. In order to discuss the case where reflections that are not kinematically forbidden are involved, we repeat, in the next section, the argument of Gjønnes & Moodie for forbidden reflections (generated by a single symmetry element).

Dynamical extinctions appear in convergent-beam patterns as lines of extinction along the locus of the appropriate conditions. As a result, the following terms have all been used as synonyms for 'dynamical extinction': Gjønnes-Moodie line, *G-M* line, dark bar and black cross. These features have come to play an important role in symmetry determination in electron microscopy. See, for example, the work of Eades (1988) and Tanaka & Terauchi (1985).

The Gjønnes–Moodie theory

It has been shown by Cowley & Moodie (1962) that the amplitude of a particular diffracted beam can be written

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$$U_g(k) = C\sum[F_1F_2F_3\ldots F_nZ(k)], \quad (1)$$

where U_g is the amplitude of the diffracted beam, g, with the incident beam at orientation k. C is a constant. The summation is over all possible diffraction routes. The F_i are the structure factors for the individual steps in each multiple-diffraction route. [It would be more accurate, if more cumbersome, to write the product $F(g_1)F(g_2)F(g_3)\ldots F(g_n)$, where $g_1+g_2+g_3+\ldots+g_n = g$.] Finally, Z is a function given explicitly by Cowley & Moodie (1962) that involves the excitation error at each vertex of the multiple-diffraction path.

$U_g(k)$ can be shown to be zero if it is possible to pair the terms in the summation such that each pair cancels. This requires two conditions. First, the function Z must be the same for the two paths. This requires the orientation of the incident beam to be such that the excitation error is the same at corresponding vertices between the two paths. Second, the products $F_1F_2\ldots F_n$ for the two paths must be of equal magnitude and opposite sign.

$$[F_1F_2F_3\ldots F_n]_A = -[F_1F_2F_3\ldots F_n]_B. \quad (2)$$

For the second condition to be fulfilled, the two paths must be chosen so that each structure factor can be paired,

$$|F_i|_A = |F_j|_B, \quad (3)$$

and at least one structure factor has opposite sign from its counterpart,

$$F_{iA} = -F_{jB}. \quad (4)$$

For a complex structure factor,

$$F_A = -F_B \quad (5)$$

implies

$$\alpha_A = \pi + \alpha_B. \quad (6)$$

A search through *International Tables for Crystallography* (1992) for the individual symmetry operations that can be included in space groups reveals that only a twofold screw (2_1) or a glide plane (a, b, c, d, n) can give $F_A = -F_B$.

The case of a glide

Consider first the case of a glide plane oriented parallel to the electron beam. Let the beam be oriented along **z** and the normal to the glide be along **y**.

If, instead of a glide, there was a true mirror, the structure factor would have the mirror relation

$$F(hkl) = F(h\bar{k}l); \quad (7)$$

however, in the case of the glide, the relation is

$$F(hkl) = (-1)^l F(h\bar{k}l). \quad (8)$$

In the special case of reflections along **x** and where l is odd,

$$F(h0l) = (-1)^l F(h0l) = -F(h0l) = 0. \quad (9)$$

These are the kinematically forbidden reflections.

Now, the multiple-diffraction routes can be paired using the mirror operation, since

$$|F(hkl)| = |F(h\bar{k}l)| \quad (10)$$

and the sign can be negative. In fact, when a multiple-diffraction route is paired with its mirror, we get

$$\begin{aligned}[F_1F_2F_3\ldots]_A &= [(-1)^{l_1}F_1(-1)^{l_2}F_2(-1)^{l_3}F_3\cdots]_B \\ &= (-1)^{\Sigma l_i}[F_1F_2F_3\ldots]_B. \quad (11)\end{aligned}$$

Since $\sum l_i$ is just the value of l for the final reflection, the negative sign will apply whenever l is odd in the final reflection. If the two multiple-diffraction routes are related by a mirror path, the final reflection must also lie on the mirror plane ($k=0$). Then, the two conditions ($k=0$ for the paths to be paired, and l odd for each pair to cancel) can only occur for the forbidden reflection. Fig. 1(a) shows one pair of multiple-diffraction routes.

We are not concerned here with the details of the excitation error term. Suffice it to say that the cancellation will occur only along the exact mirror line.

The case of a twofold screw axis

In the case of a 2_1 screw axis perpendicular to the electron beam, we can follow a similar argument. Here,

$$F(hkl) = (-1)^k F(\bar{h}k\bar{l}). \quad (12)$$

This gives forbidden reflections for k odd when $h=k=0$.

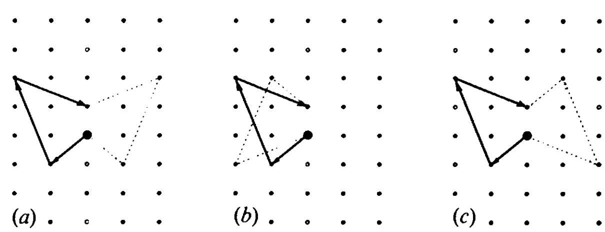

Fig. 1. Examples of the pairing of multiple-diffraction routes. (a) Glide plane parallel to the incident beam. The routes are paired by reflection in the glide plane. (b) Twofold screw axis perpendicular to the beam. The routes are paired by reflection in a plane through $g/2$. (c) Glide plane perpendicular to the beam. Multiple-diffraction routes are paired by a rotation through 180° about a vertical axis through $g/2$. To contribute intensity in this case the routes must involve out-of-zone reflections.

The diffraction routes are paired as shown in Fig. 1(*b*). Each reflection hkl in one path is replaced by the symmetry-related reflection $\bar{h}k\bar{l}$. To complete the path, the order of the reflections is reversed. This is equivalent to making one path the reflection of the other in the line at $g/2$. The extinction occurs along a line at the exact Bragg angle for the reflection.

The case of a glide plane perpendicular to the beam

The third case treated by Gjønnes & Moodie is that of a glide plane perpendicular to the beam. In this case (beam direction along **y**), we have

$$F(hkl) = (-1)^l F(\bar{h}k\bar{l}) \tag{13}$$

for a c glide. The routes are then paired in the way shown in Fig. 1(*c*).

Zero-layer diffraction

If the projection approximation is valid, then the pairing corresponding to a glide parallel to the beam can also be applied to a screw axis and *vice versa*. (This is because the result

$$|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})| \tag{14}$$

that applies to all space groups gives an additional relation provided that all reflections are in the plane.)

This gives rise to dynamical extinctions along two perpendicular directions: a black cross.

Completing this argument

Thus far, we have reproduced the argument of Gjønnes & Moodie. We consider one additional point. Gjønnes & Moodie say that all multiple-diffraction routes can be paired so that each pair cancels. However, there are some routes that cannot be paired. The multiple-diffraction routes are paired by relating one member of the pair to the other by a symmetry operation. This cannot be done for a multiple-diffraction route that transforms into itself. Such routes do exist. Examples for both glide and screw are shown in Fig. 2. The existence of these routes does not invalidate the conclusion given above, however, since such routes include at least one step for which $F=0$ (see below). A multiple-diffraction route that mirrors into itself includes at least one kinematically forbidden reflection and the Gjønnes–Moodie rules are preserved.

Gjønnes & Moodie did not draw attention to these non-pairable routes; probably they considered the point to be obvious. However, we can use it in what follows.

It is easy to see that the unpaired routes must include a forbidden reflection, provided that the route is in the zero layer, since every alternate reflection along the row must have zero structure factor. It is perhaps not immediately clear that the same result applies if out-of-zone reflections are included; however, these cannot occur in the positions that would permit the rule to be broken.

Reflections that are not forbidden

We can now give two arguments to show that cancellation of multiple-diffraction routes cannot occur for reflections that are not kinematically forbidden.

First argument

Until now, we have considered pair-wise cancellation in the presence of a single symmetry element. Suppose that, by looking at more complex space groups with several symmetry elements, we could find a case where we could develop a relation between the structure factors that would allow us to pair the multiple-diffraction routes for a reflection that is not forbidden. Even in this case, the intensity diffracted would not depend only on the structure factor for that one reflection: the unpaired routes would not now include (in general) a reflection with zero structure factor.

Second argument

In order to pair the multiple-diffraction routes, we must have a relation of the kind $F_i = -F_j$, which can be used to form the pairs. Now, relations of this kind, as seen above, are always of the kind

$$F_i = (-1)^h F_j, \tag{15}$$

and the index of the observed reflection,

$$h_g = \textstyle\sum h_i, \tag{16}$$

must be odd if the sign of the product is negative. Therefore, for the observed reflection itself, we must have

$$F_g = -F_g = 0. \tag{17}$$

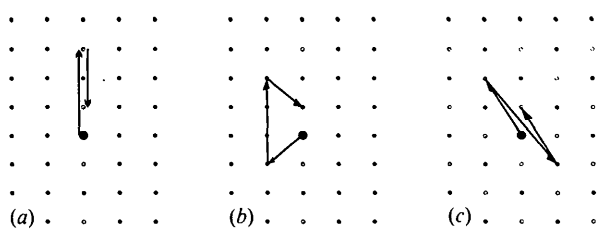

Fig. 2. Examples of multiple-diffraction routes that cannot be paired. Diagrams (*a*), (*b*) and (*c*) correspond to the symmetry operations of Figs. 1(*a*), (*b*) and (*c*), respectively.

The pairing condition itself implies that the structure factor of the observed reflection is zero. Therefore, we can conclude that the supposition of the previous section is false. No combination of symmetry elements can give rise to a pairing rule for an allowed reflection.

Summary and concluding remarks

In electron diffraction, it is difficult to use experimental intensities to solve crystal structures. This is because - unlike the case for X-rays - the intensity of a reflection does not depend only on the structure factor for that reflection but, through the complexities of dynamical diffraction, on many structure factors.

However, there are cases where the dynamical-diffraction multiple-diffraction routes can be shown to contribute nothing to the diffracted intensity. Unfortunately, these dynamical extinctions occur only when the structure factor for the observed reflection is itself zero.

Therefore, the idea that, by looking in specific circumstances and at a specific orientation, we could find an experimental intensity that would depend only on the structure factor for the observed reflection turns out not to be fruitful. The student asked a good question but one with an unhappy answer.

This conclusion should not be taken to mean that there are no methods of using electron diffraction intensities for crystal structure determination, only that the particular method proposed does not work. There are several ways of determining structure factors from electron diffraction. These have been reviewed by Gjønnes, Olsen & Matsuhata (1989) and Spence (1993). One of these methods in particular is related to the ideas of this paper: the Bristol group (Vincent & Exelby, 1994) has found situations where the intensities may be interpreted kinematically - although unfortunately only for high-order reflections.

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The Effect of a Crystal Monochromator on the Local Angular Divergence of an X-ray Beam

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Abstract

The performance of an X-ray optical system often depends critically on the local angular divergence of the X-ray beam. For example, in systems for radiography, tomography and diffraction topography, the angular divergence of the incident beam at a point in the sample determines the limiting spatial resolution. In this paper, formulas are derived for the local divergence in the diffracted beam of the non-dispersive asymmetric reflection double-flat-crystal monochromator, illuminated by synchrotron or characteristic radiation. The formulas are analyzed to determine the general behavior of the local divergence as a function of the asymmetry factors of the crystal reflections. For synchrotron radiation, one surprising conclusion is that the local divergence of the magnifying monochromator is always greater than that of the symmetric monochromator, significantly so for even moderate magnification factors. This result, which contradicts a claim in the literature, is attributed to a prismatic property of asymmetric reflection that has not previously been identified.