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Extinction Conditions in the Dynamic Theory of Electron Diffraction

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General conditions are given for the continued complete absence of kinematically space-group forbidden reflexions when the scattering is dynamic. It is shown that reflexions which are forbidden because of glide planes or twofold screw axes will remain forbidden under dynamic conditions if suitable restrictions are placed on the direction of the incident beam. These restrictions can be represented by a cross, one arm of which corresponds to the exact Bragg condition, the other arm being normal to the first and to the screw axis or glide direction. When only zero-layer interactions are taken into account the locus of zero intensity includes both arms. When higher-layer interactions are included the locus of zero intensity will be one or other arm of the cross depending on whether the incident beam is perpendicular to a screw axis or parallel to a glide plane. The case in which the incident beam is perpendicular to a glide plane, though trivial for zero-layer interactions, leads to a condition for zero intensity satisfied only at the intersection of the arms of the cross when higher layer interactions are included.

1. Introduction

Under conditions of dynamic scattering kinematically forbidden reflexions may be excited with appreciable intensity when the conditions of 'Umweganregung' are satisfied, *i.e.* when $h=h_1+h_2$ and the Bragg condition is sufficiently well satisfied for h and h_1. Here h is the reciprocal lattice vector for the forbidden reflexion and h_1 and h_2 the reciprocal lattice vectors for allowed reflexions. Nevertheless it has been shown (Cowley & Moodie 1959) that certain reflexions will remain forbidden if suitable restrictions are placed on the angle of incidence.

In a typical case it is estimated that the permissible angular deviation will be of the order of ten minutes of arc, so that the associated effects will not be readily detected in conventional diffraction experiments. Recent improvements in the technique of electron diffraction (Goodman & Lehmpfuhl, 1965) permit observation over a considerable range of angles with a resolution of the order of one minute of arc, and in consequence detailed measurements on the extinctions in CdS are now available. Precise selected area diffraction experiments have permitted qualitative observations to be made on hexagonal cobalt (Fujime, Watanabe & Ogawa, 1964). It is the purpose of this paper to lay down general conditions for the continued, complete absence of kinematically space-group forbidden reflexions when the scattering is dynamic.

In a dynamic treatment of electron diffraction it is usually sufficient to consider only those reflexions lying within a section of reciprocal space which passes through the origin. For simplicity this approximate case will be treated in some detail in § 2 and it will be shown in § 3 that the argument can be extended to include all interactions.

2. Extinction conditions for the planar groups

The symmetry elements responsible for kinematic absences in non-centred unit-cells are screw axes and glide planes. To the approximation of this section only the planar group of the appropriate projection need be considered. The only element in the planar group which can lead to absences is the glide-reflexion, corresponding to a twofold screw axis or a glide plane in the space group. From the point of view of two-dimensional symmetry the remaining absences due to three-, four- and six-fold screw axes can be regarded as accidental and the corresponding reflexions will not vanish, as was pointed out by Cowley, Moodie, Miyake, Tagaki & Fujimoto (1961) for the particular case of a fourfold screw axis.

We shall assume with no loss in generality that the projection has a symmetry *pg*. The angular conditions can be studied with the use of a general expression for dynamic scattering given by *e.g.* Cowley & Moodie (1957), Fujiwara (1959), Fujimoto (1959), Niehrs (1959). This expression can always be written as a series, the general term of which, for a reflexion $\mathbf{h}$, takes the form (see *e.g.* Cowley & Moodie, 1961).

$$F(\mathbf{h}_1)\,F(\mathbf{h}_2) - - - F(\mathbf{h}_n)\,Z\,(\zeta, \zeta_1, - - - \zeta_{n-1}), \qquad (1)$$

where ζ_r is the excitation error of the reflection $\sum_{j=1}^{r}\mathbf{h}_j$ and $\mathbf{h}=\sum_{j=1}^{n}\mathbf{h}_j$. Terms of this type may be represented

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graphically by means of a multiple scattering diagram. This is illustrated in Fig. 1(*a*) for the case $n=3$; where the lines labelled $\mathbf{h}_j$ represent the structure factors $F(\mathbf{h}_j)$ and excitation errors are associated with vertices.

Kinematically forbidden reflexions will remain at zero intensity under dynamic conditions when terms of the above type can be arranged in pairs with products of F's equal in magnitude and opposite in sign while the corresponding Z functions remain equal. Pairs satisfying the first of these two conditions result when the diagrams are reflected either over the line through the reciprocal lattice vector of the forbidden reflexion (line m in Fig. 1(*a*)) or over a line bisecting the reciprocal lattice vector [line m' in Fig. 1(*a*)].

In order to prove this, introduce the indices (h, k) of the $\mathbf{h}$'s so that the reflexions $(0, k)$, $k=2n+1$ are forbidden kinematically; that is, the glide line is parallel to the k axis. The reflexion of the diagram over m results in a change of sign in h in all the $\mathbf{h}_j$'s. In reflection over m' the sequence of the F's is also reversed. From the general properties of the planar group pg,

$$F(h, k)=F(\bar{h}, k) \quad k=2n$$
$$F(h, k)=-F(\bar{h}, k) \quad k=2n+1.$$

For a kinematically forbidden reflexion k is odd and hence equation (1) must contain an odd number of $F(h, k)$'s with k odd. Thus for the products represented by Fig. 1(*a*), (*b*), (*c*),

$$\begin{gathered} 1(a) \\ F(h_1, k_1)F(h_2, k_2) --- F(h_n, k_n)= \\ 1(b) \\ -F(\bar{h}_1, k_1)F(\bar{h}_2, k_2) --- F(\bar{h}_n, k_n)= \\ 1(c) \\ -F(\bar{h}_n, k_n)F(\bar{h}_{n-1}, k_{n-1}) --- F(\bar{h}_1, k)\ . \end{gathered}$$

Since the excitation errors are related to the vertices of the diagrams they will be unchanged on reflexion over m when the incident beam lies in the plane through

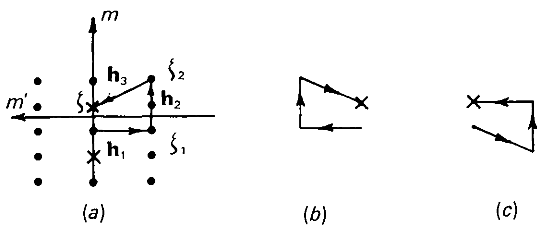

Fig. 1. Multiple scattering diagrams for third order processes associated with the kinematically forbidden reflexion marked X. (*a*) Typical third order diagram. (*b*) Diagram generated by reflexion over m. (*c*) Diagram generated by reflexion over m'.

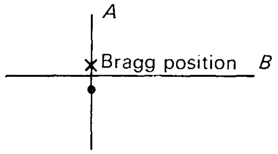

Fig. 2. Two-dimensional representation of the direction of the incident beam.

k and the axis of projection. On reflexion over m' the excitation errors will remain unchanged when the incident beam originates exactly above the line m', that is, when the Bragg condition for the forbidden reflexion is exactly satisfied.

If the direction of the incident beam is represented two-dimensionally the region of complete absence of the forbidden reflexion will therefore become cross-shaped, as shown in Fig. 2, with one arm of the cross along the line corresponding to the exact Bragg condition and the other arm normal to the first and through the axis of projection.

These results agree in detail with the observations made by Goodman & Lehmpfuhl (1964) on CdS.

In addition to the general conditions limiting reflexions considered above, additional reflexions may be forbidden kinematically when the atoms lie on special positions. These positions are not, however, described by the symmetry of the planar group and consequently terms will not cancel in the manner described above.

3. Interactions involving higher layers

In most cases of practical importance in electron diffraction dynamic interactions involving higher layers can be safely neglected. It is conceivable, however, that such interactions may become appreciable when the direction of the incident beam coincides with a long axis. For the sake of completeness we shall, in this section, extend our treatment to the general case. It is, of course, this case which corresponds to the calculation of crystal wave-functions with the full three-dimensional symmetry, a problem of some interest in solid state physics.

Three essentially different situations arise. Two derive from the inclusion of higher layer interactions in the case considered in § 1. These are (i) a projection along an axis in a glide plane, and (ii) a projection containing a twofold screw axis. In addition it is necessary to consider (iii) higher layers of a projection with a reduced or centred unit-cell. Here the projection constitutes a trivial case, but possibilities for 'Umweganregung' arise when interactions with higher layers are included.

These three cases can be discussed in terms of the diagrams of Fig. 1(*a*), (*b*), (*c*), which are now no longer restricted to the plane of the zero layer. Fig. 1(*b*) is now obtained from (*a*) by a reflexion over a *plane* m through the axis of projection and similarly (*c*) results from a reflexion over a plane m' parallel to the axis of projection plus reversal of direction. Fig. 1(*c*) may be derived from (*b*) by a rotation of 180° round the line of intersection of the planes m and m' plus rever sal of direction.

Since the corners of the diagrams will remain at the same height above the zero layer after the reflexions, equality of the Z functions still obtains under the conditions laid down in § 2. Hence the terms given by equation (1) will cancel in pairs under the geometrical conditions represented by the two arms of the cross of Fig. 2 provided the products of the structure factors cancel. It may be added that terms represented by the diagrams of Figs. 1(*b*) and (*c*) have equal Z functions for a direction of the incident beam given by the centre of the cross.

It is superfluous to demand that the reflexions over m or m' should be allowed by the point symmetry of the lattice as this will be implicit in the conditions necessary for the cancellation of the products of the structure factors. We now set out to define those conditions.

We write the arguments of the structure factors

$$\begin{array}{ccc} 1(a) & 1(b) & 1(c) \\ (h_j, k_j, l_j) & (h_j, \bar{k}_j, l_j) & (\bar{h}_j, \bar{k}_j, l_j)\ , \end{array}$$

where h lies along the axis of projection and $l=2n+1$ are the forbidden reflexions under consideration. Formulae relating to the structure factors for the above arguments in the case of a glide plane and a twofold screw axis are those relating to the space groups Pc and $P2_1$ respectively, namely:

$F(h, k, l)=(-1)^l\, F(h, \bar{k}, l)$; glide plane (010), glide $c/2$,

$F(h, k, l)=(-1)^l\, F(\bar{h}, \bar{k}, l)$; screw axis along c,

$F(h, \bar{k}, l)=(-1)^l\, F(\bar{h}, \bar{k}, l)$; glide plane (100), glide $c/2$.

By using arguments exactly analogous to those of § 2 we find that the terms represented by Fig. 1(*a*) and (*c*) will cancel for a space group with a twofold screw axis when the geometrical conditions are such as to make their excitation errors, and hence their Z functions, equal; that is, for those conditions represented by the arm labelled B in Fig. 2.

The terms represented by Fig. 1(*a*) and (*b*) will cancel for a space group with a glide plane in the given orientation under the geometrical conditions represented by the arm A of the cross in Fig. 2.

Table 1. *Conditions under which kinematically space-group forbidden reflexions remain at zero intensity when dynamic interactions are included*

A Incident beam in the plane defined by the reciprocal lattice vector of the forbidden reflexion and the axis of projection.
B Bragg condition satisfied by forbidden reflexion.

Axis of incident beam relative to symmetry element	Conditions for absence: Only zero-layer interactions	Conditions for absence: Including higher layer interactions
Perpendicular to screw axis	A or B	B
Parallel to glide plane	A or B	A
Perpendicular to glide plane	always (trivial)	A and B

Finally, the terms represented by the Fig. 1(*b*) and (*c*) cancel for a space group with a glide plane normal to the axis of projection under the conditions represented by the centre of the cross in Fig. 2, *i.e.* when the incident beam satisfies the Bragg condition of the forbidden reflexion and lies in a plane defined by the glide direction and the normal to the glide plane. These results are summarized in Table 1.

The argument relating to the situation in which the direction of the incident beam lies along an axis in the glide plane is applicable to any reflexion $(h, 0, l)$, $l=2n+1$, forbidden by the glide plane, and hence also to non-axial glide.

It may be mentioned that the geometrical conditions imposed on the incident beam, which are summarized in Fig. 2, leave one coordinate in the wave-vector space undetermined, since the results are applicable over a range of wavelengths. This contrasts with the calculation of electron wave-functions in crystals, where special points in k space are often studied. Under those conditions 'forbidden reflexions', or vanishing energy gaps also result from three-, four- and six-fold axes.

Kinematically forbidden reflexions may also appear as a result of plural scattering in mosaic crystals (*e.g.*, Cowley, Rees & Spink, 1951). The arguments given here then do not apply and, in fact it must be expected that the regions of dynamical absence will vanish for a mosaic crystal.

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