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The extinction rule for reflexions in symmetrical spot patterns of electron diffraction by crystals.

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In a recent paper of Cowley & Moodie (1959) dealing with the theory of electron diffraction by crystals, they have concluded that the forbidden reflexions due to the space group symmetry can not be generated by dynamical effects in the symmetrical spot patterns from a perfect crystal, when the incident beam is exactly parallel to a principal axis of the crystal. In the present paper, their problem is re-investigated and it is revealed the fact that their conclusion should be partly revised for completeness.

Let $V_{\mathbf{h}}$ be the Fourier component of the periodic potential $V(\mathbf{r})$ in a crystal, and $\mathbf{h}$ the reciprocal lattice vector. The wave field of electrons in $V(\mathbf{r})$ is given by a superposition of modulated plane waves

$$\Psi_{\mathbf{k}_0}(\mathbf{r}) = u_{\mathbf{k}_0}(\mathbf{r}) \exp 2\pi i(\mathbf{k}_0 . \mathbf{r}) , \quad (1)$$

where $\mathbf{k}_0$ is the wave vector of the primary wave, and $u_{\mathbf{k}_0}(\mathbf{r})$ is a periodic function which can be written in the form

$$u_{\mathbf{k}_0}(\mathbf{r}) = \sum_{\mathbf{h}} \psi_{\mathbf{h}} \exp 2\pi i(\mathbf{h} . \mathbf{r}) . \quad (2)$$

The extinction rule for the *structure amplitudes*, namely that for the Fourier components $V_{\mathbf{h}}$, comes from the invariance of $V(\mathbf{r})$ under the transformation of $\mathbf{r}$ due to the operations of screw axes and glide planes possessed by the crystal. Similarly, the extinction rule for the *reflexions*, namely that for the Fourier components $\psi_{\mathbf{h}}$, should result if $u_{\mathbf{k}_0}(\mathbf{r})$ remains invariant by these operations.

Since the ratios ψ_h/ψ_0 are uniquely determined by $\mathbf{k}_0$, the periodic function $u_{\mathbf{k}_0}(\mathbf{r})$ is invariant, except for a numerical factor, under the operation by which the potential $V(\mathbf{r})$ and the wave vector $\mathbf{k}_0$ remain invariant. It can be easily shown that the numerical factor must be unity when $\psi_0 \neq 0$. The functions $\Psi_{\mathbf{k}_0}$ for which $\psi_0 = 0$ can be disregarded in Laue case, since they are excluded by the boundary conditions.

Let us assume hereafter that $\mathbf{k}_0$ is parallel to a principal axis and the z-axis is in the same direction. If the crystal possesses, for example, the b-glide plane perpendicular to the x-axis, the wave vector $\mathbf{k}_0$ and hence $u_{\mathbf{k}_0}(\mathbf{r})$ remain invariant under the operation due to this glide plane, so that the reflexions $(0kl)$ (k: odd) should disappear.

When the wave-length of electrons is sufficiently short as assumed by Cowley & Moodie, the symmetrical spot pattern is mainly composed of the $(hk0)$ reflexions, and we can assume that the expression (2) for $u_{\mathbf{k}_0}(\mathbf{r})$ contains the $(hk0)$ terms only. In this case, we have the relation $u_{\mathbf{k}_0} = u_{-\mathbf{k}_0}$, accordingly $u_{\mathbf{k}_0}(\mathbf{r})$ is invariant also for the operations by which the wave vector $\mathbf{k}_0$ is transformed to $-\mathbf{k}_0$. Thus, when the crystal possesses, for example, the 2_1-axis parallel to the x-axis, the reflexions $(l00)$ (l: odd) should disappear in relation with this screw axis.

Summarizing the above considerations we can state: The extinction rule of reflexion spots in a symmetrical transmission pattern of electron diffraction from a perfect crystal, for short wave-length of electrons, is given in relation with those operations of screw axes and glide planes, by which the propagating direction of the primary wave is transformed to the same or opposite of the original direction.

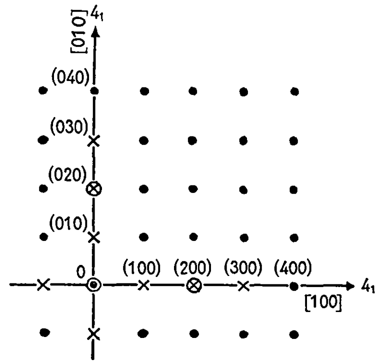

Fig. 1. The spot pattern from a crystal belonging to the space group $P4_132$. The incident beam, exactly parallel to $[00\bar{1}]$. $\otimes$: Forbidden by the kinematical theory but allowed by the dynamical theory. $\times$: Forbidden by both theories. $\bullet$: Allowed by both theories.

This result is not exactly the same as that of Cowley & Moodie. Some of the space groups of cubic symmetry contain the four-fold screw axes 4_1 and 4_2 perpendicular to the principal axes, and the extinction rule for structure amplitudes related to single-fold operations of such screw axes can not apply with respect to the *reflexions*, because the changes of the direction of $\mathbf{k}_0$ caused by these operations do not satisfy the due condition above mentioned. Fig. 1 shows schematically the spot pattern from a crystal belonging to the space group $P4_132$ given by the incident beam parallel to a cubic axis. In this pattern, the intensities of reflexions as well as the structure amplitudes vanish for (100), (300), ... etc. in relation with the $(4_1)^2 =$

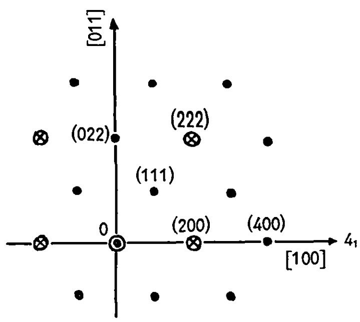

Fig. 2. The spot pattern from a crystal of diamond-type structure. The incident beam, exactly parallel to $[01\bar{1}]$. $\otimes$: Forbidden by the kinematical theory but allowed by the dynamical theory. $\bullet$: Allowed by both theories.

2_1-operation, whereas the reflexion (200), for which the structure amplitude vanishes in relation with the 4_1-operation, is not forbidden.

The present result, further, can be applied also to the symmetrical spot pattern given by the incident beam parallel to a zone axis which is not the principal axis. Fig. 2 shows the spot pattern obtained from a crystal of diamond-type structure with the incident beam parallel to $[01\bar{1}]$-axis. In this pattern, the reflexion (200), for which the structure amplitude vanishes by the presence of the screw axis 4_1 perpendicular to $[01\bar{1}]$, is not forbidden by the same reason as considered above. The reflexion (222) is also not forbidden because the extinction of the structure amplitude of it is due to the special positions of atoms and is not directly related to the symmetry operations.

An easy understanding of the above results may be obtained in the following way. The appearance of forbidden reflexions is caused by the dynamical double reflexions, and the amplitude of doubly reflected wave on the net planes (hkl) and $(h'k'l')$ may be regarded as proportional to $V_{hkl}\cdot V_{h'k'l'}$ at least approximately. In the example of Fig. 1 we have the relations $V_{hk0} = -V_{h\bar{k}0}$ (h: odd) and $V_{hk0} = V_{h\bar{k}0}$ (h: even), assuming the coordinate origin on the 4_1-axis parallel to the x-axis. Then, the double reflexions can not contribute to (100) because the products $V_{hk0}\cdot V_{1-h,\bar{k},0}$ and $V_{h\bar{k}0}\cdot V_{1-h,k,0}$ have always the opposite sign of one another, while (200) may appear because $V_{hk0}\cdot V_{2-h,\bar{k},0}$ and $V_{h\bar{k}0}\cdot V_{2-h,k,0}$ have the same sign. The similar argument can be applied to explain the appearance of (200) in Fig. 2.

Reference

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A twinning interpretation of 'superlattice' reflexions in X-ray photographs of synthetic klockmannite, CuSe.

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Introduction

X-ray diffraction studies of klockmannite were begun by Earley (1949) who observed strong X-ray reflexions consistent with a hexagonal unit cell of dimensions $a = 3{\cdot}94$ Å, $c = 17{\cdot}25$ Å, and containing six CuSe units. Its similarity with covellite (CuS) suggested that the compounds were isostructural and Berry (1954) gave a possible solution which resembled that for covellite, but the agreement between the observed and calculated reflexions was rather unsatisfactory. Earley and Berry both noted the occurrence of 'superlattice' reflexions corresponding to a much larger cell but did not investigate them further. Dr Gabrielle Donnay suggested that the extra reflexions might be investigated by optical-transform methods. She supplied us with photographs taken with Cu $K\alpha$ radiation using synthetic crystals in the form of thin hexagonal plates prepared by Dr G. Kullerud of the Geophysical Laboratory, Washington D.C. The complete structure has not been determined, but in view of the current interest in the twinning phenomena which occur in various minerals (e.g. Donnay, Donnay & Kullerud, 1958) it was thought that a short note on the progress made so far would be worth publishing.

The problem

Fig. 1 is a representation of the $hk0$ section of the weighted reciprocal lattice; there are no indications of any multiplication of the c axis and for all the three lattices discussed later the c dimension remains 17·25 Å. The very strong reflexions (indicated conventionally by encircled discs) correspond to the cell of side $a = 3{\cdot}94$ Å which will be referred to as the sub-cell. The additional reflexions lie on a hexagonal reciprocal net which corresponds in real space to a cell of side $13 \times a^{\text{sub}} = 51{\cdot}2$ Å. This would contain 1,014 CuSe units, and, at the beginning of the present investigation, was taken to be the true cell of the structure. Dr Donnay observed that the extra reflexions also lay on circles surrounding the strong reflexions (see Fig. 1). It was from this point that the optical-transform investigation began. Details of the steps

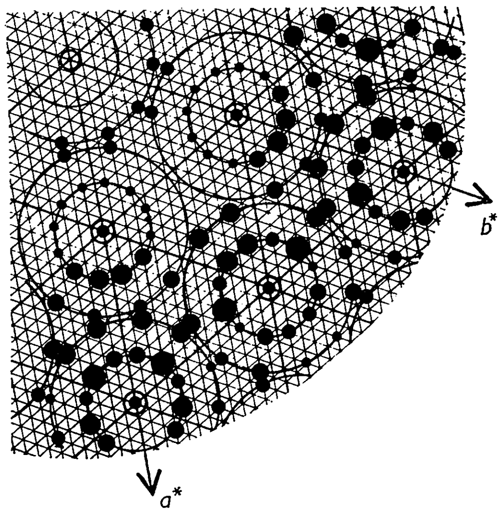

Fig. 1. Part of the $hk0$ section of the weighted reciprocal lattice; a^* and $a^*/13$ nets indicated. The encircled reflexions are very intense compared with the others.

in the solution will be published when the complete structure has been worked out, and only a brief outline will be given here.

Method of approach

The complete weighted reciprocal-lattice section was treated as the product of three functions. The first is a