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The extinction rule for reflexions in symmetrical electron-diffraction spot patterns.

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In a recent note, Miyake, Takagi & Fujimoto (1960) (M.T.F.) have considered the extinction rule for reflexions in symmetrical electron-diffraction spot patterns and have arrived at conclusions which differ in some respects from those contained in a paper by Cowley & Moodie (1959) (C. M.). The apparent differences have now been discussed and resolved by private correspondence. The present note is designed to correct any misapprehensions arising from the previous publications and present our current appreciation of the problem.

Firstly it should be made clear that both the M.T.F. and C.M. treatments apply to three-dimensional crystals of arbitrary thickness and can be developed without any short-wavelength approximation so long as the repetition distance of the crystal lattice along the beam direction is small enough.

In the M.T.F. treatment, the extinction rule for reflexions is derived by considering the symmetry of the electron wave field in relation to the symmetry of the three-dimensional space group of the crystal. It was shown that some reflexions which are space-group forbidden under kinematic diffraction conditions would not, in general, have zero intensity.

In the C.M. treatment the three-dimensional space-group symmetry is not considered explicitly. The crystal is divided into a large number of thin layers, the thickness of each in the beam direction being the repetition distance for the crystal lattice in that direction. It is then assumed that if this repetition distance is small the effect on the electron beam of each layer may be approximated by the effect of a two-dimensional projection of the layer; i.e.

$$\varphi(x, y) = \int \varphi(xyz)\,dz\ ,$$

where $\varphi(xyz)$ is the potential distribution in the layer and the beam is in the z-direction. It is then shown that the symmetry of the wave leaving the crystal is the same as the symmetry of $\varphi(x, y)$, so that the extinctions in the diffraction pattern are those corresponding to diffraction from the two-dimensional projection, $\varphi(x, y)$.

The assumption in the C.M. treatment that a layer of crystal can be approximated by a two-dimensional projection is, however, completely valid only if all atoms in the layer actually lie in a plane perpendicular to the beam, because for atoms lying at different distances from the reference plane the disturbances of the electron wave on the reference plane will be affected by different amounts by Fresnel diffraction effects. The extinction of a reflexion is complete only if the atomic peaks in $\varphi(x, y)$ which are related by the corresponding symmetry element of $\varphi(x, y)$ are identical in both their weight and Fresnel diffraction content, i.e., if they are given by the projection of identical atoms which have the same z-coordinate. In other cases the extinction may not be complete, although if the atoms are light and their z-coordinates differ only slightly, the approximation will be so good that the intensity of the reflexion will, in fact, be extremely small.

In some particular cases, such as that of the 4-fold screw axis treated in the M.T.F. paper, it happens that there is no symmetry element of the two-dimensional projection corresponding to the three-dimensional symmetry element. The relevant extinctions, or incomplete extinctions, will then occur but from the point of view of the two-dimensional lattice symmetry they must be classed as 'accidental'. For example, Fig. 1 shows the appropriate projection of the diamond structure when the incident beam is exactly parallel to the $[01\bar{1}]$ axis. The broken lines are the projections of the 4_1 screw axis, but in the projection they represent only 2-fold elements of gliding reflexion. The extinction of the 200 reflexion is, therefore, destroyed as was pointed out by M.T.F., although, by the above arguments, the actual 200 intensity may not be appreciable.

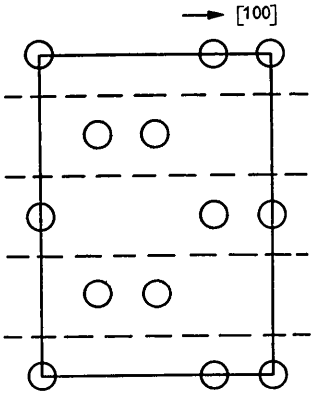

Fig. 1. Projection of the diamond structure along the $[01\bar{1}]$ axis. Projections of 4-fold screw axis are indicated by broken lines.

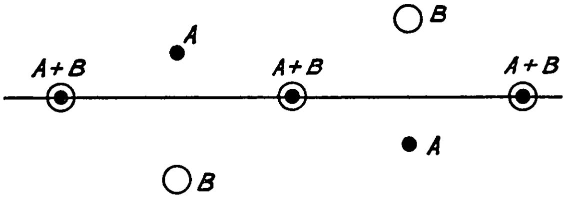

Fig. 2. A possible projection of a system in which a 4-fold screw axis acts on two unequal atoms.

Mr J. Gjønnes has pointed out that additional special cases may arise. For example, when a four-fold screw axis acts simultaneously on two separate atoms, projections such as shown in Fig. 2 may be obtained. If we consider $\exp\{i\sigma\varphi(x, y)\}$, as in the C.M. treatment, it is seen that the $A+B$ peak has different weight from the A and B peaks taken together. Then the 'accidental' extinction of the (200) reflexion is destroyed and the 200 reflexion may have appreciable intensity, especially if the atoms concerned are heavy so that the value of $\sigma\varphi(x, y)$ becomes comparable with unity. The condition for extinction of a reflexion in the diffraction pattern from a crystal is therefore given more exactly by specifying that the intensity of the reflexion given by the Fourier transform of $\exp\{i\sigma\varphi(x, y)\}$ should be zero.

After taking account of the above remarks, we see that the predictions of the M.T.F. and C.M. treatments are in essential agreement as to which of the kinematic extinction conditions will be retained for the dynamic scattering conditions under consideration, (i.e., when the incident electron beam is in a principal lattice direction or otherwise when the repetition distance in the beam direction is small) and which of these extinction conditions will not be rigorously maintained. In the latter case the C.M. treatment allows some sort of rough estimate of the intensities of the 'incompletely extinguished' reflexions to be made, but for more quantitative estimates we must await detailed calculations for particular cases.

References

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Sur la structure de l'alizarine.

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L'Alizarine cristallise par sublimation sous vide en aiguilles de couleur jaune orangé.

La maille monoclinique présente les caractéristiques suivantes:

$$a = 21{,}04 \pm 0{,}04,\ b = 3{,}75 \pm 0{,}01,\ c = 20{,}12 \pm 0{,}04\ \text{Å}\,,\quad \beta = 104^\circ\ 30' \pm 10'.$$

Volume de la maille = 1540 Å^3.

Nombre de molécules par maille: $Z = 6$.

Une pseudosymétrie orthorhombique provoque une macle très fréquente des cristaux, qui apparait dans au moins 95% des cas.

Les réflexions ont été observées pour:

hkl à tous les ordres,
$h0l$ si $h = 2n$,
$0k0$ si $k = 4$.

Ces lois d'extinction pourraient correspondre au groupe spatial $P2_1/a$, mais celui-ci exige quatre points homologues par maille alors que six molécules y sont présentes. Par ailleurs, l'asymétrie de la molécule élimine l'hypothèse d'une position spéciale. Nous avons donc été conduits à adopter le groupe spatial non centré Pa, avec deux groupes de trois molécules. L'extinction des taches 010 et 030 serait alors accidentelle.

La faible valeur du parametre b impliquant l'existence d'une seule couche moléculaire, nous avons abordé en premier lieu l'étude des projections de Patterson et de densité électronique $x0z$.

Les intensités des taches $h0l$ n'ont subi aucune correction d'absorption, le cristal utilisé étant petit (0,4 mm.) et peu absorbant ($\mu = 9{,}5$ cm.$^{-1}$ pour la radiation utilisée Cu $K\alpha$).

Le coefficient de température moyen, calculé par la méthode de Wilson, est égal à $4{,}9 . 10^{-16}$ cm^2.

Sur la demi-projection de Patterson (Fig. 1) les sommets voisins de l'origine forment une figure qui se retrouve affaiblie, mais avec la même orientation autour de deux pseudo-origines situées aux points de coordonnées ($u = \frac{2}{3} . a/2,\ v = \frac{1}{3} . c$) et ($u = \frac{1}{3} . a/2,\ v = \frac{2}{3} . c$). Ceci ne peut s'expliquer que dans l'hypothèse où les centres des trois molécules se déduiraient les uns des autres par des translations voisines de $(\frac{2}{3} . \mathbf{a}/2,\ \frac{1}{3} . \mathbf{c})$ et $(\frac{1}{3} . \mathbf{a}/2,\ \frac{2}{3} . \mathbf{c})$.

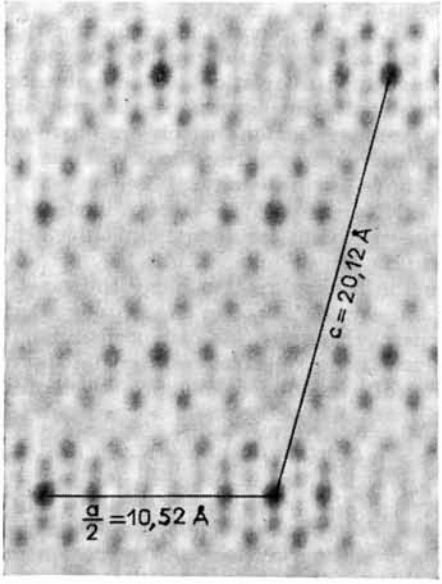

Fig. 1. Projection de Patterson $z0x$ calculée au moyen du photosommateur harmonique de G. v. Eller.

En outre, les six sommets entourant l'origine indiquent l'existence d'un ensemble de cycles benzéniques inclinés d'environ 25° autour d'un de leurs diamètres perpendiculaire à $0x$.

Dans nos premiers calculs de facteurs de structure, nous n'avons pas tenu compte des oxhydriles substitués en 1–2. Les centres des noyaux anthraquinoniques dont la formule est figurée ci-dessous furent placés aux points (0, 0), $(\frac{2}{3} . a/2,\ \frac{1}{3} . c)$, $(\frac{1}{3} . a/2,\ \frac{2}{3} . c)$ et leurs grands axes parallèlement à $0x$. C'est en effet, parmi les diverses orientations possibles, la seule qui conduise à une reconstitution théorique de la projection de Patterson ayant un aspect voisin de celle qui fut obtenue à partir des données ex-