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Multiple Bragg Reflection Areas in Single Crystals Determined by Image Fringes

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Experimental observations of fringes having twice the planar spacings on single organic crystal light-field images in the electron microscope are briefly discussed with reference to the multiple beam dynamical theory of electron diffraction. Similarly spaced fringes are demonstrated on dark-field images, using several strong permitted Bragg reflections in the other-than-zero layer lines and interpreted as resulting from the simultaneous production of adjacent Bragg reflections in the same crystal area. This simultaneous production of adjacent Bragg reflections with indices of h_1k_10 and h_2k_10 requires, by the dynamical theory, the production of a third coupled reflection h_2-h_1, 0, 0 from the same area. The diffraction image through this latter reflection combines with the zero order image to produce fringes which appear experimentally to be complementary to the $h_1k_10-h_2k_10$ image fringes from the same area. These light- and dark-field image fringes having the structurally false periodicity of twice the planar spacings would disappear if all Bragg reflections leaving the crystal could be combined to form the image without any spherical aberration.

Introduction

The fringe patterns first observed on images in the electron microscope of properly oriented single crystals whose molecular plane spacings are within the instrument resolution could be directly correlated with the planar spacings (Menter, 1956). These fringes were therefore initially assumed to be a direct image of the crystal lattice. Further experimental work soon demonstrated that the fringe separation could also be half (Labaw & Wyckoff, 1957; Labaw, 1960) or twice (Neider, 1956; Espagne, 1960; Labaw, 1961) the pertinent crystal plane spacing. The explanation for this involves the two basically different ways that image fringes can be produced from the interaction of the electrons with the crystal planes. The first of these obtains when the crystal planes are oriented parallel to the beam direction and produce no Bragg reflections or when the crystal order has deteriorated under bombardment until the crystal acts as a two-dimensional object. Such crystal areas will produce energy through all diffraction spots in the back focal plane of the objective lens, yielding an image similar to one obtainable in light optics from a grating. Experimentally in the electron optical case these fringes disappear in exact focus (Labaw, 1960) so that under these conditions the crystal behaves predominantly as a phase grating yielding out-of-focus fringes having the separation of the molecular planes or half of this (Cowley & Moodie, 1960). The second way that image fringes can be produced is for the crystal to diffract electrons as a three-dimensional lattice giving Bragg reflections. Thus, a hypothetical crystal area oriented for Bragg reflection but still transmitting some energy in the direction of the incident beam would produce two images (one through the particular Bragg reflection diffraction spot and one through the zero diffraction spot) of the same area which would interfere in the image plane to produce fringes, neglecting spherical aberration. The fringe separation would be directly related to the distance in reciprocal lattice space between the Bragg reflection spot and the zero order beam. Unlike fringes of the first type, these image fringes will exist in, as well as around, focus (Hashimoto, Mannami & Naiki, 1961).

Crystal image fringes of the second type will be used in this paper to demonstrate that a single area of a real crystal often produces comparable energy in several diffraction spots simultaneously as predicted by the dynamical theory of electron diffraction (Heidenreich, 1949, 1950). The fringes on crystal images having twice the planar spacing will be shown to result from this multiple Bragg reflection from the same crystal area.

Results and discussion

The crystals used in this study were selected for their long planar spacing and for their capability of producing image fringes of about twice the planar spacing. All crystals having this latter property have a structure in which the repeating unit in the direction of the resolvable spacing is twice the planar separation and give a normal diffraction pattern having a spot frequency in the first and higher layer lines twice that in the zero layer line. Whenever images of these crystals show fringes twice the planar spacing, their selected area diffraction patterns show 'forbidden' or 'perturbation' reflections in the zero layer line for which the structure factor is zero. A typical selected area diffraction pattern of an indanthrone ($C_{28}H_{14}O_4N_2$) crystal using low beam current with the beam direction down the *c* axis is shown in Fig. 1. This crystal is monoclinic with

$$a=30\cdot83,\ b=3\cdot833,\ c=7\cdot845\ \text{Å};\ \beta=91°\ 55'$$

and belongs to the $P2_1/a$ space group (Bailey, 1955). The diffraction pattern shows strong 100 forbidden reflections. The intense 310, 410, and 510 reflections agree with the X-ray data and reflect the planarity of these large molecules. The large number of spots present shows that the crystal producing this pattern was probably randomly bent over the area of the selector aperture (triangular, each side 1700 Å). The pattern was taken at the crossover setting of the condenser lens with a 125μ condenser aperture, to match the conditions under which the crystal images were photographed. This diagram shows that an indanthrone crystal image photographed with a centrally placed 50μ aperture in the back focal plane of the objective lens, which would limit image contributions to diffraction spots from spacings greater than 5 Å, should be noticeably deficient in electrons over the areas producing the strong reflections in the first layer lines.

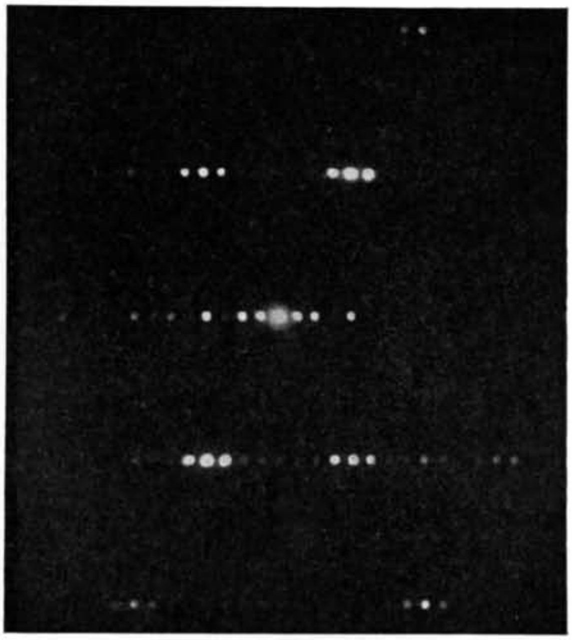

Fig. 1. Selected-area electron diffraction pattern from an indanthrone crystal showing intense 100 perturbation reflections.

The image of a similarly oriented indanthrone crystal photographed with such an objective aperture is shown in Fig. 2. The fringes at the top of the image have the spacing of the (200) planes. These could result from the coincidence of the beam direction and the *c* crystal axis in this area or from the orientation of the (200) planes at the Bragg angle to the beam. One should be able to tell which choice is correct by photographing the crystal again in exact focus. Practically, however, this is almost impossible because the rapid deterioration of the three-dimensional order in the electron beam for organic molecules such as this permits time for only one micrograph to be taken while Bragg reflections are operative. The high contrast fringes over the lower part of the crystal have the spacing one would expect from interference of the diffraction image through the perturbation 100 reflection with the zero order image. The fringes are not quite parallel over the whole crystal but this could reflect phase differences in the energy from the different crystal areas passing through the 100 reflection. These 30 Å fringes generally occur in image areas deficient in electrons (extinction contours) indicating their association with the strong first or higher layer line reflections excluded by the objective aperture. This suggests further that the 100 reflection is also associated with the excluded reflections. Associations of this type are quite common in electron diffraction and are predicted by the multiple beam dynamical theory of electron diffraction (Heidenreich, 1950). The 100 reflection could be a compound reflec-

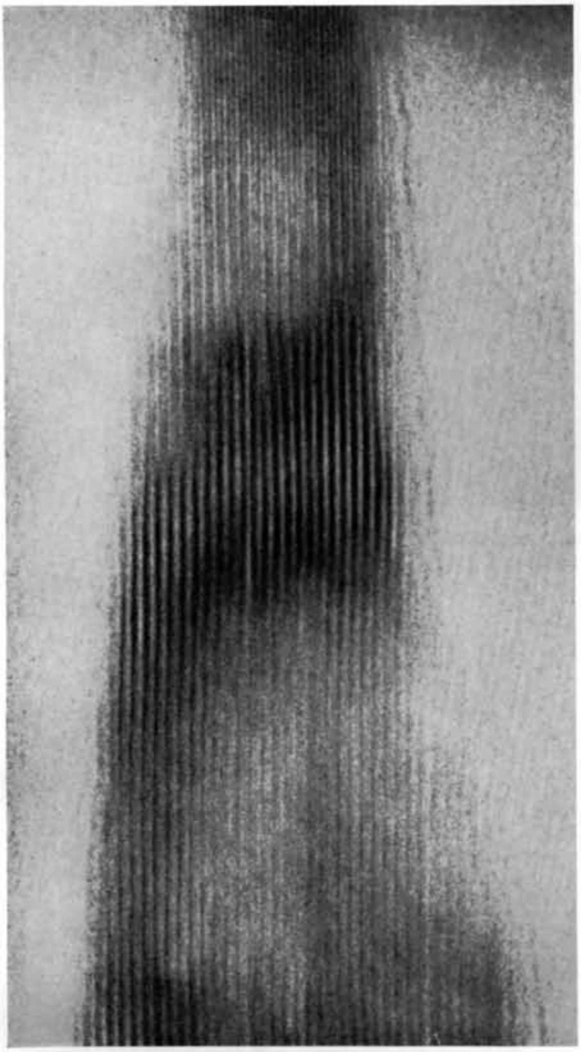

Fig. 2. A typical image of an indanthrone crystal producing a diffraction pattern like Fig. 1 photographed through a centered 50μ back-focal-plane objective aperture to exclude the first and higher layer lines. The image shows both the 15 Å planar spacing fringes and the 30 Å fringes associated with the 100 perturbation reflections. 495,000 ×.

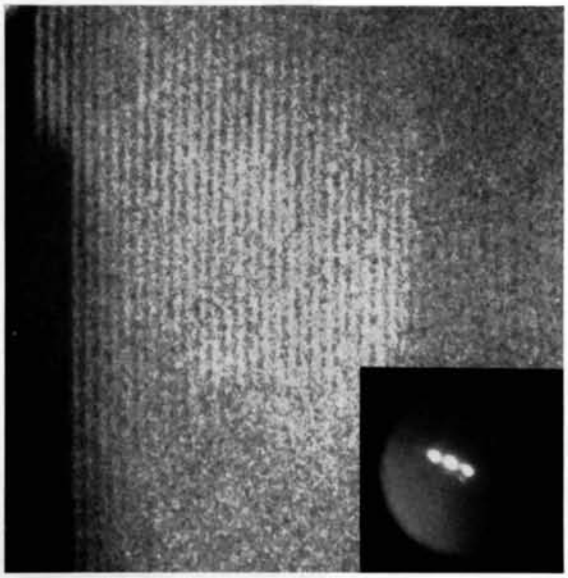

Fig. 3. A dark-field image of an indanthrone crystal showing 30 Å fringes photographed through a 50μ objective aperture positioned to pass the intense 310–510 reflections as shown in the insert. 555,000 ×.

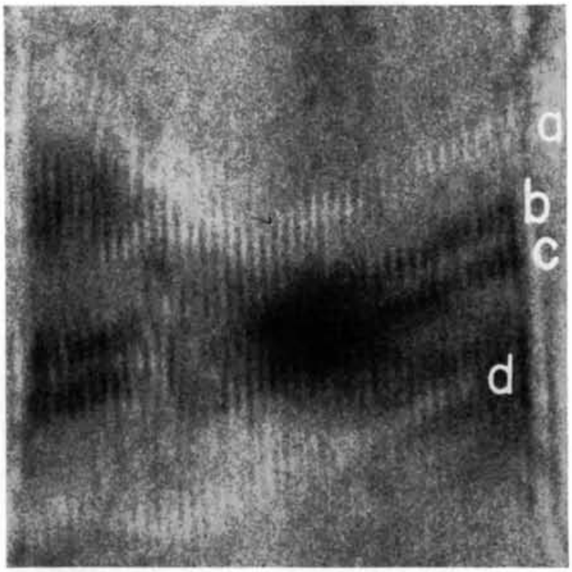

Fig. 4. The image of an indanthrone crystal through a centered 150μ objective aperture showing on the right two light 30 Å fringes, *a* and *d*, associated with the 310–510 reflections and the complementary dark 30 Å fringes, *b* and *c*, associated with the related 100 reflections. 505,000 ×.

tion from the interaction of the 410 and 310, for example, where all three reflections would necessarily originate in the same crystal area. This has been checked experimentally by forming crystal images in the electron microscope using different parts of the diffraction pattern.

A dark-field image of an indanthrone crystal using only the 310, 410, and 510 reflections is shown in Fig. 3, along with an image of the back focal plane aperture and the transmitted reflections in the insert. Since some areas in the image show 30 Å fringes, these crystal areas must be the origin of two or three adjacent Bragg reflections which are separated by a distance corresponding to 30 Å in reciprocal lattice space. Having thus demonstrated that some areas of these bent crystals can simultaneously give rise to strong adjacent permitted reflections one can now show that such areas are also the origin of the associated 100 perturbation reflection by including reflections in the first as well as zero layer line to form the image.

The indanthrone crystal image in Fig. 4 was obtained with a 150μ centered objective aperture which passes all reflections down to 2·2 Å. The limited regions on the right side of this image showing the light 30 Å fringes, *a* and *d*, from reflections in the first layer line (like Fig. 3) are separate from the dark fringes from reflections in the zero layer line, *b* and *c*, because of spherical aberration in the objective. Fringe *a* is shifted up and to the right from its complementary dark fringe so is probably caused by reflections around 410. Fringe *d* is shifted down and to the left and could result from reflections around $\bar{4}\bar{1}0$. The dark fringes would thus result from interaction of the 100 and $\bar{1}00$ reflections with the zero order beam. The apparent complementarity of the light and dark fringes on this and similar images suggests that if all the Bragg reflections from a crystal were utilized by an electron optical system to form an image without spherical aberration, there would be no fringes present whose periodicities were other than the planar spacings.

Similar results have been obtained for the α form of phthalocyanine ($C_{32}H_{18}N_8$) and indanthrene olive T ($C_{45}H_{22}N_2O_5$) crystals, both of which give diffraction diagrams similar to Fig. 1. The planar spacings indicated in the zero layer lines are 11·8 Å for α-phthalocyanine and 25 Å for olive T crystals. These have been checked by X-ray powder patterns (Labaw, 1961). The repeating unit in this same direction is twice these values. Dark-field images of α-phthalocyanine crystals which show 23·6 Å fringes with the dominant 210, 310, and 410 reflections in the first-layer-line are more difficult to obtain than the corresponding ones for indanthrone crystals. This reflects the smaller relative intensity of the prominent first-layer-line reflections in α-phthalocyanine. The intense first-layer-line reflections for olive T crystals are the 210, 310, 410, 610, and 710. Fringe patterns on first-layer-line dark-field images are as easily obtained as for indanthrone. They occasionally show 25 Å fringes as well as the usual 50 Å ones. These 25 Å fringes would be from areas producing Bragg reflections separated by a distance corresponding to 25 Å such as the 410 and 610.

Dark-field olive T crystal images showing 25 Å fringes have been obtained with the zero layer line reflections of higher order than the 400. These could be caused by Bragg reflections from the same area of a bent crystal. This follows from calculations of the widths of the primary diffraction maxima for the 600 and higher order reflections using the dynamical theory of electron diffraction for a bent crystal (Heidenreich, 1949). These primary diffraction maxima from several orders of the (200) spacing overlap so the same crystal area could contribute to several zero layer diffraction spots simultaneously.

This work illustrates the usefulness of the multiple beam dynamical diffraction theory to explain observable image phenomena from single crystals with resolvable molecular plane spacings, even though only a small portion of the diffraction pattern around the central spot is included. It should apply to crystals such as the β form of phthalocyanine where the interaction of two permitted reflections gives a reflection for which the structure factor is not zero, as well as the crystals considered here.

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