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Subsidiary maxima in electron-diffraction net patterns from molybdenite. By Ryozi Uyeda, Takeo Ichinokawa and Yasushige Fukano, *Physical Institute, Nagoya University, Nagoya, Japan*

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It is well known that in the case of thin films the intensity region in the reciprocal lattice is extended in the direction normal to the film. The interference function along this direction is given by the well known formula

$$\sin^2 \pi M l / \sin^2 \pi l \,, \quad (1)$$

where M is the number of atom layers in the film and l the parameter indicating the distance along the direction in the reciprocal lattice. Equation (1) has principal maxima at $l = L$, L being integral, and has a number of subsidiary maxima at

$$l_N = L \pm (n+\tfrac{1}{2})/M \,, \quad (2)$$

where $n = 1, 2, \ldots, (M-2)$, and N is defined as $\pm n$ according to the double sign on the right-hand side.

According to the dynamical theory of diffraction (Thomson & Cochrane, 1939; Kato & Uyeda, 1951), equation (1) near principal maxima corresponding to L is to be modified to

$$\sin^2 \pi M \sqrt{\{l'^2+(2dq)^2\}} / \pi^2\{l'^2+(2dq)^2\} \,, \quad (3)$$

where $l' = l-L$, d is the spacing of the net plane parallel to the film, and q is given by

$$q = \lambda m e |V_{hkl}| / h^2 \sqrt{\{\cos\theta_1 \cos\theta_2\}} \,; \quad (3a)$$

here (hkl) is the index of the principal maximum, V_{hkl} the (hkl)th Fourier coefficient of the periodic field in the crystal, and θ_1 and θ_2 are the angles between the normal of the film and the direction of incident and diffracted beam respectively. The other symbols λ, m, e and h have their usual meaning. Equation (3) has the subsidiary maxima at

$$l'_N = \pm \sqrt{\{(n+\tfrac{1}{2})^2/M^2-(2dq)^2\}} \,, \quad (4)$$

where n takes positive integral values. We can calculate M (thickness of film Md) and $|V_{hkl}|$ from (4) if the l'_N's are determined by experiment.

These maxima are observed in divergent-beam electron-diffraction patterns of thin crystals (Kossel & Möllenstedt, 1939; MacGillavry, 1940; Raether, 1949). They are also expected in ordinary (parallel-beam) electron-diffraction patterns of a thin crystal flake if it is rotated during the exposure about an axis not parallel to the normal of the flake or if it is adequately curved. In this case, however, the angular distances between the observed subsidiary maxima are expected to be very small compared with those obtained with a divergent beam because of the geometrical relation between the diffracted angle and the parameter l. A high-resolution diffraction camera is therefore required to observe them.

Finch & Wilman (1936*a*) observed fractional-order rings in the patterns from polycrystalline graphite and attributed them to the subsidiary maxima, as discussed above. These rings, however, might preferably be ascribed to the particular structure of graphite, as found by Lipson & Stokes (1942). The former investigators obtained very beautiful patterns from rotated and curved single crystals of graphite and molybdenite (Finch & Wilman,

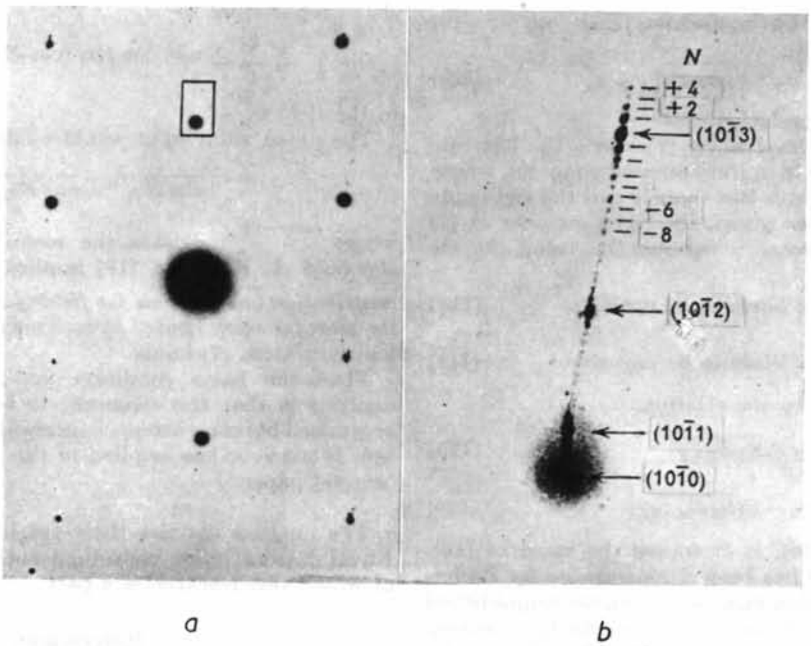

Fig. 1. High-resolution electron-diffraction pattern from a thin molybdenite film (210 Å). (*a*) Camera length 40 cm., accelerating voltage 45 kV., magnification 3×. (*b*) Enlargement (10×) of the marked part of (*a*); effective camera length about 12 m.

1936*b*, *c*, 1937) and stated that some subsidiary maxima were observed, but they did not analyse in detail the series of maxima arising from different N.

Recently we obtained the maxima in question with our newly-designed electron-diffraction camera of high resolution. Fig. 1(*a*) is a net pattern from a thin molybdenite crystal. Although the crystal was not rotated, a series of spots was recognized in the neighbourhood of the ($10\bar{1}0$) spot due to a curving of the crystal. Fig. 1(*b*) is an enlarged picture of the marked part of Fig. 1(*a*). In this figure, a number of spots are clearly observed on both sides of the ($10\bar{1}3$) spot. We have deduced from this figure, by applying the formula (4), that $Md = 210$ Å and $|V_{10\bar{1}3}| = 7\cdot2$ volts. The latter value is in good agreement with the theoretical value, 7·4 volts. The anomalous splitting observed in the peak $N = -2$ can be explained as an effect of the ($20\bar{2}6$) reflexion which happens to occur simultaneously at this point. Thus, the pattern we obtained is without doubt that caused by the subsidiary maxima of the interference function in the dynamical theory of electron diffraction. We did not observe in our experiment the effect of the elastic bending of the crystal discussed by Blackman (1951).

The similar pattern was also observed independently by Hashimoto (1952) in the case of a thin MoO_3 crystal and by Ueda (1953) in the case of specially prepared colloidal gold.

Finally it is to be noted that Rees & Spink (1950) have also obtained similar subsidiary maxima in diffraction patterns from a ZnO crystallite. The maxima they obtained, however, are due to the small lateral extension of the crystallite, while the present ones are due to the small thickness of the crystalline film.

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Subsidiary maxima of Kikuchi pattern.

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In the foregoing note (Uyeda, Ichinokawa & Fukano, 1954) we reported our observation on the subsidiary spots in a diffraction pattern, and showed that they can be explained in a similar way to those in a K.–M. pattern (Kossel & Möllenstedt, 1939) by the subsidiary maxima of the interference function in the dynamical theory. It is pointed out here that the subsidiary maxima of extinction fringes due to Bragg reflexion in electron micrographs of curved crystalline films (Heidenreich, 1949; Hashimoto, 1952) can be accounted for also by the same function.

The Kikuchi pattern has a different origin from the diffraction patterns mentioned above and, according to Kainuma (1954), it has an interference function as follows:

$$M\{1-\sin 2\pi M\sqrt{[l'^2+(2dq)^2]}/2\pi M\sqrt{[l'^2+(2dq)^2]}\}\,, \quad (1)$$

where M, l', d and q have the same meaning as in equation (3) of the previous note. Subsidiary maxima of this function appear at

$$l'_N = \pm\sqrt{[(n+\tfrac{3}{4})^2/M^2-(2dq)^2]}\,, \quad (2a)$$

where n is a positive integer and N is defined as $\pm n$ according to the double sign on the right-hand side. It must be mentioned here that the subsidiary maxima on the photographic plate coincide with (2) if the factor multiplying (1) is positive. When, however, the factor is negative, they appear at

$$l'_N = \pm\sqrt{[(n+\tfrac{1}{4})^2/M^2-(2dq)^2]}\,. \quad (2b)$$

The subsidiary maxima of Kikuchi patterns were reported by Heidenreich & Shockley (1948) to occur in a reflexion pattern from an aluminium single crystal. However, no observable subsidiary maxima are expected theoretically in reflexion patterns, and we suppose that the crystal studied by these authors might have been composed of several blocks with slightly different orientations. No subsidiary maxima have ever been observed, as far as we are aware, in parallel-beam transmission patterns. They are observable, though faint, in divergent-beam patterns taken by Kossel & Möllenstedt (1939) and by Hoerni (1950); but these authors apparently failed to take notice of the phenomenon.

We observed the maxima more clearly in divergent-beam diffraction patterns from a thin film of molybdenite; an example is reproduced in Fig. 1, where the ($20\bar{2}2$)-