Acta Cryst. (1950). **3**, 314

An exception to Friedel's law in electron diffraction. By Shizuo Miyake,* *Kobayashi Institute of Physical Research, Kokubunji, Tokyo, Japan*, and Ryozi Uyeda, *Physical Institute, Faculty of Science, Nagoya University, Nagoya, Japan*

(*Received* 26 *February* 1949 *and in revised form* 28 *December* 1949)

As is well known for X-ray diffraction by crystals, Friedel's law ceases to hold when the X-ray wave-length lies in the range of anomalous dispersion of any of the constituent atoms, in which case the atomic form-factors have to be regarded as complex quantities. The effect was actually observed for zincblende (ZnS), a crystal having no centre of symmetry, by Nishikawa & Matsukawa (1928), Coster, Knol & Prins (1930), and Geib & Lark-Horowitz (1932).

The present writers have observed a similar effect in the electron diffraction by zincblende. This amounts to having found a method of determining the sense of the polar axes of this crystal solely by a diffraction phenomenon, in spite of Friedel's law which prohibits this. Using fresh cleavages (110), and applying the reflexion method with the grazing incident beams, directed strictly in [1$\bar{1}$0] or [$\bar{1}$10] azimuth (the arrow A or A' in Fig. 1), we

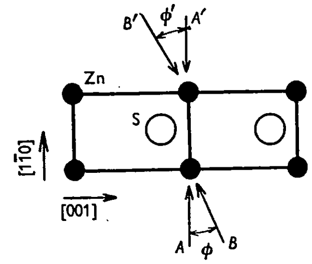

Fig. 1. (110) plane of zincblende. The arrows A, A', B and B' show the projection of incident electron beams on this plane, ϕ (or ϕ') being the azimuthal angle.

obtained diffraction patterns that are always *asymmetric* in respect to the (001) plane (which coincides with the plane of incidence in the present cases), for stationary (Fig. 2(*a*)), as well as for rotating crystals with [001] as the rotation axis (Figs. 3 and 4).

Asymmetric features of the patterns are always well correlated with the sense of the polar axes of the crystal. The latter can be determined from the piezo-electric effect, or by the electron-diffraction study of the crystal growth of zinc oxide formed upon surfaces by oxidation (Aminoff & Broome, 1938; Uyeda, Takagi & Hagihara, 1941), or of metallic films deposited on surfaces by the evaporation method (Miyake, to be published; Kubo & Miyake, 1948). Let us take the crystal axes in respect to the atomic arrangement in the plane of cleavage as indicated in Fig. 1. Then, generally speaking, the asymmetry in the diffraction patterns takes place in such a way that the diffraction intensities, including spots and Kikuchi lines, are stronger in the half of the pattern corresponding to the [001] side in respect to the (001) plane, than in the other half (the [00$\bar{1}$] side). The geometrical asymmetry is also observed in the rotation photographs as indicated in Fig. 4.

The phenomenon was confirmed, without a single exception, on about one hundred samples from different origins. Temperature variation (room temperature to 450° C.) and change of electron voltage (35–60 kV.) had no effect on the phenomenon. The asymmetry, however, could not be shown (Uyeda *et al.* 1941) for etched surfaces so long as the integrated intensity is concerned.

The unfavourable influence of the mis-setting of crystals was undoubtedly eliminated. The deviation of the azimuthal angle (Fig. 1) of the incident beam from the correct direction can be precisely determined from the position of the Kikuchi band (004). Fig. 3 shows the stationary and rotation photographs taken at $\phi' = -35'$, $0'$ and $+20'$. Although the intensity distribution in rotation photographs changes a little with ϕ', the asymmetry is always visible. Especially, (331) is always remarkably stronger than (33$\bar{1}$) in this region of ϕ'. The asymmetry is not due to some secondary effect, for example, a warping of the surface, because the feature of the asymmetry is the same for all samples and, moreover, none of the samples showed any asymmetry for electron beams in the [001] azimuth (Fig. 2(*b*)). The phenomenon might be interpreted theoretically, for instance, by considering the phase change of the scattered wave in the collision problem, the displacement of ions at the extreme surface, as discussed by Lennard-Jones (1930), the effect of two-dimensional diffraction by the uppermost layers, the dynamical theory of diffraction taking account of the absorption effect of electrons, etc. But we have failed, so far, to arrive at a satisfactory understanding of the phenomenon.

Note added in November 1949. An extended calculation by the dynamical theory of diffraction performed recently by K. Kohra seems to explain this phenomenon in its general features. A brief note will be published shortly.

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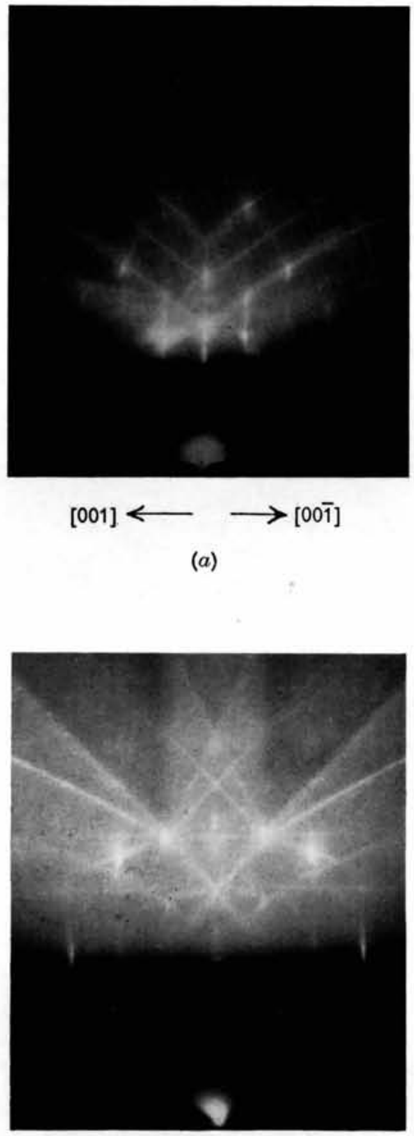

Fig. 2. Reflexion patterns by cleavage surface of zincblende (stationary crystal), with incident electron beams in (*a*) [$\bar{1}$10] azimuth (arrow *A′* in Fig. 1), (*b*) [001] azimuth.

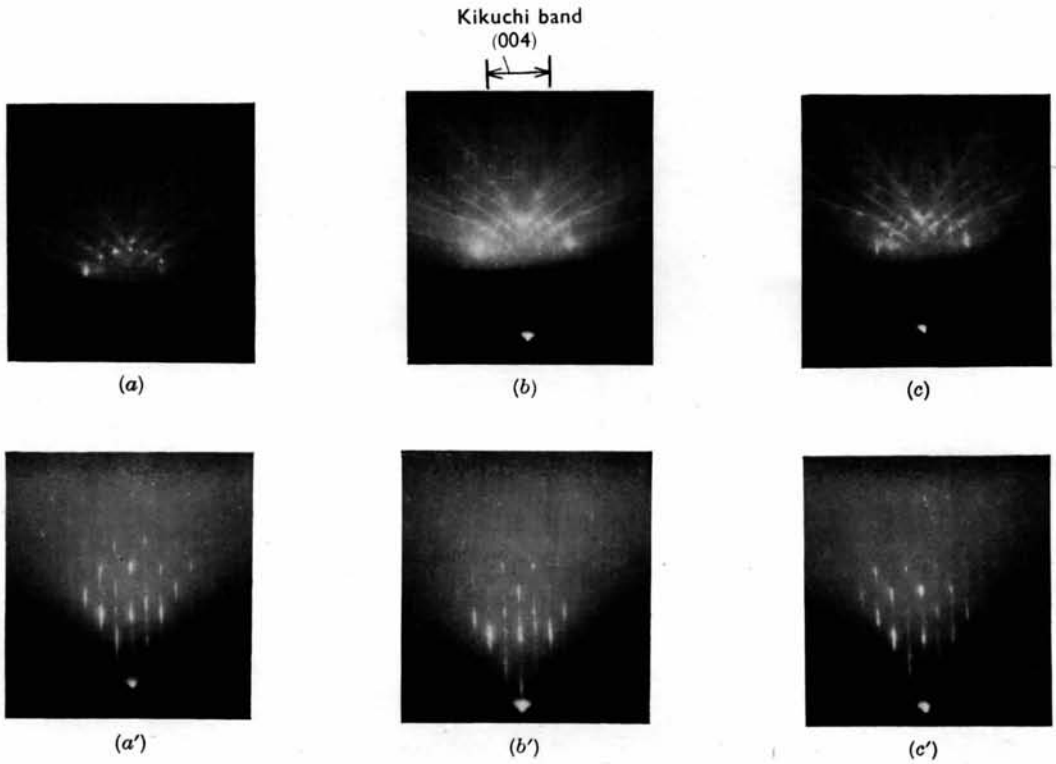

Fig. 3. Reflexion patterns obtained by (a), (b) and (c) stationary crystal and (a′), (b′) and (c′) rotating crystal with incident beams in the following azimuthal angles: (a) and (a′), $\phi' = -35'$; (b) and (b′), $\phi' = 0$; and (c) and (c′), $\phi' = +20'$.

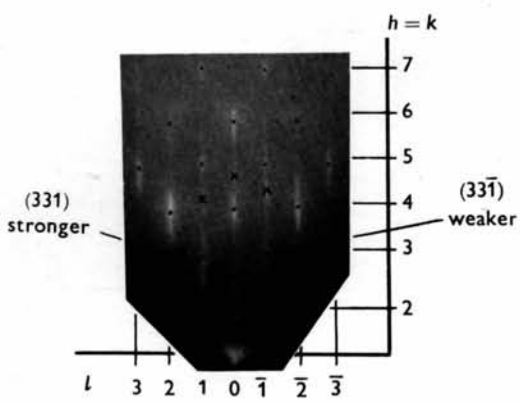

Fig. 4. Magnified picture of Fig. 3(b′), a pattern obtained by rotating crystal with incident beam in [$\bar{1}$10] azimuth. Asymmetry of intensity between (331) and (33$\bar{1}$) reflexion is indicated. The reflexions (111), (11$\bar{1}$), (222), etc., are absent owing to the refraction effect. The maxima indicated by × are anomalous ones (Kikuchi & Nakahawa, 1938).