

anhydrous conditions, in the cold, by passing dry NH_3 gas into water-free chloroacetic acid dissolved in freshly-distilled absolute ethyl alcohol. Form I can be prepared from cold aqueous solutions (a rise in temperature leads to hydrolysis and a number of unwanted products). Form II was obtained only once from cold aqueous solution, and we have not been able to repeat the experiment.

Form II shows a dielectric anomaly at -150°C . The dielectric constant along b is 5 at room temperature, and reaches a maximum of 15 at -150°C . Below this temperature the crystals show spontaneous polarization and ferroelectric hysteresis. The coercive field is $\sim 10\text{ kV.cm.}^{-1}$ at -170°C . The spontaneous polarization is in the neighborhood of $0.1\text{ microcoul.cm.}^{-2}$. The observed hysteresis loops are often unsymmetric. The transition is apparently of first order. The symmetry of the low-temperature phase is apparently C_2 , the glide plane

of the upper phase disappearing as does the mirror plane in the case of triglycine sulfate and isomorphs (Pepinsky, Okaya & Jona, 1957) and in ferroelectric silver glycinate (Pepinsky, Eastman & Mitsui, 1957).

The crystal structure of the room-temperature phase of Form II is under X-ray examination.

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A method of correcting the primary extinction effect in electron diffraction. By SIGEMARO NAGAKURA, *Tokyo Institute of Technology, Oh-okayama, Meguroku, Tokyo, Japan*

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A serious difficulty in applying the electron-diffraction method to crystal structure analysis arises from the effect of primary extinction or dynamical diffraction. Although Pinsker (1949) and Jamzin (1949) held that the effect is not significant in practice, Lennander (1954) and Kuwabara (1957) showed that the effect is hardly negligible. Recently, Honjo & Kitamura (1957) showed that the variation of diffraction intensity with wavelength is in accordance, at least approximately, with the theory of primary extinction given by Blackman (1939), and they proposed a method to eliminate the effect by extrapolating the observed intensity to zero wavelength. The present author proposes another method to correct the primary extinction effect, utilizing Wilson's intensity statistics (Wilson, 1949) combined with the theory of primary extinction. This paper describes briefly the method, with the result of its application to the structure analysis of nickel carbide, Ni_3C .

Electron-diffraction patterns of Ni_3C suggest that the structure belongs to the space group $R\bar{3}c$. Nickel atoms are in $18(e)$ positions with $x = \frac{1}{3}$ and carbon atoms in $6(b)$ positions (Nagakura, 1957). Fig. 1(a) shows the two-dimensional Fourier map of the carbide calculated by assuming that the observed intensity I_{obs} is proportional to the square of the structure amplitude F for electrons. The intensity data were obtained from powder patterns taken with 40 kV. electrons (wavelength $\lambda = 0.06\text{ \AA}$). While nickel peaks appear in reasonable positions corresponding to a close-packed hexagonal arrangement (Jacobson & Westgren, 1933), there is no indication of carbon peaks in spite of the fact that the scattering amplitude of carbon atoms for electrons is as large as one-third of that of nickel atoms. The fact that carbon atoms did not appear on the map is due to the primary extinction effect participating strongly in the diffraction intensity, as shown below.

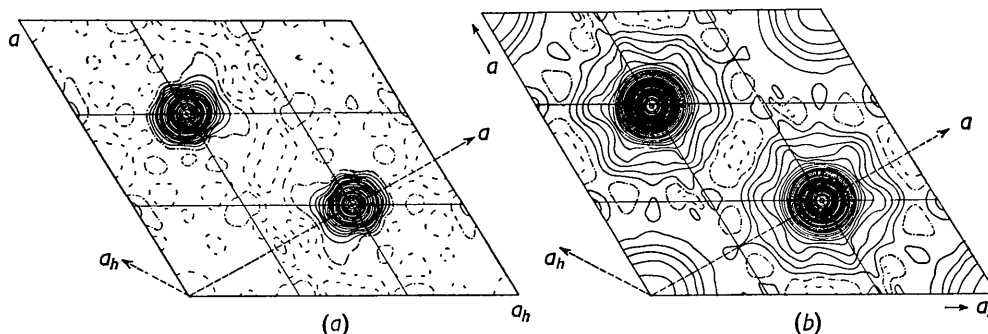


Fig. 1. (a) Two-dimensional Fourier map of Ni_3C synthesized from uncorrected intensity data. The map shows a part of the basal-plane projection, corresponding to Jacobson & Westgren's unit cell (Nagakura, 1957). The contours are drawn at arbitrary intervals. (b) Two-dimensional Fourier map of Ni_3C synthesized from the final values of the corrected intensity. The contours are drawn at intervals of $0.5\text{ V.}\text{\AA}^{-2}$. The chain lines indicate zero level and the broken lines negative regions.

Wilson's relation, given by

$$\langle I \rangle = \sum_{i=1}^n f_i^2$$

for X-ray diffraction, can be written in the case of electron diffraction in the form

$$K \langle s^4 I \rangle = \sum_{i=1}^n (Z - f_X)_i^2, \quad (1)$$

where n is the total number of atoms in a unit cell, Z is the atomic number, f_X is the atomic scattering amplitude for X-rays, $s = 1/d = 2 \sin \theta / \lambda$, $K = (h^2/2mc^2)^2$, I is the intensity and $\langle \rangle$ means the local average in the reciprocal lattice.

When the primary extinction occurs, $K \langle s^4 I \rangle$ becomes smaller than

$$\sum_{i=1}^n (Z - f_X)_i^2.$$

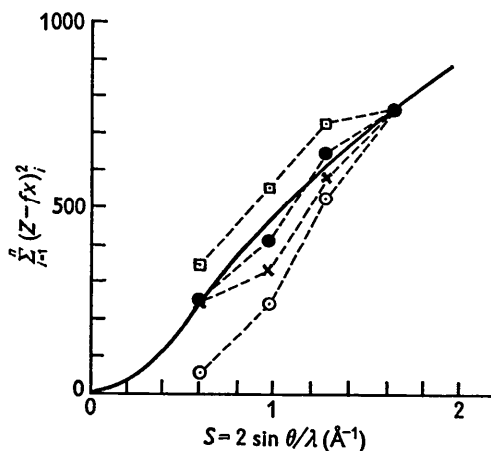


Fig. 2. Local averages of the intensity of Ni_3C . Open circles are the plots of the local averages $\langle s^4 I_{\text{obs.}} \rangle$. Other plots are the local averages $\langle s^4 I_{\text{cor.}} \rangle$: crosses correspond to $\bar{\rho} = 190 \text{ \AA}$, filled circles to $\bar{\rho} = 240 \text{ \AA}$ and squares to $\bar{\rho} = 285 \text{ \AA}$. The local averages for $\bar{\rho} = 240 \text{ \AA}$ show the best fit with the curve.

In Fig. 2, the values of $\langle s^4 I_{\text{obs.}} \rangle$ for Ni_3C are compared with the curve

$$\sum_{i=1}^n (Z - f_X)_i^2;$$

they are normalized with the curve at the outermost s -range. The local averages for the lower angles deviate downward from the curve. This deviation is evidently due to primary extinction, since the lower the scattering angle the greater the effect, on the average, on account of the rapid increase of the scattering amplitude with decreasing scattering angle.

According to the theory of the primary extinction effect, the intensity is written as

$$I = f(x)|F|^2. \quad (2)$$

The function $f(x)$ for the Laue case of electron diffraction is given by

$$f(x) = \sum_{n=0}^{\infty} J_{2n+1}(2x)/x, \quad (3)$$

$$x = \bar{\rho} \lambda |F| / v, \quad (4)$$

where J_{2n+1} is the Bessel function of odd order, $\bar{\rho}$ is the effective thickness of crystallites, and v is the unit-cell volume.

Though the values of F are not given beforehand, its approximate values can be determined when an approximate structure of the crystal is known: for example, when the positions of heavy atoms are given. $\bar{\rho}$ can be considered to be approximately equal to the particle size determined by the line-breadth. Using the values of $f(x)$ calculated from these approximate values of F and $\bar{\rho}$, $I_{\text{obs.}}$ can be corrected to $I_{\text{cor.}}$, which can be used to deduce the structure to a higher approximation.

The value of $\bar{\rho}$ can also be corrected by using the intensity statistics: we calculate $I_{\text{cor.}}$ for several values of $\bar{\rho}$ and choose the value which makes the local averages fit the curve

$$\sum_{i=1}^n (Z - f_X)_i^2$$

most closely (Fig. 2). The observed intensities are corrected successively by repeating the refinements of F and $\bar{\rho}$.

The Fourier map for Ni_3C , synthesized from the final values of $I_{\text{cor.}}$ is shown in Fig. 1(b), where the carbon peaks appear clearly. In this example, the final result was obtained after a few steps of refinement. The initial value of $\bar{\rho}$ was 290 \AA and the final value was 240 \AA . This map coincides very well with the structure already proposed.

The merit of the detection of the primary extinction effect by intensity statistics is that it can be performed without any knowledge of the crystal structure. When no knowledge of the structure is given at first, $\sqrt{I_{\text{obs.}}}$ may be used as the initial value of F to calculate $f(x)$ for the correction of the primary extinction effect, provided that $I_{\text{obs.}}$ is known in absolute units. The method described above can be applied also in X-ray diffraction.

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