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»Anomalous dispersion« effects in electron diffraction and their possible applications.*

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In a recent article on the structure determination by Fourier methods in electron diffraction, Cowley & Rees (1958) have emphasized the fact that the dynamical effects occurring due to strong interaction of the electron waves and lattice potentials give a method of estimating the intensity of the diffracted spots from a simple measurement of the fine structure of the diffracted spots. In a similar way the pseudo-kinematical and dynamical effects can help us in estimating the phases of the Fourier waves and in fixing the absolute configuration of non-centric crystals. The purpose of this note is to discuss this possibility. Except for a suggestion by Miyake & Uyeda (1950) and Miyake & Kambe (1954), no systematic study of this seems to have been made. It is pointed out that, unlike the X-ray case, it should be possible under suitable conditions to find the absolute configuration of a non-centric crystal like tellurium, which contains only one type of atom in its structure.

As in the anomalous dispersion method of finding the phases of X-ray reflections (Ramachandran & Raman, 1956; Raman, 1959; Okaya & Pepinsky, 1956), the possibility of finding the phases in electron diffraction rests on the violation of Friedel's law. The failure of Friedel's law in electron diffraction has been investigated by a number of authors, chiefly by Miyake & Uyeda (1950), Miyake & Kambe (1954), Kohra (1954), Niehrs (1955), Fujimoto (1959) using the dynamical theory and by Hoerni (1956*b*) using the pseudo-kinematical as well as the dynamical theory. Unlike the X-ray case, the violation of Friedel's law can occur in electron diffraction because of two different reasons, namely due to effects occurring from the changes in phase in the scattering by single atoms (the so-called pseudo-kinematical theory-PKT) and due to dynamical interactions in a non-centrosymmetric crystal, which can be worked out by the dynamical theory (DT).

The calculation of the diffracted amplitude in the simple kinematical theory (KT) is carried out in two stages. Firstly, the scattering amplitude $f(\theta)$ for an isolated atom is obtained by solving the Schrödinger equation using the first Born approximation. Secondly, the Fourier transform of one unit cell is calculated using this scattering factor and the effect of a number of such cells is added, which is equivalent to taking the Fourier transform of the whole crystal. This second step amounts to applying the first order Born approximation in calculating the scattering of the crystal as a whole from the scattering of a unit cell. Thus the first order Born approximation is used at both stages of calculating the diffracted amplitude in the KT. This approximation is justified at the first stage only if the multiple scattering *within an atom* is neglected, and at the second stage, only if the multiple scattering *within a volume element* of the crystal is neglected. The failure of this approximation both at the first and the second stages has been recognized and taken into account in the rigorous dynamical theory of Bethe. The possibility that the first Born approximation may not be valid at the atomic level itself was first pointed out by Schomaker & Glauber (1952), and this has been subsequently investigated in detail by Hoerni (1956*a*, *b*). The more detailed theory (PKT) results in the atomic scattering factor $f(\theta)$ being complex, rather than real, which is closely analogous to the complex atomic scattering factor which occurs in X-ray scattering when there is anomalous dispersion. In the electron scattering also $f(\theta)$ takes the form $|f_B(\theta)| \exp [i\eta(\theta)]$ where f_B denotes the first Born approximation value, $\eta(\theta)$ is a phase factor which increases with increasing atomic number Z, increasing angle of scattering θ, and decreasing accelerating voltage, i.e., increasing λ. In the X-ray case

$$f = f' + i\Delta f'' = (f'^2 + \Delta f''^2)^{\frac{1}{2}} \exp [i(\Delta f''/f')]$$
$$= |f| \exp [i\eta(\theta)] ,$$

where

$$\eta(\theta) = \tan^{-1} \Delta f''/f' .$$

Here also the phase shift η increases with θ (since $\Delta f''$ is independent of θ while f' decreases with increasing θ), and for backward scattering it may assume a fairly large value. Taking a typical case, we may compare the values of phase shifts for the scattering of X-rays and electrons by chlorine atoms, for $\theta = 0$. For $\lambda = 1{\cdot}54, f(0) = 17, \Delta f'' = 0{\cdot}66$ and $\eta(0) = 0{\cdot}038$ radians. From the calculation of Ibers & Hoerni (1954), we have for the electron scattering for an element with $Z = 15$, $\eta(0) = 0{\cdot}07$ radians for 40 kV electron. The comparison given above shows that the effect of phase shift in electron diffraction can be as pronounced as, if not more than, what is observed with X-rays. However, although the phase shift can give a considerable difference between the intensities of inverse reflections, namely $\Delta I = |V_H|^2 - |V_{\bar{H}}|^2$, it may not appreciably affect the average $\langle |V_H|^2 \rangle = \frac{1}{2}[|V_H|^2 + |V_{\bar{H}}|^2]$ in the non-centric case and $|V_H|^2$ in the centric case, as compared with the corresponding quantities calculated without phase shift. Moreover, as compared with the X-ray case, the situation here would be somewhat more complicated because there is a phase shift for every atom, unlike for X-rays for which they are important only for atoms whose absorption limits are close to the wavelength used. In addition, dynamical effects would be more strongly present in electron diffraction than in X-ray diffraction.

If a non-centric crystal contains only one type of atom, for example tellurium, then even including 'anomalous dispersion' effects, there is no violation of Friedel's law, both for X-rays and electrons (PKT). However, a scrutiny of the DT for non-centric crystals indicates an interesting possibility of finding the absolute configuration of such crystals. It is found that Friedel's law is violated if, in the dynamical theory, the effect of weak waves are also taken into account. Fujimoto (1959) has in fact derived expressions for the diffracted intensity

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for a pair of inverse reflections under these conditions. His formulae are

$$\mathrm{I}_H = (D/2k)^2|V_H|^2 + (D/2k)^3\,\mathrm{Im}\,\{V_H \sum_G{}' V_{-G}V_{G-H}\} - \ldots$$

$$\mathrm{I}_{\overline{H}} = (D/2k)^2|V_H|^2 - (D/2k)^3\,\mathrm{Im}\,\{V_H \sum_G{}' V_{-G}V_{G-H}\} - \ldots$$

where H stands for h, k, l, D = crystal thickness, $k = 2\pi/\lambda$, Im { } denotes the imaginary part of { } and the prime after the symbol Σ indicates the absence of terms with $G = 0$ or H. This difference arises because of the fact that though $|V_H| = |V_{\overline{H}}|$ the phases of V_H and $V_{\overline{H}}$ are different. Consequently, if V_H can be obtained from the structure, it should be possible to find the absolute configuration from the difference in intensity of inverse reflections using a thick crystal to accentuate the effect of dynamical interactions.

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References

Cowley, J. M. & Rees, A. L. G. (1958). *Rep. Phys. Soc. Progr. Phys.* **21**, 165.

Fujimoto, F. (1959). *J. Phys. Soc. Japan*, **14**, 1558.

Hoerni, J. A. (1956*a*). *Phys. Rev.* **102**, 1530.

Hoerni, J. A. (1956*b*). *Phys. Rev.* **102**, 1534.

Ibers, J. A. & Hoerni, J. A. (1954). *Acta Cryst.* **7**, 405.

Kohra, K. (1954). *J. Phys. Soc. Japan*, **9**, 690.

Miyake, S. & Uyeda, R. (1950). *Acta Cryst.* **3**, 314.

Miyake, S. & Kambe, K. (1954). *Acta Cryst.* **7**, 220.

Niehrs, H. (1955). *Z. Phys.* **140**, 106.

Okaya, Y. & Pepinsky, R. (1956). *Phys. Rev.* **103**, 1645.

Ramachandran, G. N. & Raman, S. (1956). *Curr. Sci.* (*India*), **25**, 348.

Raman, S. (1959). *Proc. Ind. Acad. Sci.* A **50**, 95.

Schomaker, V. & Glauber, R. (1952). *Nature, Lond.* **170**, 290.

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The crystal structure of $MoTe_2$.*

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An investigation of the Mo–Te system has been undertaken to determine the thermoelectric properties of its constituent phases. Our work confirms the existence of $MoTe_2$ and Mo_2Te_3, the two phases previously reported by Morette (1942). This paper describes a refinement of the molybdenum ditelluride structure.

$MoTe_2$ was prepared from the elements, using 99·999% pure Te and Mo, further purified by heat treatment in H_2 at 850 °C., Stoichiometric quantities of the elements were sealed in vacuo in carbonized quartz ampules. The specimen was reacted and homogenized for several hours at 1100 °C. using R–F induction heating. Chemical analysis of the resultant product, a loosely sintered polycrystalline specimen, yielded 33·44 at.% Mo, 66·56% Te. The specimen was crushed and the specific gravity of the powder measured as $7{\cdot}8 \pm 0{\cdot}2$. $MoTe_2$ oxidizes slowly when exposed to air at room temperature; the powder pattern of finely divided $MoTe_2$ begins to show molybdenum dioxide lines after about a week in air.

The crystal structure of $MoTe_2$ was determined from its powder pattern, using a diffractometer and filtered Cu $K\alpha$ radiation. The diffraction spectra were easily indexed by comparison with the MoS_2 pattern and the lattice parameters were computed from several high-angle lines, using graphic extrapolation to $\theta = 90°$. $MoTe_2$ has a hexagonal unit cell, space group $P6_3/mmc$, with $a = 3{\cdot}519 \pm 0{\cdot}001$, $c = 13{\cdot}964 \pm 0{\cdot}004$ Å, and a calculated specific gravity of 7·78 g.cm.$^{-3}$. It is isomorphous with molybdenite, with Mo at $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and with Te at $\pm(\frac{1}{3}, \frac{2}{3}, z)$ and $\pm(\frac{2}{3}, \frac{1}{3}, z+\frac{1}{2})$, where $z \simeq \frac{5}{8}$. The positional parameter of tellurium, z, was determined from the powder-pattern intensities. Preferred orientation of the $MoTe_2$ powder parallel to the (00·1) cleavage face made accurate intensity determination difficult, but consistent results were obtained by sifting the powder ($< 44\mu$) onto a glass slide covered with glue. A comparison of the observed intensities for specimens with preferred and random orientations is given in Table 1.

The random-orientation intensities were compared with calculated structure factors to obtain the tellurium coordinate. The calculated structure factors were computed from

$$F_c(hkl) = 2[p(hkl)]^{\frac{1}{2}} \sum_i f_i \cos 2\pi(hx_i + ky_i + lz_i)\,,$$

where p is the multiplicity factor and the summation was carried out over one formula unit. The observed intensities were scaled to the F_o values to give an observed structure factor

$$F_o(hkl) = K(\theta)P(\theta)[I_0(hkl)]^{\frac{1}{2}},$$

where $P(\theta)$ is the Lorentz polarization correction and $K(\theta)$ a scaling factor which includes, among other things, the Mo and Te temperature factors. $K(\theta)$ was calculated by scaling the observed and calculated structure factors in zones. The structure factors were computed for various values of z; the best agreement between theory and experiment was obtained for $z = 0{\cdot}620$, as shown in Fig. 1. The lowest R factor is still quite large (17%), but much of the discrepancy can be attributed to preferred orientation or to anisotropic temperature factors, since the

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