the point of view of saving machine time it seems to be convenient to code it in the most economical way, *e.g.* in machine code with possibilities of skipping matrix operations with zero matrices M of higher symmetries of electron-density maps. On the other hand the 'crystallographic' part of the calculation containing the formation of matrices M according to algorithms dependent on the symmetry of a plane group or space group can be easily written in particular cases in any symbolic language with regard to small numbers of arithmetic operations.

The described method was used in programming three-dimensional Fourier syntheses for space groups $P2/m$, $C2/m$ and $P2/c$, $P2_1/c$, $C2/c$ for a National Elliott 803B computer. More detailed descriptions of programs for space groups $P2/m$ and $C2/m$ are published elsewhere (Tichý, 1966).

I am indebted to Dr Karel Toman for suggesting the problem and for helpful discussions, and to Dr Blahoslav Sedláček for his kind interest.

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# Electron diffraction determination of the ionization of the carbon atom in β-Mo$_2$C crystal.

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Recently, the state of atomic ionization in crystals has been studied by precise intensity measurements of X-ray reflexions, and, in particular, successful results have been reported on some nitrides of transition metals (Fe$_4$N, Elliott, 1963; Mn$_4$N, Kuriyama, Hosoya & Suzuki, 1963; VN, Yamagishi, Nakajima, Hosoya & Tokonami, 1965). The atomic ionization has also been studied by the electron diffraction method (Vainshtein & Dvoryakin, 1956; Pinsker & Abrosimova, 1958), in which less elaborate intensity measurements are needed because the effect of atomic ionization on reflexion intensities is stronger for electrons than for X-rays. A difficulty encountered is that the available number of useful reflexions is limited because the effect appears strongly only in the angular range as low as $\sin\theta/\lambda \sim 0{\cdot}1$ Å$^{-1}$ ($\theta$: Bragg angle, $\lambda$: wavelength). In the course of electron diffraction studies on transition metal carbides, the present authors found that $\beta$-Mo$_2$C, which gives superstructure reflexions, happens to be a favourable case for such a purpose. The analysis led to the conclusion that the carbon atom is almost in the state of C$^{1-}$, as described below.

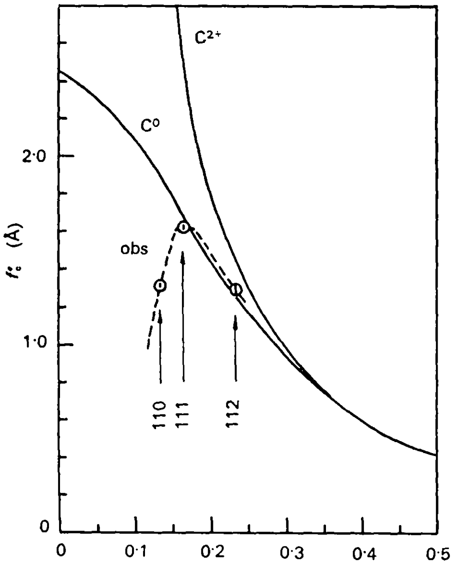

Fig. 1. Comparison of the observed scattering amplitude of the carbon atom for electrons with theoretical curves for neutral atom C$^0$ and the ion C$^{2+}$. Probable errors are indicated by vertical bars in the circles.

$\beta$-Mo$_2$C exists in a narrow range of chemical composition (31 ~ 33·75 at. %C). Its crystal structure has been determined by neutron diffraction (Parthé & Sadagopan, 1963) and also by electron diffraction (Kikuchi, 1966). The crystal is orthorhombic, with the lattice parameters and space group $a=4{\cdot}748$, $b=6{\cdot}020$, $c=5{\cdot}213$ Å and *Pbcn*. Molybdenum atoms occupy 8($d$) positions with $x=\frac{1}{4}$, $y=\frac{1}{8}$ and $z=\frac{1}{12}$, and carbon atoms 4($c$) with $y=\frac{3}{8}$. The arrangement of molybdenum atoms is close packed hexagonal, while the carbon atoms occupy regularly half of the octahedral interstices. In the diffraction pattern of this crystal the three low order reflexions, 110, 111 and 112, appear at angles corresponding to $\sin\theta/\lambda=0{\cdot}135$, $0{\cdot}166$ and $0{\cdot}235$ Å$^{-1}$, respectively. They are superstructure reflexions and their intensities are contributed only by carbon atoms. The crystal structure factor is given by

$$|\Phi_g| = 2\sqrt{2} f^e_{\mathrm{C}},$$

where $f^e_{\mathrm{C}}$ is the scattering amplitude of carbon atom for electrons.

Polycrystalline films of $\beta$-Mo$_2$C were prepared by carburizing evaporated molybdenum films of about 500 Å in thickness in a stream of carbon monoxide at about 850°C for 15 min. The molybdenum films were produced by the vacuum-arc evaporation method (Kikuchi, Nagakura, Ohmura & Oketani, 1965). Transmission electron diffraction patterns were taken with 63 kV electrons ($\lambda=0{\cdot}045$ Å), and the intensity curves were obtained by the microphotometric method. Peak height intensities were measured, since all the observed reflexions had the same half-width. Accuracy in the intensity measurement was 5 %.

Although relative values of several observed intensities are almost enough for detecting the effect of atomic ionization, the observed values were put on the absolute scale by comparing the observed superstructure reflexion intensity $I_s$ with the intensities of ten first-order reflexions in the range of $\sin\theta/\lambda = 0{\cdot}49 \sim 0{\cdot}74$ Å$^{-1}$. These reference reflexions, all being main reflexions, are contributed by both molybdenum and carbon atoms and free from the effect of the atomic ionization. The temperature effect was corrected by assuming $B = 0{\cdot}5$ Å$^2$ (Parthé & Sadagopan, 1963), and the dynamical effect on the basis of Blackman's formula (Blackman, 1939). These effects may influence the reference intensities fairly strongly but the intensities $I_s$ only weakly.

In Fig. 1, $f^e_C$ values observed for 110, 111 and 112 reflexions are plotted against $\sin\theta/\lambda$ and compared with the theoretical curves for neutral carbon atom and for $C^{2+}$ ion. The observed value for 110 deviates downwards from the theoretical curve for the neutral atom. This shows evidently that the carbon atom is negatively ionized. The slight discrepancy of the observed value from the neutral one for the 112 reflexion is possibly due to an error in the scale factor. This factor may depend strongly on the temperature and dynamical corrections for the reference intensities, and also on the carbon content of the crystal. The degree of order in the carbon atom arrangement may also affect the observed values. Such errors, however, do not result in appreciable change in the shape of the curve.

For estimating the degree of atomic ionization, $f^e_C$ was converted to $f^X_C$, the atomic scattering amplitude for X-rays, by the relation

$$(Z-f^x)_C = \frac{2h^2}{me^2}\left(\frac{\sin\theta}{\lambda}\right)^2 f^e_C\,,$$

where the symbols have the usual meanings. In Fig. 2, the observed values of $(Z-f^X)_C$ are plotted and compared with the theoretical curves, the full lines being drawn from the $f^e_C$ values in *International Tables for X-ray Crystallography* (1962), while the broken ones are those obtained by conventional interpolation and extrapolation of the known theoretical values, as they have not yet been calculated. Fig. 2 reveals that the observed values are almost on the curve for $C^{1-}$ ion.

Rundle (1948) discussed the atomic bonding in carbides and nitrides of transition metals. According to him, the carbon atom in an octahedral interstice makes a bond to each of six surrounding metal atoms with a bond number $\frac{2}{3}$. However, he did not take the atomic ionization into consideration. According to the present result, the electron configuration in the carbon ion in $\beta$-$Mo_2C$ may be $(1s)^2(2s)^2(2p_x)(2p_y)(2p_z)$ and the bond between the carbon and metal atoms may be partly ionic and partly covalent. The covalent bonding may be due to three outer electrons in the state $(2p_x, 2p_y, 2p_z)$ making resonating bonds to the six surrounding molybdenum atoms with a bond number $\frac{1}{2}$. It should be added that the effect of aspherical electron distribution on the atomic scattering amplitude (Harada & Kashiwase, 1962) does not need to be considered in the present case, because the electron distribution is spherically symmetric in the above ion.

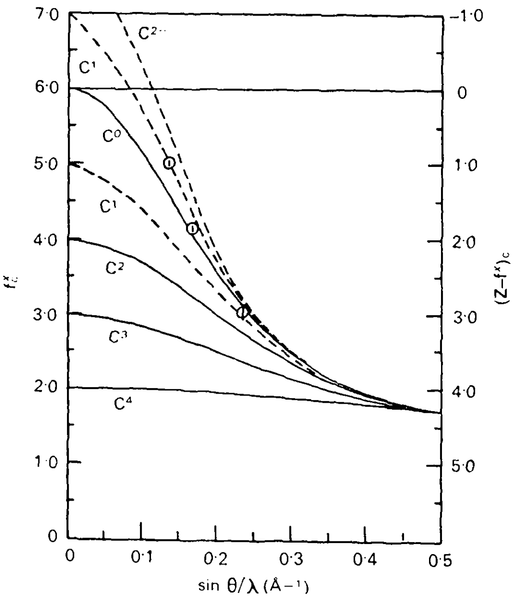

Fig. 2. Comparison of the observed $(Z-f^X)_C$ values (circles) with theoretical $f_C{}^X$ curves (full and broken lines.) Full lines are taken from *International Tables* (1962) and broken lines are obtained by conventional interpolation and extrapolation of the known theoretical curves.

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