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Calculation of electron density maps of all 230 space groups according to one matrix equation.

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As Jaggi (1960) pointed out, matrix formalism enables the compilation of a program for electron-density calculations to be greatly simplified. The calculation of three-dimensional Fourier series with sections parallel to any unit-cell surface is then processed in two steps:

(*a*) Formation of matrices **M** from structure factors and cosine and sine matrices **C** and **S**.

(*b*) Execution of a sequence of matrix operations.

The aim of this contribution is to point out that calculation of electron density maps of all plane groups and of all space groups can be performed according to one general matrix equation.

The electron density of the plane group of lowest symmetry $p1$ is given by the following expression (*International Tables for X-ray Crystallography*, 1952):

$$\varrho(X,Y)=\frac{2}{A_c}\sum_h\sum_k\{|F(hk)|\cos[2\pi(hX+kY)-\alpha(hk)] + |F(\bar{h}k)|\cos[2\pi(-hX+kY)-\alpha(\bar{h}k)]\}\quad(1)$$

which can be transformed into the matrix form:

$$\mathbf{R}=\frac{2}{A_c}\{\mathbf{C}^{(x)}\mathbf{M}^{(cc)}\mathbf{C}^{(y)}+\mathbf{S}^{(x)}\mathbf{M}^{(ss)}\mathbf{S}^{(y)}+\mathbf{C}^{(x)}\mathbf{M}^{(cs)}\mathbf{S}^{(y)} + \mathbf{S}^{(x)}\mathbf{M}^{(sc)}\mathbf{C}^{(y)}\}\quad(2)$$

where **R** is a matrix, whose elements are values of the electron density $\varrho(X,Y)$ at equidistant points X,Y. Matrices $\mathbf{C}^{(x)}$ and $\mathbf{S}^{(x)}$ ($\mathbf{C}^{(y)}$ and $\mathbf{S}^{(y)}$) are cosine and sine matrices X by h (k by Y), whose elements are $\cos 2\pi hX$ and $\sin 2\pi hX$ ($\cos 2\pi kY$ and $\sin 2\pi kY$) respectively; $\mathbf{M}^{(cc)}$, $\mathbf{M}^{(ss)}$, $\mathbf{M}^{(cs)}$ and $\mathbf{M}^{(sc)}$ are matrices h by k. Their elements $m_{hk}^{(cc)}$, $m_{hk}^{(ss)}$, $m_{hk}^{(cs)}$ and $m_{hk}^{(sc)}$ are formed from structure factors according to the following equations

$$\begin{aligned} m_{hk}^{(cc)} &= A'_{hk}+A'_{\bar{h}k}\\ m_{hk}^{(ss)} &= -A'_{hk}+A'_{\bar{h}k}\\ m_{hk}^{(cs)} &= B'_{hk}+B'_{\bar{h}k}\\ m_{hk}^{(sc)} &= B'_{hk}-B'_{\bar{h}k}\end{aligned}\quad(3)$$

where A'_{hk} and B'_{hk} are the real and imaginary parts of the structure factor $F(hk)$

$$\begin{aligned} A'_{hk} &= |F(hk)|\cos\alpha(hk)\\ B'_{hk} &= |F(hk)|\sin\alpha(hk)\end{aligned}\quad(4)$$

The structure factors enter in equation (4) with appropriate weights according to their multiplicity.

Differences in symmetries of plane groups are represented by certain symmetries of the matrices **M**. Formulae for matrix elements of those matrices are summarized in Table 1 for all plane groups.

Sections of all space groups have symmetries of plane groups; therefore it is possible to perform the calculation of their maps according to the same matrix equation as for plane groups, matrices **M** which are results of summation over one index being prepared in advance. The elements $m_{hk}(Z_i)$ for calculation of electron density in sections $Z=Z_i$ ($i=1,2,\ldots$) in space group $P1$ are given by expressions such as:

$$m_{hk}^{(cc)}(Z_l)=\sum_{l=0}^{\infty}[(A'_{hkl}+A'_{\bar{h}kl}+A'_{h\bar{k}l}+A'_{hk\bar{l}})\cos 2\pi lZ_l + (B'_{hkl}+B'_{\bar{h}kl}+B'_{h\bar{k}l}-B'_{hk\bar{l}})\sin 2\pi lZ_l]\,.\quad(5)$$

Higher symmetries of space groups simplify the formulae for elements $m_{hk}(Z_l)$.

'Arithmetical' procedure [multiplication and addition of matrices according to the matrix equation (2)] in calculation of electron density is common to all symmetries and from

Table 1. *Classification of plane groups in 7 sets according to algorithms of formation of matrices* **M** *used in matrix calculation of the electron density map*

No.	Symbol	$m^{(cc)}{}_{hk}$	$m^{(ss)}{}_{hk}$	$m^{(sc)}{}_{hk}$	$m^{(cs)}{}_{hk}$
1	$p1$	$A'_{hk}+A'_{\bar{h}k}$	$-A'_{hk}+A'_{\bar{h}k}$	$B'_{hk}-B'_{\bar{h}k}$	$B'_{hk}+B'_{\bar{h}k}$
13	$p3$				
14	$p3m1$				
15	$p31m$				
4	pg	A'_{hk} (for k even)	$-A'_{hk}$ (for k odd)	B'_{hk} (for k odd)	B'_{hk} (for k even)
2	$p2$	$F(hk)+F(\bar{h}k)$	$-F(hk)+F(\bar{h}k)$	0	0
10	$p4$				
16	$p6$				
17	$p6m$				
7	pmg	$F(hk)$ (for h even)	$-F(hk)$ (for h odd)	0	0
8	pgg	$F(hk)$ (for $h+k$ even)	$-F(hk)$ (for $h+k$ odd)	0	0
12	$p4g$				
3	pm	A'_{hk}	0	0	B'_{hk}
5	cm				
6	pmm	$F(hk)$	0	0	0
9	cmm	$F(hk)$ (for $h+k$ even)			
11	$p4m$	$F(hk)$			

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).

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Electron diffraction determination of the ionization of the carbon atom in β-Mo₂C 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_4N, Elliott, 1963; Mn_4N, 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} (θ: Bragg angle, λ: wavelength). In the course of electron diffraction studies on transition metal carbides, the present authors found that β-Mo_2C, 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.

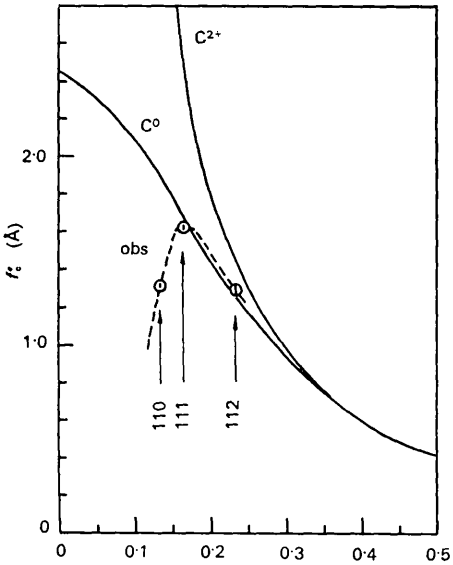

Fig. 1. Comparison of the observed scattering amplitude of the carbon atom for electrons with theoretical curves for neutral atom C^0 and the ion C^{2+}. Probable errors are indicated by vertical bars in the circles.

β-Mo_2C exists in a narrow range of chemical composition ($31 \sim 33{\cdot}75$ 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

$$|\Phi_g| = 2\sqrt{2} f_C^e ,$$

where f_C^e is the scattering amplitude of carbon atom for electrons.

Polycrystalline films of β-Mo_2C 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