

On Some Errors in X-ray Analysis. I. Systematic Errors in Observed Structure Factors

By F. JELLINEK

*Laboratorium voor Kristalchemie der Rijks-universiteit, Utrecht, The Netherlands**

(Received 14 April 1958)

Systematic errors in F_o may be due to, for example, extinction or inaccurate absorption corrections. It is shown that the influence of these errors can be largely suppressed and that in principle they can be corrected for by a modification of the difference-synthesis method. Some examples are given of applications to organic structures containing a heavy atom. Finally it is shown how the enhancement of weak reflexions by double reflexion can be recognized.

1. Introduction

In a recent paper Kitajgorodskij (1957) recalls one of the dangers that threaten accurate X-ray structure analyses, namely systematic errors in F_o due to extinction and incorrect absorption factors. Kitajgorodskij even expresses the opinion that these errors are so serious that they deprive structure refinement beyond the Fourier stage of any physical meaning. Lonsdale, Mason & Grenville-Wells (1957) and Cox & Cruickshank (1957) pointed out that this view is far too pessimistic; although the existence of systematic errors in F_o cannot be denied, 'super-refinement' has yielded quite reasonable interatomic distances and individual anisotropic temperature factors in numerous investigations.

This paradox is not surprising, since derivations of atomic positions and temperature factors depend mainly on the intensities of reflexions with high diffraction angles, while it is with low diffraction angles that the systematic errors in F_o are largest. Therefore it is such structure parameters as hydrogen positions, bonding electrons, ionization, depending largely on the low-angle reflexions, that are most seriously influenced by the systematic errors.

2. A modified difference-synthesis method

The very difference of the θ range of the reflexions determining atomic (except hydrogen) positions and temperature factors on the one hand, and those most susceptible to systematic errors on the other, gives us a means of estimating these errors from the F_o values themselves. If accurate atomic positions, temperature factors and the scale factor have been determined from moderate- and high-angle reflexions (say with $\sin \theta/\lambda > 0.35$) only, a subsequent difference synthesis of the low-angle reflexions will reveal the systematic errors. After these errors have been appropriately

corrected for (the procedure can be reiterated), hydrogen positions etc. may be derived from a new low-angle-reflexions difference synthesis.

Although what is stated above is in principle applicable to any structure analysis (in crystals with small absorption the dependence on θ of the systematic absorption errors is not pronounced, but in that case absorption errors are negligible anyway), the point is most clearly demonstrated for compounds containing a heavy atom: the errors in F_o will accumulate around the heavy-atom position. A few examples may serve as an illustration.

3. Extinction

After atomic (except hydrogen) positions, scale and temperature factors in the b -axis projection of monoethylamine hydrobromide (Jellinek, 1958) had been determined from high-angle reflexions ($\sin \theta/\lambda > 0.355$) alone, a difference synthesis of low-angle reflexions was calculated (Fig. 1(a)). This synthesis showed a minimum around the bromine position, which was ascribed to extinction. By application of a semi-

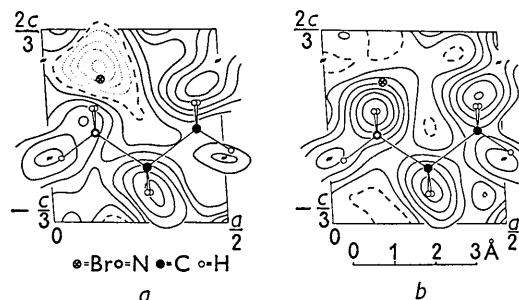


Fig. 1. (a) Difference synthesis of $(h0l)$ reflexions with $\sin \theta/\lambda < 0.355$ of monoethylamine hydrobromide. The calculated Br, N and C contributions have been subtracted from the (uncorrected) observed structure factors. Contours are at intervals of $0.2 \text{ e.}\text{\AA}^{-2}$; positive contours are full lines, negative contours are dotted, and the zero line is broken. (b) The same synthesis after the application of a correction for secondary extinction to the observed structure factors.

* Present address: Anorganisch- en Fysisch-Chemisch Laboratorium der Rijksuniversiteit, Groningen, The Netherlands.

empirical correction for secondary extinction the minimum was effectively removed and the positions of hydrogen atoms, close to bromine in the projection, were now clearly indicated (Fig. 1(b)). The reliability factor was improved from 3.9% to 2.4% (for details see Jellinek, 1958).

4. Absorption

Minima and maxima around the atomic positions in low-angle difference syntheses can also be caused by inaccurate absorption factors. If no correction is applied the systematic errors in F_o , due to this inaccuracy, lead to the derivation of incorrect temperature factors; the errors in the latter, however, are small even for rather strongly absorbing crystals, and equal for all atoms.

As an example may be given the case of an equatorial diagram about the axis of a cylindrical crystal with μR in the range 1.3–1.9; then the transmission factor A can be analytically approximated by

$$A \approx 0.22/(\mu R)^2 - 0.0055 + 0.11 \sin^2 \theta.$$

As F_o^2 is inversely proportional to A we have:

$$(F + \Delta F)/F \approx 1 + \Delta R/R \times \left\{ 1 - \frac{1}{40}(\mu R)^2 + \frac{1}{2}(\mu R)^2 \sin^2 \theta \right\}^{-1}, \quad (1)$$

where ΔR and ΔF are the errors in R and F_o respectively. For the reflexions used for the derivation of atomic positions and temperature factors (with say $\sin^2 \theta > 0.25$) expression (1) can be fairly well represented by

$$(1 + p \times \Delta R/R) \times \exp(-q \times \sin^2 \theta \times \Delta R/R); \quad (2)$$

if $\mu R = 1.6$, $p \approx 0.92$ and $q \approx 0.46$ (see Fig. 2).

If $\Delta R/R$ is constant (specimen cylindrical, but radius incorrect), (2) has the form of an extra isotropic temperature (and scale) factor for all atoms. For $|\Delta R/R| < 0.2$, this—physically incorrect—'heat' cor-

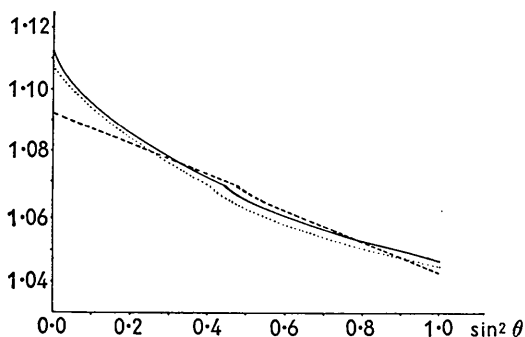


Fig. 2. The error in F_o due to the assumption of an incorrect cylinder radius and its partial compensation by an extra temperature factor, for the case $\mu R = 1.6$; $\Delta R/R = 0.1$. The drawn line represents $(F + \Delta F)/F$ calculated from Bradley's (1935) tables; the dotted line is calculated by approximation (1). The compensating 'temperature' factor $1.092 \exp(-0.046 \sin^2 \theta)$ is plotted as a broken line.

rection compensates the error in F_o of reflexions with $\sin^2 \theta > 0.25$ except for a few tenths of a percent. In a subsequent difference synthesis of low-angle reflexions shallow maxima (if $\Delta R/R > 0$) or minima (if $\Delta R/R < 0$) may appear around the atomic positions, as can be deduced from Fig. 2. (In practice, however, inaccuracies in the atomic scattering factors may obscure this effect.) By a comparison of F_o and F_c such minima can be distinguished from those due to extinction (which mainly affects the strong reflexions).

If $\Delta R/R$ is not constant (specimen not ideally cylindrical) the shapes of all atomic peaks will be distorted in the same ways. In a low-angle-reflexion difference synthesis both maxima and minima will be found around the atomic positions, forming peculiar 'absorption figures' which reflect the crystal cross section. As an illustration (Fig. 3(a)) may be given

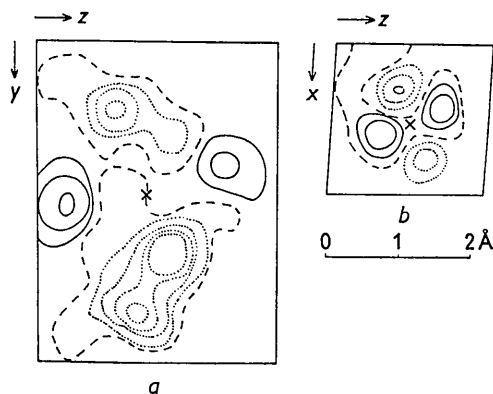


Fig. 3. (a) Absorption figures around the iodine position (indicated by a cross) in the final $(0kl)$ difference synthesis of muscarine iodide. Contours are at intervals of $0.5 \text{ e.}\text{\AA}^{-2}$; in the corresponding electron-density map the iodine peak height is $85 \text{ e.}\text{\AA}^{-2}$. (b) Anisotropic temperature movement of bromine (position indicated by a cross) in monoethylamine hydrobromide, as found in a $(h0l)$ difference synthesis. Contours are at intervals of $0.5 \text{ e.}\text{\AA}^{-2}$; the peak height of bromine in the corresponding electron-density map is $64 \text{ e.}\text{\AA}^{-2}$.

the final difference synthesis along the a axis of muscarine iodide (Jellinek, 1957). The specimen section was more or less elliptically deformed; therefore the absorption figures around the iodine position are somewhat reminiscent of the 'four-leaved clovers', which are due to anisotropic temperature movement, but the latter are far less extended (compare Fig. 3(b), which is on the same scale as Fig. 3(a)). In this case no high precision was aimed at and no correction for the systematic error was attempted.

5. Double reflexion

Another error in F_o may also be mentioned in this context—the one that is due to double reflexion. With crystals of the quality generally used in structure

analysis, this error will be important only if the double reflexion caused by two strongly reflecting lattice planes coincides with a very weak (or absent) reflexion. The occurrence of this effect can be recognized in single-crystal diagrams taken with unfiltered radiation: if—with the given crystal setting—the azimuth conditions for double reflexion via a certain pair of lattice planes are fulfilled for the α radiation, this will not hold for the β radiation. So weak reflexions whose intensities are enhanced by double reflexion can be unmasked by a comparison of their α and β components.

The author wishes to thank Prof. J. M. Bijvoet for his stimulating interest and advice in the course of this investigation.

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Acta Cryst. (1958). **11**, 679

On the Structure of Uranium in Thin Film

BY S. N. CHATTERJEE

Institute of Nuclear Physics, Calcutta, India

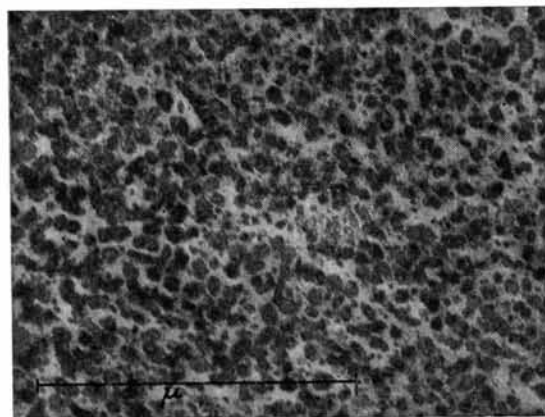
(Received 18 February 1958)

Thin film of uranium, prepared by the vacuum evaporation technique, was studied with the help of electron microscopy and electron diffraction. The analysis shows that uranium in thin film assumes the β -phase structure (tetragonal; $a = 10.52$, $c = 5.57$ Å; $P4nm$).

X-ray crystallographic study of uranium has been done at different temperatures by different authors (Jacob & Warren, 1937; Tucker, 1951; Wilson & Rundle, 1949). It is found that uranium assumes the orthorhombic structure (α -phase; $a = 2.852$, $b = 5.865$, $c = 4.945$ Å and space group $Amam$) up to 660 °C., tetragonal (β -phase; $a = 10.52$, $c = 5.57$ Å and space group $P4nm$) between 660 °C. and 760 °C. and body-centred cubic (γ -phase; $a = 3.474 \pm 0.005$ Å and space group $Im3m$) between 760 °C. and the melting point. In the present work investigation is made on the structure of uranium in thin film with the help of electron microscopy and electron diffraction technique.

Thin film of uranium was prepared by the evaporation of a weighed quantity of the metal from a tungsten bucket inside a vacuum chamber (pressure 10^{-4} mm.Hg.). The evaporated metal was allowed to deposit on a collodion film covering a steel wire-mesh. Fig. 1(a) is the electron micrograph ($54,000\times$) of the uranium film taken with an accelerating potential of 60 kV. using the Siemen's Elmiskop I. The micrograph shows the uranium microcrystals well resolved. Fig. 1(b) is the electron diffraction photograph of the film. The diffraction length was 587 mm. and the accelerating potential 60 kV. The indexing of the diffraction rings is shown in the figure. The diffraction pattern is found to correspond with the tetragonal structure (β -phase) of uranium. Table I shows the

agreement between the theoretical and experimental ring diameters and also the relative intensities of the



(a)



(b)

Fig. 1. (a) Electron micrograph of the uranium film. (b) Electron diffraction photograph of the uranium film.