fragments were isolated, were prepared by Dr C. J. Raub. One of the two crystal spheres was ground by Miss H. A. Plettinger. The least-square refinement was carried out on the IBM 704 computer of the Argonne National Laboratory. The work was in part supported by the Advanced Research Projects Agency.

The investigation reported in this paper was begun during a visit to the University of California at San Diego. The writer thanks Prof. B. T. Matthias and other La Jolla friends for valuable discussions in a hospitable milieu.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1963). **16**, 1255

The crystal structure of KI.Hg(CN)$_2$. A correction.

By F. H. Kruse, *Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.*

(*Received* 21 *March* 1963)

The paper of the above title (Kruse, 1963) contains an error in Table 4 — *Final observed and calculated structure factors for* KI.Hg(CN)$_2$.

The F_o values for reflections 001, 003, 005, and 009 should be marked with a minus sign denoting 'less than' for these unobserved values, thus making the data table compatible with the space group, *Cmcm*.

Reference

Kruse, F. H. (1963). *Acta Cryst.* **16**, 105.

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Treatment of anomalous dispersion in X-ray diffraction data.

By A. L. Patterson, *The Institute for Cancer Research, Fox Chase, Philadelphia* 11, *Pennsylvania, U.S.A.*

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The purpose of this note is to reemphasize and to amplify the remarks made by Templeton (1955) concerning the importance of the correction of X-ray data for anomalous dispersion effects in the refinement of crystal structures. We are not concerned here with the important uses of such data in the initial approach to the solution of the phase problem.

First, let us assume that there is only one element in the crystal which shows appreciable dispersive effects. This element may be located in one or more sets of general or special positions and is assumed to have structure factor components $A_d = f_d H_d$ and $B_d = f_d K_d$ where f_d is the non-dispersive part of the scattering factor for the dispersive atom at rest and the geometrical components H_d and K_d are assumed to contain isotropic or anisotropic temperature factors appropriate for the thermal motion of the atoms of the dispersive element in the crystal. The structure factor components for the non-dispersive part of the crystal are taken as A_n and B_n. We define F_+ as the structure factor for the plane hkl for which A_n, B_n, A_d, B_d are calculated. Then F_- is that for the plane $\bar{h}\bar{k}\bar{l}$ the inverse of the first. The structure factors for these two planes may then be written in the well known form (*cf.* James, 1948)

$$F_\pm = A_n + i\sigma B_n + (H_d + i\sigma K_d)(f_d + \Delta f'_d + i\Delta f''_d)\,, \quad (1)$$

in which $\sigma = +1$ corresponds to F_+, $\sigma = -1$ corresponds to F_-, and $\Delta f'_d$ and $\Delta f''_d$ are the real and imaginary components of the dispersive effect for the given atom. The result (1) may then be rewritten in the forms

$$\begin{aligned} F_\pm &= A_n + i\sigma B_n + (A_d + i\sigma B_d)(1 + \delta_1 + i\delta_2) \\ &= (A + \delta_1 A_d - \sigma\delta_2 B_d) + i\sigma(B + \delta_1 B_d + \sigma\delta_2 A_d)\,, \end{aligned} \quad (2)$$

where A and B are the non-dispersive structure factor components for the whole structure, and

$$\delta_1 = \Delta f'_d / f_d\,; \quad (2a)$$

$$\delta_2 = \Delta f''_d / f_d\,. \quad (2b)$$

We now calculate

$$\begin{aligned} |F_\pm|^2 = A^2 + B^2 + (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2) + 2\delta_1(AA_d + BB_d) \\ - 2\sigma\delta_2(AB_d - BA_d) \end{aligned} \quad (3)$$

and define the quantities S and D as

$$\begin{aligned} S = \tfrac{1}{2}\{|F_+|^2 + |F_-|^2\} = A^2 + B^2 + 2\delta_1(AA_d + BB_d) \\ + (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2) \end{aligned} \quad (4a)$$

and

$$D = \tfrac{1}{2}\{|F_+|^2 - |F_-|^2\} = -2\delta_2(AB_d - BA_d)\,. \quad (4b)$$

One could of course make use of formula (3) to calculate the structure factors for $|F_+|$ and $|F_-|$ separately but it seems simpler to use (4*a*) to obtain an 'experimental' value of $|F|_0^2$ by applying a correction for the dispersion of the observed values of S, *i.e.* to $S_0 = \frac{1}{2}\{|F_+|_0^2 + |F_-|_0^2\}$. In making this correction we use the calculated factors at the given stage of the refinement, and we have

$$|F|_0^2 = S_0 - 2\delta_1(AA_d + BB_d) - (\delta_1^2 + \delta_2^2)(A_d^2 + B_d^2) \,. \quad (5)$$

Thus it is neither $|F_+|_0$ nor $|F_-|_0$ nor $S_0^{\frac{1}{2}}$ but the quantity $|F|_0$ defined by (5) which must be alloted a phase by an ordinary structure factor calculation and used as a coefficient in Fourier series calculation of the true electron density in the crystal.

If this same value $|F|_0$ is used in constructing the difference vector in least-squares analysis, the normal equation matrix will be in exactly the same form as for a non-dispersive crystal. In the earlier stages of the refinement it is probable that $S_0^{\frac{1}{2}}$ will be an adequate approximation to $|F|_0$ but in the later stages when the essential features of the structure are precisely defined it will be necessary to calculate a new set of values $|F|_0$ between each stage of refinement of the positional, thermal, and scale parameters.

In making the correction (5) the tabulated values (Dauben & Templeton, 1955; Templeton, 1962) of $\Delta f_d'$ and $\Delta f_d''$ can be used. It is suggested however that parameters corresponding to δ_1 and δ_2 may be introduced into the least-squares treatment of structures for which accurate intensity measurements have been made, as for instance in a full matrix correlating δ_1 and δ_2 with the scale factor and an overall temperature factor. In this way, experimental values for the dispersion constants may be obtained (*cf.* Parthasarathy, 1962). Further details of such procedures must await experimental test.

In the case of a centrosymmetric crystal (5) reduces to

$$|F|_0^2 = S_0 - 2\delta_1 AA_d - (\delta_1^2 + \delta_2^2)A_d^2 \,. \quad (6)$$

For rock salt with Cu $K\alpha$ radiation the correction in (6) reaches 18% for the plane (311) for the 'all odd' reflections and 10% (640) for the 'all even' reflections; with Mo $K\alpha$ the corresponding figures are 7% (331) and 4% (880) respectively. The larger part of these corrections comes from $\Delta f'$ but the correction due to $\Delta f''$ is not negligible.

In the case of several dispersive atoms the above argument is readily generalized (Bijvoet, 1962). If $A_r, B_r, \delta_{1r}, \delta_{2r}$ are the structure factor components and dispersion constants of the rth dispersive element, and other notation is unchanged, the expression (3) becomes

$$\begin{aligned}|F_\pm|^2 = A^2 + B^2 &+ 2\sum_r \delta_{1r}(AA_r + BB_r) - 2\sigma\sum_r \delta_{2r}(AB_r - BA_r) \\ &+ \sum_{r,s}\sum (\delta_{1r}\delta_{1s} + \delta_{2r}\delta_{2s})(A_rA_s + B_rB_s) \\ &- \sigma\sum_{r,s}\sum (\delta_{1r}\delta_{2s} - \delta_{1s}\delta_{2r})(A_rB_s - A_sB_r) \,. \quad (7)\end{aligned}$$

From this result, expressions for S, D, and the correction for S_0 can easily be written down.

While we wish to emphasize strongly the importance of the corrections for dispersive effects in both Fourier and least-squares analyses we hold no particular brief for the methods which we have suggested for carrying out these corrections, since there are many other ways of doing this.

Thanks are due to eighteen colleagues, who were good enough to comment on a first draft of this note, for the clarifications which they suggested; but particularly I wish to thank Drs Jenny P. Glusker, Dick van der Helm and Carroll K. Johnson for assistance in calculations and for discussions which helped in the original formulation.

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On the weighting of reflexions in least-squares calculation of non-cubic unit-cell dimensions.

By B. R. LAWN, *Department of Physics, University of Western Australia, Western Australia*

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It is well known that extrapolation for non-cubic cell dimensions inherently requires that weight be allocated to individual *hkl* reflexions in accordance with the particular parameter being determined. This is usually practised to some extent in graphical extrapolation but not in the more sophisticated 'least-squares' techniques developed by Cohen (1935), Hess (1951) and others. Hess has made provision in the 'least-squares normal equations' to include a weighting term W, which is the product of two factors, $W(\theta)$ and $W(s)$. These respectively take into account the influence of Bragg angle θ and the accuracy of the linear film distances s upon the ultimate precision of cell dimensions.

With the advent of high-speed computers the objection to lengthy computations associated with the analytical procedures no longer arises. It is therefore little extra trouble to incorporate a third weight factor $W(hkl)$ into W, which facilitates h, k, l weighting. In establishing such a factor it is desirable that certain boundary conditions be satisfied. For instance, consider the following expression for hexagonal cells, the terms retaining their conventional meaning: