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

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

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

$$|F|_0^2=S_0-2\delta_1AA_d-(\delta_1^2+\delta_2^2)A_d^2\,. \qquad (6)$$

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

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

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.

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

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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:

$$4 \sin^2 \theta/\lambda^2 = 4(h^2+hk+k^2)/3a^2 + l^2/c^2 .$$

$hk0$ lines render a exempt from any error in the term containing c whereas $00l$ lines are completely independent of a. This implies $W_a(hk0)=1$, $W_a(00l)=0$.

The following is the simplest expression which complies with the two above extreme specifications and is adaptable to the general hkl reflexion:

$$W_a(hkl) = \frac{4(h^2+hk+k^2)/3a^2}{4(h^2+hk+k^2)/3a^2+l^2/c^2} .$$

a is then determined by solving the 'normal equations' weighted with $W=W(s).W(\theta).W_a(hkl)$. Parameter c is obtained similarly. It will be noted that at least a crude approximation to c/a is presupposed.

Table 1. *Cell parameters a and c of β-AgI, with standard error, using various W functions*

Film	Cohen (Å)	Hess (Å)	Modified (Å)
1	4·59085 ± 0·00056	4·59063 ± 0·00039	4·59059 ± 0·00038
	7·50358 ± 0·00092	7·50363 ± 0·00064	7·50281 ± 0·00105
2	4·59217 ± 0·00031	4·59196 ± 0·00025	4·59190 ± 0·00021
	7·50764 ± 0·00051	7·50789 ± 0·00041	7·50818 ± 0·00059
3	4·59400 ± 0·00029	4·59381 ± 0·00016	4·59376 ± 0·00014
	7·50894 ± 0·00048	7·50943 ± 0·00027	7·50912 ± 0·00036
4	4·59341 ± 0·00041	4·59346 ± 0·00022	4·59346 ± 0·00022
	7·51153 ± 0·00068	7·51192 ± 0·00037	7·51261 ± 0·00036
5	4·59415 ± 0·00042	4·59415 ± 0·00030	4·59405 ± 0·00033
	7·51079 ± 0·00069	7·51096 ± 0·00049	7·51086 ± 0·00033
6	4·59371 ± 0·00026	4·59355 ± 0·00015	4·59355 ± 0·00012
	7·51320 ± 0·00042	7·51325 ± 0·00024	7·51448 ± 0·00041
7	4·59326 ± 0·00022	4·59324 ± 0·00014	4·59324 ± 0·00013
	7·51160 ± 0·00036	7·51195 ± 0·00024	7·51279 ± 0·00039
8	4·59311 ± 0·00023	4·59327 ± 0·00014	4·59329 ± 0·00012
	7·51033 ± 0·00038	7·51000 ± 0·00022	7·50960 ± 0·00027
9	4·59420 ± 0·00034	4·59401 ± 0·00020	4·59398 ± 0·00019
	7·51150 ± 0·00055	7·51181 ± 0·00033	7·51229 ± 0·00049
10	4·59357 ± 0·00045	4·59340 ± 0·00023	4·59337 ± 0·00017
	7·50924 ± 0·00074	7·50947 ± 0·00039	7·51008 ± 0·00072

As a test of the function W, data from ten powder photographs of hexagonal β-AgI, taken at temperatures ranging from 30 °C to 150 °C, were in turn subjected to the Cohen, Hess and modified weighting procedures, extrapolating against the Nelson–Riley function and setting $W(s)=1$ for all lines. The problem was coded in FORTRAN II language for solution on an IBM 1620 computer. Results are illustrated in Table 1. Although the Hess method yields consistently smaller standard errors than does that of Cohen, there is no further significant overall reduction resulting from the modified scheme. However, an unsatisfactory feature of the Cohen and Hess methods, the identity of the relative errors in both a and c, does not arise with the modified procedure. In the exposures tested there were no $00l$ lines and an average of only 5 observations in about 20 were more favourable to a c extrapolation. Furthermore, these were generally found to be faint and therefore of comparatively poorer quality. It is to be expected that the relative error in c will exceed that in a, as is indeed reflected by the trend of the standard errors listed in Table 1.

The various weighting systems may be examined for sensitivity by removing (*a*) $hk0$ reflexions (average of. 5 per film) or (*b*) all reflexions favouring c extrapolation. It would be desirable that situation (*a*) have no effect on parameter c and (*b*) very little effect on a. Table 2 summarizes the result of such an analysis with the Hess and Modified systems.

Table 2. *Results of sensitivity test*

	Average change in c as a result of (*a*)	Average change in a as a result of (*b*)
Hess	0·00061 Å	0·00006 Å
Modified	zero	0·00003

The latter is found to be more insensitive to the absence of reflexions unfavourable to extrapolation for a particular cell dimension.

The above proposed weighting system is readily applicable to orthorhombic and higher-symmetry crystals, which comprise the practical limit for powder X-ray diffraction. Extension to lower symmetries in which the angles become variables is difficult owing to the appearance of cross terms in the expression for cell parameters.

The author is indebted to Dr E. N. Maslen and Mr S. R. Hall for discussions. The latter is at present working on weighting functions for lower-symmetry crystals in conjunction with single-crystal techniques.

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