Table 12. *Neutron scattering amplitudes and thermal parameters obtained for* CaF_2, SrF_2 *and* BaF_2

	CaF_2	SrF_2	BaF_2	
b_M	0·488	0·688 (0·013)	0·522 (0·13)	$\times 10^{-12}$ cm
α_M	6·30	5·63 (0·011)	4·71 (0·04)	$\times 10^{-12}$ erg. Å^{-2}
α_F	4·58	3·77 (0·06)	3·04 (0·01)	$\times 10^{-12}$ erg. Å^{-2}
$-\beta_F$	5·66 (1·16)	3·95 (0·46)	3·06 (0·26)	$\times 10^{-12}$ erg. Å^{-3}
$-\beta_F/\alpha_F$	1·24 (0·25)	1·05 (0·12)	1·01 (0·09)	Å^{-1}
α_M/α_F	1·38	1·49 (0·03)	1·55 (0·01)	
B_M	0·507	0·567 (0·011)	0·678 (0·005)	Å^2
B_F	0·697	0·846 (0·013)	1·048 (0·004)	Å^2
B_M/a^2	1·70	1·69 (0·03)	1·76 (0·01)	$\times 10^{-2}$
B_F/a^2	2·34	2·51 (0·04)	2·73 (0·01)	$\times 10^{-2}$

for the nuclear scattering amplitude of strontium of $b_{Sr}=0{\cdot}688\ (\pm 0{\cdot}013)\times 10^{-12}$ cm, assuming a value of $b_F=0{\cdot}560\ (\pm 0{\cdot}010)\times 10^{-12}$ cm. The new value of b_{Sr} is appreciably larger than the previously tabulated values of $0{\cdot}57\times 10^{-12}$ cm (*International Tables for X-ray Crystallography*, 1962) and $0{\cdot}656\times 10^{-12}$ cm (The Neutron Diffraction Commission, 1969), but is in excellent agreement with the value of $0{\cdot}683(\pm 0{\cdot}007)\times 10^{-12}$ cm given by Loopstra & Rietveld (1969).

The present measurements give further confirmation of the importance of anharmonic effects for atoms occupying tetrahedral sites in the fluorite structure and it is to be expected that these considerations can be extended to other types of structure. Neutron diffraction measurements on a number of other relatively simple structures are in progress to investigate this further.

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An Improved Absorption Correction Procedure for X-ray Intensity Data from a Poorly Defined Single Crystal

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A mathematical technique is described which combats the innacuracies in absorption corrections applied to single-crystal X-ray diffraction data due to indefinite location of the crystal faces.

Introduction

The purpose of this paper is to demonstrate the feasibility of correcting errors inherent in the calculation of absorption corrections. Here a method is described for calculating the magnitude of the absorption error associated with the fixing of the planes defining a crystal. The effectiveness of the method is studied by using a least-squares correlation of common reflexions obtained from different data collection geometries. The orientation of the defining planes of a crystal may reasonably be regarded as without error and only the

distances of these planes from an internal origin were corrected.

Theory

Intensities of X-ray reflexions from one or more single crystals of a compound may commonly be separated into zones. The ith zone is that collection of intensities with a common scale constant k_i. Correlation of these zones of data is obtained by having values of $|F(hkl)|^2$ measured in more than one zone. Since it is possible to measure $|F(hkl)|^2$ with different geometries (implying either a different crystal or different directions of the incident and emergent beam with respect to the unit-cell axes), it is also possible to make minor corrections to the size and shape of the crystal to improve the estimation of the absorption factors and to calculate correct values of $|F(hkl)|^2$. Indeed, both of these procedures may be carried out in the same single cycle least-squares calculation.

The correct values of $|F(hkl)|^2$ in the ith zone may be written as

$$F^2_{hi}=k_i\left(\frac{A_{0hi}}{A_{hi}}\right)F^2_{0hi}$$

where k_i is the scale constant, F^2_{0hi} is the almost correct value of $|F(hkl)|^2$ using the almost correct absorption coefficient A_{0hi}. A_{hi} is the correct absorption coefficient.

$$A_{hi}=\frac{\int \exp\{-\mu(r_{\text{in}}+r_{\text{out}})\}\mathrm{d}V}{\int \mathrm{d}V}$$

where the integrations are over the crystal.

We minimize the sum of the weighted residuals squared.

$$R=\sum_{h,i,j} W_{hij}\{\ln(F^2_{hi})-\ln(F^2_{hj})\}^2$$

where the sum is over the reflexions, h, having independent measurements in zones i and j. By using the logarithms we are looking at ratios of values of $|F(hkl)|^2$ rather than absolute differences between values (Rae, 1965).

The residuals $\Delta_{hij}=\ln(F^2_{hi})-\ln(F^2_{hj})$ may be expanded as

$$\Delta_{hij}=\ln k_i-\ln k_j-\ln\left(\frac{A_{hi}}{A_{0hi}}\right)+\ln\left(\frac{A_{hj}}{A_{0hj}}\right)+\ln\left(\frac{F^2_{0hi}}{F^2_{0hj}}\right).$$

We can express $\ln(A_{hi})$ in a Taylor expansion using as variables $d_q=(R_q-R_{0q})/R_{0q}$ where R_q is the correct distance from the internal origin to the qth defining plane, and R_{0q} is the assumed value.

$$\ln(A_{hi})=\ln(A_{0hi})+\sum_q a_{hiq}d_q+\text{higher terms}$$

where

$$a_{hiq}=\left(\frac{\partial}{\partial d_q}\ln A_{hi}\right)_0=\frac{1}{A_{0hi}}\left(\frac{\partial}{\partial d_q}A_{hi}\right)_0 \qquad (1)$$

evaluated for the assumed parameters R_{0q}.

The orientation of the defining planes, usually defined by Miller indices, are regarded as without error. Higher terms in the Taylor expansion can be ignored if the assumed crystal is almost correct: otherwise an iterative procedure is necessary.

We thus obtain a residual

$$\Delta_{hij}=\ln k_i-\ln k_j-\sum_q(a_{hiq}-a_{hjq})d_q+\ln\frac{F^2_{0hi}}{F^2_{0hj}}$$

which is linear in the variables $\ln k_i$ and d_q. The summation of q is over all planes of all crystals, a_{hiq} being zero when the qth plane is not involved in calculating F^2_{0hi}.

We may generalize the expression to

$$\Delta_{hij}=V_{0hij}+\sum_{k=1}^{N}V_{khij}u_k$$

where

$$V_{0hij}=\ln\left(\frac{F^2_{0hi}}{F^2_{0hj}}\right) \quad\text{and}\quad V_{khij}=\frac{\partial}{\partial u_k}\Delta_{hij}.$$

u_k is the kth of the total N variables.

$$u_1, u_2, \ldots u_n, u_{n+1}, u_{n+2}, \ldots u_{n+n'}, u_{n+n'+1}, u_{n+n'+2}, \ldots u_{n+n'+n''}$$

corresponds to

$$\ln k_1, \ln k_2, \ldots \ln k_n, d_1, d_2, \ldots d_{n'}, d_{n'+1}, d_{n'+2}, \ldots d_{n'+n''}$$

where there are n zones, n' faces on the first crystal, n'' faces on the second crystal, *etc.*

By putting

$$\frac{\partial}{\partial u_k}\sum_{h,i,j}W_{hij}(\Delta_{hij})^2=0 \qquad k=1,N$$

we obtain the linear equations

$$\sum_{m=1}^{N}B_{km}u_m=C_k \qquad k=1,N$$

where

$$B_{km}=\sum_{h,i,j}W_{hij}V_{khij}V_{mhij}$$

$$C_k=-\sum_{h,i,j}W_{hij}V_{0hij}V_{khij}.$$

The calculation of the coefficients a_{hiq}

The absorption calculation routine is a modified version of the program *DATAP*2 by Coppens; the method used by this program is described in detail elsewhere (Coppens, Leiserowitz & Rabinovich, 1965).

In general, if the distances R_{0q} to the defining planes of the crystal are incremented to $R_{0q}(1+d_q)$ then the increment $\mathrm{d}\varphi$ in any quantity φ may be expressed in the form

$$\mathrm{d}\varphi=\sum_q\varphi_q d_q \quad\text{where}\quad \varphi_q=\left(R_q\frac{\partial\varphi}{\partial R_q}\right)_0. \qquad (2)$$

The R_q are regarded as independent variables and the

values of R_q $\partial\varphi/\partial R_q$ are evaluated for the assumed crystal. From equation (1) we see

$$a_{hiq}=\frac{1}{A_{0hi}}\left(R_q\frac{\partial A_{hi}}{\partial R_q}\right)_0 . \qquad (3)$$

It is necessary to express, at each stage in the calculation of A_{hi}, the variables in terms of R_q, the components of the differential increment then follow from (2).

The increment may be considered in two parts. That part associated with a change in the path length due to the change in position of the faces of incidence and emergence, and that correspondent with the change in position and weighted volume of the grid point.

Consider the Gaussian integral and the approximate method used to evaluate it (Busing & Levy, 1957).

$$\int_a^b \mathrm{d}x\int_{c(x)}^{d(x)}\mathrm{d}y\int_{(ex,y)}^{f(x,y)} g(x,y,z)\mathrm{d}z$$
$$\simeq \sum_{i=1}^{m}\sum_{j=1}^{m}\sum_{k=1}^{m}(b-a)\,[d(x_i)-c(x_i)]$$
$$\times[f(x_i,y_j)-e\,(x_i,y_j)]R_iR_jR_kg(x_i,y_j,z_k) \qquad (4)$$

where

$$x_i=a+(b-a)u_i \qquad (4a)$$
$$y_j=c(x_i)+[d(x_i)-c(x_i)]u_j \qquad (4b)$$
$$z_k=e\,(x_i,y_j)+[f(x_i,y_j)-e\,(x_i,y_j)]u_k\,. \qquad (4c)$$

Change in position of grid point

The calculation of a and b, the limits of integration over x, depend on the intersection, at a point that is not external to the crystal, of three crystal defining planes, q_1, q_2 and q_3. The maximum and minimum values of x so obtained yield b and a respectively. Thus, a is of the form

$$a=\alpha_1R_{q_1}+\alpha_2R_{q_2}+\alpha_3R_{q_3}$$

where the α's are numerical constants, and

$$a_q=\left(R_q\frac{\partial a}{\partial R_q}\right)_0=\alpha_1R_{0q_1}\delta_{qq_1}+\alpha_2R_{0q_2}\delta_{qq_2}+\alpha_3R_{0q_3}\delta_{qq_3}$$

where

$$\delta_{qq_i}=0 \text{ for } q\neq q_i \text{ and}=1 \text{ for } q=q_i\,.$$

The b_q values can be obtained similarly giving, from equation (4a)

$$(x_i)_q=a_q+(b_q-a_q)u_i\,.$$

The limits $c(x_i)$ and $d(x_i)$ of the integration over y depend on the intersection of two crystal defining planes and the plane $x=x_i$. The maximum and minimum values of y, not external to the crystal, yield $d(x_i)$ and $c(x_i)$ respectively. Thus, $c(x_i)$ is of the form

$$c(x_i)=\alpha_4R_{q_4}+\alpha_5R_{q_5}+\alpha_6x_i$$

and

$$c(x_i)_q=\alpha_4R_{0q_4}\delta_{qq_4}+\alpha_5R_{0q_5}\delta_{qq_5}+\alpha_6(x_i)_q\,.$$

The $d(x_i)_q$ values can be obtained similarly giving, from equation (4b)

$$(y_j)_q=c(x_i)_q+[d(x_i)_q-c(x_i)_q]u_j\,.$$

The limits $e\,(x_i,y_j)$ and $f(x_i,y_j)$ of the integration over z are evaluated as the minimum and maximum values z, not external to the crystal, defined by one crystal defining plane and the planes $x=x_i$, $y=y_j$. Thus, $e\,(x_i,y_j)$ is of the form

$$e\,(x_i,y_j)=\alpha_7R_{q_7}+\alpha_8(x_i)+\alpha_9(y_j)$$

and

$$e\,(x_i,y_j)_q=\alpha_7R_{0q_7}\delta_{qq_7}+\alpha_8(x_i)_q+\alpha_9(y_j)_q\,.$$

The $f(x_i,y_j)_q$ values can be obtained similarly giving, from equation (4c)

$$(z_k)_q=e\,(x_i,y_j)_q+[f(x_i,y_j)_q-e\,(x_i,y_j)_q]u_k\,.$$

The weighted volume of the ijk element of the crystal is given by

$$V_{ijk}=(b-a)\,[d(x_i)-c(x_i)]\,[f(x_i,y_j)-e\,(x_i,y_j)]R_iR_jR_k$$

and $(V_{ijk})_q$ follows directly from equation (2)

$$(V_{ijk})_q=V_{ijk}\left\{\frac{b_q-a_q}{b-a}+\frac{d(x_i)_q-c(x_i)_q}{d(x_i)-c(x_i)}+\frac{f(x_i,y_j)_q-e\,(x_i,y_j)_q}{f(x_i,y_j)-e\,(x_i,y_j)}\right\}.$$

Change in path length

The incident and emergent path lengths r_{ijk1} and r_{ijk2} are given by an expression of the form

$$r_{ijk}=\beta_1x_i+\beta_2y_j+\beta_3z_k+\beta_4R_{q_4}$$

where β's are numerical constants.
It follows that

$$(r_{ijk})_q=\beta_1(x_i)_q+\beta_2(y_j)_q+\beta_3(z_k)_q+\beta_4R_{0q_4}\delta_{qq_4}$$
$$A_{ijk}=V_{ijk}\exp\,[-\mu(r_{ijk1}+r_{ijk2})]$$

so

$$(A_{ijk})_q=A_{ijk}\left\{\frac{(V_{ijk})_q}{V_{ijk}}-\mu(r_{ijk1})_q-\mu(r_{ijk2})_q\right\}.$$

Since the absorption coefficient is defined as

$$A=\sum_{i,j,k}A_{ijk}(\sum_{i,j,k}V_{ijk})^{-1}$$

we have

$$A_q=\frac{\sum_{i,j,k}V_{ijk}\sum_{i,j,k}(A_{ijk})_q-\sum_{i,j,k}A_{ijk}\sum_{i,j,k}(V_{ijk})_q}{(\sum_{i,j,k}V_{ijk})^2}$$

and A_q/A gives us the value of a_{hiq} [equation (3)] that we need for equation (1).

The linear dependence of variables

The residual is unaltered if $\ln k_i-\ln k_j$ is replaced by $\ln k_i/k-\ln k_j/k$. We can change our variables to

$\ln k_i - \ln k_1 = l_i$, thus reducing the number of scale constant variables by one.

$$\frac{\partial \Delta_{hij}}{\partial l_i} = \frac{\partial \Delta_{hij}}{\partial(\ln k_i)}, \quad i \neq 1 .$$

We also require the origin to be fixed in space for each crystal. Our method of doing this alters the covariance between the parameters d_q but does not alter the size and shape of the corrected crystal. The fixing of the origin is achieved most easily by saying the distances R_q from the origin to three planes intersecting at a point must be fixed for each crystal. We thus set three values of d_q identically equal to zero without error for each crystal.

We now have the problem expressed in terms of linearly independent variables, achieved by simply deleting the relevant rows and columns from the matrix of the least-squares equations. However, we still have to fix an overall scale constant for the data.

Further redundancy in the equations may be accidentally introduced. For example, Weissenberg data about (100), (010), (001) and (111) axes for a F-centred crystal give zones in which h, k, l are either all even or all odd leading to a scale factor redundancy. Data collected about the [011] direction are necessary to remove this redundancy.

Error analysis

Standard procedures are applicable for the unbiased estimation of the variance and covariance of the reduced set of variable parameters required for linear independence. The variance of the nth parameter u_n is given by

$$\text{var}\,(u_n) = a^{nn}\sigma^2$$

while the covariance of the parameters u_n and u_m is given by

$$\text{cov}\,(u_n, u_m) = a^{nm}\sigma^2 .$$

a^{nm} is the nm element of the inverse of the matrix of the least-squares equations for the linearly independent variables, and σ^2 is the unbiased estimate of the variance of an observation of unit weight, and should be unity for an absolute set of weights.

$$\sigma^2 = \sum_{h,i,j} W_{hij}\Delta^2_{hij}/(M-N)$$

where M is the total number of observations and N is the number of linearly independent variables.

Let us consider now a least-squares correlation between our corrected values of F^2_{hi} and the truly correct values of F^2_h

$$R = \sum_{h,i} W_{hi}[\ln(\hat{k}_i \,.\, F^2_{hi}) - \ln(F^2_h)]^2 .$$

By saying $\partial R/\partial \ln(F^2_h) = 0$ we see that the least-squares estimate of $\ln(F^2_h)$ is $\sum_i W_{hi} \ln(\hat{k}_i F^2_{hi})/\sum_i W_{hi}$ where W^{-1}_{hi} $=$ var $[\ln(F^2_{hi})] = m^2_{hi} = \text{var}\,(F^2_{hi})/F^4_{hi}$ $\hat{k}_i$ is an estimate of the overall scale constant for the ith zone. Thus var $[\ln(F^2_h)] = m^2_h = {}^1/\sum_i m^{-2}_{hi}$ where m^{-2}_{hi} is zero, if F^2_{hi} is unobserved in the ith zone.

Likewise we can show that var $(\ln \hat{k}_i)$ is ${}^1/\sum_h m^{-2}_{hi}$ and thus the best value of the overall scale constant is given by

$$\ln k = \sum_i \{ \sum_h m^{-2}_{hi} \ln \hat{k}_i \} .$$

From this result we can infer that we should fix the overall scale of the data in the original least-squares equations by saying $\sum_i\{\sum_h m^{-2}_{hi} \ln k_i\}$ is a constant without error, say zero. This enables us to evaluate how the scale constant errors are spread over the various zones of data, since

$$\begin{aligned}\sum_{h,i} m^{-2}_{hi} \ln k_j &= \sum_{h,i} m^{-2}_{hi}\{(\ln k_j - \ln k_1) - (\ln k_i - \ln k_1) \\ &\quad + \ln k_i\} \\ &= \sum_{h,i} m^{-2}_{hi}\{(\ln k_j - \ln k_1) - (\ln k_i - \ln k_1)\} \\ &\quad + \text{constant}\end{aligned}$$

if $\sum_{h,i} m^{-2}_{hi} \ln k_i$ is set equal to a constant without error.

Thus,

$$\begin{aligned}(\sum_{h,i} m^{-2}_{hi})^2 \,\text{var}\,(\ln k_j) &= (\sum_{h,i} m^{-2}_{hi})\,\text{var}\,(\ln k_j - \ln k_1) \\ &+ \sum_i (\sum_h m^{-2}_{hi})^2 \,\text{var}\,(\ln k_i - \ln k_1) \\ &- 2\sum_{i \neq j} \sum_h m^{-2}_{hi} \sum_{h,k} m^{-2}_{hi}\,\text{cov}\,(\ln k_i - \ln k_1, \ln k_j - \ln k_1)\end{aligned}$$

and

$$\begin{aligned}&\sum_{h,i} m^{-2}_{hi}\,\text{cov}\,(\ln k_j, d_q) \\ &= \sum_{h,i} m^{-2}_{hi}\{\text{cov}\,(\ln k_j - \ln k_1, d_q) - \text{cov}\,(\ln k_i - \ln k_1, d_q)\} .\end{aligned}$$

We should note that $\sum_h m^{-2}_{hi}$ includes data not used in correlations.

It is often assumed that $m^2_{hi} = \text{var}\,[\ln(F^2_{0hi})]$ and is simply the error arising from counting statistics. This can result in an over-emphasis of the reliability of intense reflexions by ignoring errors in crystal size and other errors such as secondary extinction which have not been considered here. Rather, since

$$\begin{aligned}\ln(F^2_{hi}) &= \ln k_i + \ln(F^2_{0hi}) - \sum_q a_{hiq} d_q \\ &+ \text{other ignored terms} \\ m^2_{hi} &= \text{var}\,[\ln(F^2_{0hi})] + \text{var}\,(\ln k_i) + \sum_q a^2_{hiq}\,\text{var}\,(d_q) \\ &+ 2\sum_{q>q'} a_{hiq} a_{hiq'}\,\text{cov}\,(d_q, d_{q'}) \\ &- 2\sum_q a_{hiq}\,\text{cov}\,(\ln k_i, d_q) + \text{other terms.}\end{aligned}$$

Likewise $W_{hij}=1/\mathrm{var}\,(\Delta_{hij})$, and though W_{hij} may be approximated to by $W_{hij}=1/(m_{hi}^2+m_{hj}^2)$, it also involves covariance terms. The variance–covariance matrix is unknown in the initial cycle and so the incorporation of these ideas necessarily involves iterative procedures.

Results and discussion

To test the procedure described, 20 reflexions were arbitrarily chosen for an orthorhombic crystal with $a=26{\cdot}75$, $b=12{\cdot}41$, $c=7{\cdot}24$ Å; linear absorption coefficient $\mu=256\ \mathrm{cm}^{-1}$, $\lambda=1{\cdot}54182$ Å. A reference crystal was chosen, its dimensions being defined by the planes (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), (00$\bar{1}$), the spacing between parallel pairs of planes being 0·10, 0·18 and 0·38 mm respectively.

A four-circle geometry was selected, with the crystal mounted about the b axis (data set A) and the c axis (data set B). The intensities of data set B were all made to be 4 above the background. The intensities of data set A were chosen to give perfect agreement between the two data sets after correction had been made for both collection geometry and absorption. The absorption was calculated for both data sets using the reference crystal.

Two incorrect crystals were chosen to test the ability of the program to bring these incorrect crystals back to the correct size (that is, the size of the reference crystal). The crystal for data set A was of dimensions $0{\cdot}09\times0{\cdot}18\times0{\cdot}38$ mm and the crystal for data set B was of dimensions $0{\cdot}10\times0{\cdot}14\times0{\cdot}38$ mm. Unit weights were used.

To test the success of correlations it is more useful to consider the quantity

$$R'=\exp\left[\left\{\frac{\sum\limits_{h,i,j} W_{hij}\Delta_{hij}^2}{\sum\limits_{h,i,j} W_{hij}}\right\}^{1/2}\right]-1$$

rather than $R=\sum\limits_{h,i,j} W_{hij}\Delta_{hij}^2$. R' approximates to a root-mean-square fractional difference between correlated reflexions.

We note that for data set A only the distance to the (100) plane is altered, whereas for data set B only the distance to the (010) plane is altered from the correct dimension. In this way we can investigate the effect of the refinement on correct crystal dimensions when this dimension either is or is not correct in the other crystal. Also both crystals are of smaller volume than the reference crystal so that we can investigate whether the program brings each of the crystals back to an average crystal (of dimensions $0{\cdot}095\times0{\cdot}16\times0{\cdot}38$ mm) or back to the correct volume.

In correlation 1 only scale constants were varied for a best least-squares fit. A value of $R'=9{\cdot}27\times10^{-2}$ (9·3 %) was obtained.

In correlation 2 the maximum number of parameters were varied, one scale constant and three planes per crystal. Correcting the data using the values of a_{hiq} previously obtained, a value of $R'=7{\cdot}99\times10^{-3}$ was obtained.

We can test the linearity of our expansion of $\ln\,(A_{0hi}/A_{hi})$ by using the values of d_q and $\ln k_i$, which are known to be correct, to correlate the data. A value of $R'=4{\cdot}06\times10^{-2}$ was obtained. By not using the values of a_{hiq} but by recalculating the values of F_{hi}^2 using the scale constants and crystal dimensions indicated in correlation 2, a value of $R'=2{\cdot}13\times10^{-2}$ was obtained.

Correlation 3 was an iteration, recalculating the absorption factors and the coefficients a_{hiq} before again varying the maximum number of parameters. Using the new values of a_{hiq} to make the corrections indicated, a value of $R'=7{\cdot}53\times10^{-4}$ was obtained.

Agreement with the standard crystal was much improved. Details of the calculation are given in Tables 1 and 2.

We note that there is a definite tendency for the crystals to distort in a compensatory manner such that the correct ratio of dimensions between the two crystals is more closely approximated than the correct absolute values. Correlation 3 successfully corrected this fault though after correlation 2 the value of R' was already quite low. With data experimentally obtained the main advantages of iteration would be to obtain better values of a_{hiq} to be used in a final least-squares structure refinement using all independently observed F_{obs} values. This is feasible since

$$\left(\frac{\partial F_{hi}}{\partial d_q}\right)_0=\tfrac{1}{2}F_{0hi}\left(\frac{\partial \ln F_{hi}^2}{\partial d_q}\right)_0=-\tfrac{1}{2}F_{0hi}a_{hiq}$$

or

$$\frac{\partial F_{hi}}{\partial R_{0q}}=-\tfrac{1}{2}F_{0hi}a_{hiq}/R_{0q}$$

and has the advantage that other errors may also be included, and any covariance correctly accounted for.

The calculation of the values of a_{hiq} does not increase the time involved for the absorption correction by more than 20 to 30 % though the storage requirements are greatly increased since each grid point has associated with it the number of planes minus 2 parameters.

The most time consuming step in the absorption program is in establishing the faces of incidence and emergence for each grid point, not in evaluating the distance to the correct plane. Obviously the more faces on the crystal the smaller the proportion of time used in evaluating the a_{hiq} values. This is obviously faster than shifting the defining planes one at a time to evaluate the a_{hiq} values.

The ability to define the distance to the qth plane will depend approximately on the proportion of the total surface area associated with the qth plane. Difficulties in the method can be envisaged when this proportion of the total area is too small. In the cases of tabular and needle crystals this can easily be rem-

edied by excluding those data obtained with geometries involving long path lengths in the crystal, which can be done without any loss of availability of data, by either using four-circle geometry or by remounting the crystal about another axis. One would then not attempt to refine those planes defining the long directions within the crystal and if the remaining directions are so small as to make the standard deviations of the calculation of R_q approach R_q, then there is probably no need to modify the crystal size, nor maybe to apply an absorption correction at all. The procedure previously described was repeated for a thin crystal, see Table 3, using the same reflexions, unit-cell dimensions, and geometries as before. Only $hk0$ reflexion data about the c axis gave long distances in the crystal and, owing to the lack of such data, the expected inaccuracies were evident. However, the refinement of the data in the short (001) direction was well behaved when $hk0$ reflexions were omitted and the (001) spacings and one scale constant were varied.

There are two good arguments for applying a data correlation procedure early in refinement rather than simply incorporating the parameters a_{hiq} in a final structure refinement. Firstly, if we have a non-centric space group and anomalous scatterers cause $|F(hkl)|^2$ to no longer equal $|F(\bar{h}\bar{k}\bar{l})|^2$ and we have to use more than one crystal, then this program should enable us to correctly assign the hkl indices, even when large absorption corrections have to be made. Secondly, as discussed earlier, a more realistic weighting system can be

Table 1. *Comparison of F^2 values*

h	k	l	Reference crystal	Data set A	Data set B	Correlation 1	Correlation 2	Correlation 3
22	1	7	10·68	9·86	10·55	10·19	10·53	10·65
4	0	5	133·20	110·22	111·81	111·02	131·92	132·53
24	0	5	32·01	29·11	31·49	30·26	31·61	31·91
6	1	7	120·86	109·03	108·52	108·72	118·46	120·30
22	2	5	40·35	36·72	39·16	37·90	39·52	40·22
10	6	4	85·75	79·31	73·24	76·18	81·91	85·29
3	4	1	29·57	25·81	27·10	26·43	28·54	29·39
6	0	0	38·72	32·10	26·95	29·40	37·73	38·53
29	2	0	34·40	31·20	33·37	32·25	33·92	34·31
7	1	0	38·70	32·86	28·28	30·47	37·48	38·52
2	4	4	61·78	53·28	58·05	55·59	59·76	61·47
10	5	5	91·07	83·67	78·74	81·13	87·75	90·66
28	0	0	40·18	36·29	39·36	37·78	40·00	40·07
13	2	2	67·85	62·57	55·87	59·10	65·26	67·51
11	3	2	57·98	53·60	46·75	50·04	55·26	57·63
15	0	0	44·58	39·90	40·67	40·27	44·22	44·44
5	5	6	98·85	91·13	89·46	90·25	95·31	98·31
2	3	4	56·44	48·07	52·49	50·21	54·66	56·11
0	7	2	49·39	43·51	43·85	43·66	47·72	49·11
1	1	1	11·03	8·73	9·99	9·34	10·69	10·97

Table 2. *Comparison of crystal dimensions*

Spacing between parallel planes (mm), volume (mm³).

	Initial dimensions	Correlation 2	Correlation 3	Ideal dimensions
(*a*) Crystal for data set *A*				
(100)	0·090000	0·098547	0·099732	0·100000
(010)	0·180000	0·165360	0·178720	0·180000
(001)	0·380000	0·378293	0·378928	0·380000
Volume	0·006156	0·006165	0·006751	0·006840
(*b*) Crystal for data set *B*				
(100)	0·100000	0·098845	0·099870	0·100000
(010)	0·140000	0·169718	0·178185	0·180000
(001)	0·380000	0·371703	0·378298	0·380000
Volume	0·005220	0·006233	0·006766	0·006840
(*c*) Ratio of dimensions (crystal for data set *A*/crystal for data set *B*)				
(100)	0·900	0·997	0·999	1·000
(010)	1·286	0·975	0·997	1·000
(001)	1·000	1·017	1·002	1·000
Volume	1·180	0·989	0·998	1·000
(*d*) Ratio of dimensions (mean of crystal for data sets *A* and *B*/ideal crystal)				
(100)	0·950	0·987	0·998	1·000
(010)	0·889	0·930	0·994	1·000
(001)	1·000	0·987	0·996	1·000
Volume	0·831	0·906	0·988	1·000

Table 3. *Refinement of a thin crystal*

Dimensions in mm. Dimensions (1) are from a single-cycle least-squares refinement varying all allowed parameters. Dimensions (2) are from a single-cycle least-squares refinement omitting ($hk0$) reflexions from data set B'.

	Initial dimensions	Dimensions (1)	Dimensions (2)	Ideal Dimensions
Data set A' (b rotation axis)				
(100)	0·096000	0·089645	0·096000	0·100000
(010)	0·140000	0·192937	0·140000	0·140000
(001)	0·004000	0·001590	0·001588	0·002000
Data set B' (c rotation axis)				
(100)	0·100000	0·098257	0·100000	0·100000
(010)	0·144000	0·140046	0·144000	0·140000
(001)	0·004000	0·001600	0·001590	0·002000

obtained by evaluating the random error implicit in the absorption correction.

Extension of the methods here, differentiating the absorption correction for the additional parameters involved for the case of a crystal in the presence of its mother liquor in a capillary (Wells, 1960) appears quite feasible.

It should be noted that using a four-circle geometry, geometrically different measurements of F_h^2 may be made for a single zone. We could label these observations:

$$F^2_{hii'} = k_i \frac{A_{0hii'}}{A_{hii'}} F^2_{0hii'}$$

where the i' refers to the i'th observation of F_h^2 in the ith zone.

$$R = \sum_{h,i,j,i',j'} W_{hijj'} \{\ln F^2_{hii'} - \ln F^2_{hjj'}\}^2$$

and our simultaneous equations are

$$\frac{\partial R}{\partial u_k} = 0 \text{ as before.}$$

The arguments used are still true if we only have one data zone and

$$R = \sum_{h,i',j'} W_{hi'j'} \{\ln (F^2_{hi'}) - \ln (F^2_{hi'})\}^2$$

where i' and j' refer to geometrically different measurements in one zone. The one scale constant k_1 is set to unity.

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X-ray Compton–Raman Scattering

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X-ray Compton–Raman scattering is reviewed from an original point of view. The differential cross section for X-ray inelastic scattering from crystals is derived from first principles to explain the coexisting Compton and Raman scattering in solids. This derivation makes it possible to express the cross section in terms of the current correlation of electrons in a crystal. All the electrons, including the core electrons, are treated on an equal basis in this formulation. The relationship between the X-ray absorption spectrum and the inelastic scattering spectrum is discussed in detail. This formulation provides a theoretical justification to the importance of X-ray inelastic scattering experiments in connection with an experimental determination of the two-particle Green's function. In the Appendices the theoretical formulations are given in detail, which apply not only to the ordinary inelastic scattering process, but also to the processes involving Bragg diffraction.

1. Introduction

Recently, interest in X-ray inelastic scattering from crystals has been renewed for several reasons. From a theoretical point of view, this scattering process may be used to check the validity of the one electron model in solids, and to study the many body effects, if any, among the electrons. From an experimental point of