

An Experimental Absorption–Extinction Correction Technique

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An extension of the experimental method of absorption correction of Flack [*Acta Cryst.* (1974), A30, 569–573; *J. Appl. Cryst.* (1975), 8, 520–521] is presented. The technique may now be applied to crystals of any symmetry and may also correct for extinction. The correction is based on intensity data of all forms of a few reflexions measured at varying values of the azimuthal angle. The correction is written as a polynomial-Fourier series, polynomial in intensity and trigonometric in the four diffractometer setting angles. The coefficients of this series are determined by least squares with the condition that all corrected intensity measurements of a form of reflexions should be ‘as nearly equal as possible’. The least squares is implemented with the (modified) Gram–Schmidt transformations in a Fortran program called *CAMEL JOCKEY WITH THREE HUMPS*. The extended method has been tested on six crystals, some without and some with extinction. In one case it is shown that the method may also be used as a misalignment correction.

1. Introduction

The object of this paper is to describe an absorption–extinction correction method based on intensity measurements from the crystal under study. Notions such as the shape or mosaic distribution of the crystal do not enter into the theory and thus knowledge of parameters describing these phenomena are not required. This makes the method particularly suitable for crystals of irregular shape or crystals contained within a support (e.g. glass capillary with mother liquor, opposed anvils of a high-pressure cell, housing of a liquid-helium cryostat or one crystal inside another).

The use of azimuthal scans as the basis of an experimental absorption correction has been described (Flack, 1974, 1975). In this method, the absorption correction is expanded as a Fourier series of the diffractometer angles and the coefficients of this series are determined by least-squares from the experimental intensities. We have found this method useful in the study of alloy crystals (Flack, Moreau & Parthé, 1974; Leroy, Moreau, Paccard & Parthé, 1977; Moreau & Paccard, 1976; Moreau, Paccard & Parthé, 1976; McNear, Vincent & Parthé, 1976) which suffer from high absorption and are of irregular shape. However, the formalism that has been used in the previous versions of this method limits its application to crystals of high symmetry. We have thus attempted to reformulate the method in order to extend its applicability to crystals of any symmetry and to incorporate a correction for anisotropic extinction at the same time.

The data necessary for the current method of absorption–extinction correction are intensity measurements of a set of reflexions which in the absence of absorption–extinction would have exactly the same intensity. Such measurements may be obtained from a form of reflexions and from azimuthal scans of all reflexions

of a form. Fuller details concerning the choice of suitable reflexions have been given by Flack (1976).

2. Theory of absorption–extinction correction

(a) The basic model

Let H_{nm} be the observed intensity of the reflexion $h_n k_n l_n$ measured at the angular position $\omega_n, 2\theta_n, \chi_n, \varphi_n$ of a four-circle diffractometer, where n is an integer ($n=1, 2, \dots, N$) indexing the different intensity measurements and m is an integer ($m=1, 2, \dots, M$) grouping symmetry-equivalent reflexions together (i.e. all reflexions in a form have the same value of m). Let G_{nm} be the corrected intensity of the observation n , obtained by multiplying by a correction factor A_n . Thus we have

$$G_{nm} = A_n H_{nm}. \quad (1)$$

The form of A for an absorption correction is suggested by the observation that A is a function of the four diffractometer setting angles ω , 2θ , χ and φ , and that the correction should be cyclic in these angles. Hence a four-dimensional Fourier series should be suitable. If we further wish the correction to take care of extinction, the terms of the Fourier series need to be multiplied by polynomials in the observed intensity. Thus we may write

$$A = \sum_{h=0}^{\infty} \sum_{i=-\infty}^{+\infty} \sum_{j=-\infty}^{+\infty} \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \{ a'_{hijkl} H^h \times \cos(i\omega + j2\theta + k\chi + l\varphi) + b'_{hijkl} H^h \sin(i\omega + j2\theta + k\chi + l\varphi) \}. \quad (2)$$

The coefficients a' and b' in this expression are to be found from the experimental intensity measurements as described below. (2) may be written more succinctly by collecting the five summations together into a single summation such as

$$A_n = \sum_{p=0} C_p f_{pn}, \quad (3)$$

where C_p represents one of the coefficients a_{hijkl} or b_{hijkl} and f_p represents one of the functions

$H^h \cos(i\omega + j2\theta + k\chi + l\varphi)$ or $H^h \sin(i\omega + j2\theta + k\chi + l\varphi)$.

(b) *An exact constraint on the model*

An inherent weakness of absorption–extinction corrections made from intensity measurements of equivalent reflexions may be illustrated by considering observations made on a highly absorbing spherical crystal also suffering anisotropic extinction. There is no variation of intensity amongst symmetry-equivalent reflexions even if the azimuthal angle is changed. Thus the method ‘sees’ no absorption or extinction under these conditions and the necessary correction for all reflexions would have to be an arbitrary constant. Even in the general case of an irregular crystal suffering anisotropic extinction, the fact that symmetry-equivalent reflexions are measured at the same value of 2θ means that the Camel method is incapable of ‘seeing’ contributions to the absorption–extinction which are a function of 2θ only. We thus do not have an absolute correction and must devise some means to fix an (arbitrary) scale for A .

The arbitrary scale may be fixed by constraining the least-squares determination of the coefficients C_p so that the mean absorption–extinction correction over the observations should be unity. Formally we wish to impose

$$\frac{1}{N} \sum_{n=1}^N A_n = 1. \quad (4)$$

Substituting (3) into (4) gives

$$\frac{1}{N} \sum_{n=1}^N \sum_{p=0} C_p f_{pn} = 1.$$

Let us define the function f_0 to have a value of unity and thus obtain

$$C_0 = 1 - \frac{1}{N} \sum_{p=1} C_p \sum_{n=1}^N f_{pn}. \quad (5)$$

Eliminating C_0 from (3) and (5) we obtain

$$\begin{aligned} A_n &= 1 - \frac{1}{N} \sum_{p=1} C_p \sum_{n=1}^N f_{pn} + \sum_{p=1} C_p f_{pn} \\ &= 1 + \sum_{p=1} C_p \left\{ f_{pn} - \frac{1}{N} \sum_{n=1}^N f_{pn} \right\}. \end{aligned} \quad (6)$$

Writing

$$g_{pn} = f_{pn} - \frac{1}{N} \sum_{n=1}^N f_{pn}, \quad (7)$$

we obtain

$$A_n = 1 + \sum_{p=1} C_p g_{pn}, \quad (8)$$

which is a form similar to (3) but now with a constant term.

(c) *Least squares on the model*

We require a least-squares method capable of determining the coefficients C_p . Furthermore, although the limits on the summations in (2) extend to infinity for an exact representation of the absorption–extinction correction, we may expect that, with data of limited precision, only a relatively small number of the functions f_p will be significant in the description of A . A further objective of the method will thus be to find the functions necessary to describe A at a certain level of significance.

Substituting (8) into (1) gives

$$G_{nm} = H_{nm} + H_{nm} \sum_{p=1} C_p g_{pn}. \quad (9)$$

Consider the G_{nm} to be arranged into sets of values of constant m . We require values of C_p which make the values of G_{nm} within a set ‘as nearly equal as possible’ for all sets. As we cannot expect the values of G_{nm} within a given set m to be exactly equal, we may write

$$G_m + \varphi_{nm} = H_{nm} + H_{nm} \sum_{p=1} C_p g_{pn} \quad (10)$$

and determine G_m ($m=1, 2, \dots, M$) and C_p ($p=1, 2, \dots$) in such a way as to minimize

$$\sum_{n=1}^N \omega_n^2 \varphi_{nm}^2,$$

where ω_n is the square root of the weight applied to the n th equation (10) (Erskine, 1975). Rearranging (10), we obtain

$$\varphi_{nm} = \{ -G_m + H_{nm} \sum_{p=1} C_p g_{pn} \} + H_{nm}. \quad (11)$$

Now compare (11) to the conventional linear least-squares problem (without weights) of finding the best values of a vector \mathbf{C} for which $\mathbf{D} \simeq \mathbf{FC}$. This is achieved by minimizing Φ^2 where $\Phi = \mathbf{D} - \mathbf{FC}$. Writing (11) in the approximate form, we obtain

$$-H_{nm} \simeq -G_m + H_{nm} \sum_{p=1} C_p g_{pn}, \quad (n=1, 2, \dots, N) \quad (12)$$

where $-H_{nm}$ corresponds to \mathbf{D} , G_m ($m=1, 2, \dots, M$) and C_p ($p=1, 2, \dots$) correspond to \mathbf{C} and (-1) , $H_{nm} \cdot g_{pn}$ ($n=1, 2, \dots, N$) correspond to \mathbf{F} . (12) represents an overdetermined system of equations, for which the normal equations method of solution (unweighted) would be

$$\mathbf{C} = (\mathbf{F}'\mathbf{F})^{-1} \mathbf{F}'\mathbf{D}. \quad (13)$$

The weighted solution of (12) may be obtained by multiplying (12) by the square root of the weight and applying (13)

$$-\omega_n H_{nm} \simeq -\omega_n G_m + \sum_{p=1} C_p g_{pn} \omega_n H_{nm}. \quad (14)$$

By this method, it may be shown that

$$G_m = \frac{\sum \omega_n^2 G_{nm}}{\sum \omega_n^2}, \quad (15)$$

where the summations are over n for all observations with the same value of m , *i.e.* G_m is the weighted-mean-corrected intensity of the m th equivalent reflexion (Erskine, 1975). The sum of squares minimized may be written as

$$S_1 = \sum_{n=1}^N \omega_n^2 (G_{nm} - G_m)^2. \quad (16)$$

The normal-equations solution of (14) (for C_p only) was used in the previous Camel program (Flack, 1975). In brief, the method may be described as follows. Suppose that we already have P functions f_p ($p = 1, 2, \dots, P$) significant in describing A and that we wish to know whether a new function, f_{p+1} , will further reduce the sum of squares significantly. The normal equations of dimension $(P+1) \times (P+1)$ are formed and solved for the coefficients C_p ($p = 1, 2, \dots, P+1$). The reduction in the sum of squares after including the new function f_{p+1} will tell us whether it is significant or not. If it is not, the function is temporarily rejected and a new one is tried. If the function is significant, it is added to the list of already accepted functions and a further new function is tried. In this way a list of significant functions can be built up.

The great disadvantage of the normal-equations solution of (14) is that a matrix inversion must be carried out for each function tried. Furthermore, the dimension of the normal-equations matrix increases with the number of functions already accepted. However, there exists an alternative least-squares method of solution of $\mathbf{D} \approx \mathbf{FC}$ which enables the sum of squares to be calculated prior to matrix inversion. This is the (modified) Gram-Schmidt transformation and is described in the Appendix. Further details of the strategy of function choice are given in § (f) below.

(d) Approximate constraints

Let us define

$$H_m = \sum \omega_n^2 H_{nm} / \sum \omega_n^2$$

in a similar way to (15). Some preliminary tests on the method thus far described showed that sometimes the weighted-mean equivalent intensities before and after correction (H_m and G_m) differed by a physically unreasonable amount. We thus modified the model to incorporate the approximate equality of these quantities as additional constraints. These constraints were implemented by the method of weighting (Lawson & Hanson, 1974) which introduces M additional observational equations as follows. We wish

$$\frac{\sum \omega_n^2 H_{nm}}{\sum \omega_n^2} = \frac{\sum \omega_n^2 G_{nm}}{\sum \omega_n^2}. \quad (17)$$

Substituting (9) into (17) gives

$$\frac{\sum \omega_n^2 H_{nm}}{\sum \omega_n^2} = \frac{\sum \omega_n^2 H_{nm}}{\sum \omega_n^2} + \frac{\sum_{p=1}^N C_p \sum_{n=1}^N \omega_n^2 g_{pn} H_{nm}}{\sum \omega_n^2}. \quad (18)$$

(18) may be written

$$0 = (0)G_m + \sum_{p=1}^N C_p \left\{ \frac{\sum \omega_n^2 H_{nm} g_{pn}}{\sum \omega_n^2} \right\} \quad (m = 1, 2, \dots, M)$$

or

$$0 = (0)G_m + \sum_{p=1}^N C_p \left\{ \frac{\varepsilon \omega_m \sum \omega_n^2 H_{nm} g_{pn}}{\sum \omega_n^2} \right\} \quad (m = 1, 2, \dots, M). \quad (19)$$

There are M equations of this type which have been written in the same form as the observational equations (14). Here ω_m is the square root of the weight of the weighted-mean equivalent reflexion H_m . ε is a 'down-weighting' factor applied to all M equations (19) which controls the strength with which the approximate constraints are enforced. The (19) are introduced as additional observational equations in the least squares making $N + M$ observations in all. The sum of squares minimized is now

$$S_2 = \sum_{n=1}^N \omega_n^2 (G_{nm} - G_m)^2 + \sum_{m=1}^M \varepsilon^2 \omega_m^2 (H_m - G_m)^2. \quad (20)$$

(e) Weighting schemes

The choice of the weighting schemes ω_n and ω_m has been based on a consideration of the sum of squares S_2 minimized in the constrained model. We have chosen $\omega_n = 1/H_{nm}$ and $\omega_m = 1/H_m$ so that the sum of squares is a measure of the relative deviation of each measurement from its associated mean. In this way, the weak and strong intensities contribute approximately equally to the sum of squares. We have not experimented with other weighting schemes.

(f) Function choice

As the functions are tested sequentially for their significance in the representation of A , we need an operational strategy to know in which order to test them. We have used the method proposed by Wind (1972). In this method the maximum values H, I, J, K, L of h, i, j, k, l are fixed at the outset. The functions are then ordered according to their value of Q , where

$$Q = \frac{h}{H} + \frac{i}{I} + \frac{j}{J} + \frac{k}{K} + \frac{l}{L}, \quad (21)$$

retaining only those functions for which $Q \leq Q(\max)$. $Q(\max)$ is a parameter chosen at the outset and would normally have a value of between 1 and 2. The functions are tested in order of ascending Q thus ensuring that low-order functions are tested first.

Because of the multi-monovariate nature of the function-testing algorithm for what should in theory be a multivariate analysis it is necessary to run through the list of trial functions several times to retest those functions which have been temporarily rejected on a previous attempt. Following Wind (1972), we have chosen to cycle over the list of candidate functions three times.

A function is accepted if it produces a significant reduction in the sum of squares S_2 . Let R be the current residual sum of squares, D be the reduction in S_2 produced on introducing the new function, I_{FF} be the number of functions desired in the representation of A and I_{FN} be the number of functions already accepted. Following Wind (1972), we accept those functions for which

$$D \geq R/(I_{FF} - I_{FN}). \quad (22)$$

It should be pointed out, however, that the functions G_m ($m=1, 2, \dots, M$) are always accepted regardless of the value D . The Gram-Schmidt transformations also lend themselves readily to a multiple correlation test (Flack, 1975). The length squared (W_k^2) of the Gram-Schmidt vector k is an inverse measure of the correlation (or direct measure of the linear independence) of the k th function with all the other accepted functions. We have chosen to reject all those functions for which W_k^2 is smaller than a quantity

$$Z = k \cdot S_0, \quad (23)$$

where k is a constant chosen by the user and S_0 is the value of S_2 remaining when the G_m ($m=1, 2, \dots, M$) are the only functions included in the model.

(g) *Candidate functions*

The inherent symmetry of a four-circle diffractometer permits a simplification in the general polynomial-Fourier series (2). Let us assume a conventional four-circle diffractometer with setting angles ω , 2θ , χ and φ . We suppose $\omega=0$ when the machine is set in the bisecting position for measurement of a reflexion. We further assume that diffraction is symmetric with respect to reversal of the directions of the incident and reflected beams. Under these conditions, given directions for the incident and reflected beams with respect to the crystal may be attained by one of eight equivalent angular settings.

- (1) $\omega, 2\theta, \chi, \varphi$
- (2) $\omega, -2\theta, -\chi, \varphi + \pi$
- (3) $-\omega, -2\theta, \chi + \pi, \varphi$
- (4) $-\omega, 2\theta, -\chi + \pi, \varphi + \pi$
- (5) $\pi + \omega, -2\theta, \chi, \varphi$
- (6) $\pi + \omega, 2\theta, -\chi, \varphi + \pi$
- (7) $\pi - \omega, 2\theta, \chi + \pi, \varphi$
- (8) $\pi - \omega, -2\theta, -\chi + \pi, \varphi + \pi$. (24)

(Positions 2, 4, 5 and 7 represent a reversal of the incident and reflected beam directions with respect to positions 1, 3, 6 and 8. Current physical theories of extinction do not predict symmetry with respect to this reversal although experimental differences seem very small (Thornley & Nelmes, 1974).

We thus wish to construct a Fourier series which contains the symmetry represented by (24). Substitut-

ing (24) into (2) to find equal coefficients and then rearranging the result, one obtains

$$\begin{aligned} A(H, \omega, 2\theta, \chi, \varphi) = & \sum \sum^e \sum \sum^e \sum^e (afcccc + bfcccs) \\ & + \sum \sum^e \sum \sum^e \sum^e (afccsc + bfccss) \\ & + \sum \sum^e \sum \sum^e \sum^e (afscce + bfscce) \\ & + \sum \sum^e \sum \sum^e \sum^e (afscsc + bfscss) \\ & + \sum \sum^e \sum \sum^e \sum^e (afsssc + bfssss) \\ & + \sum \sum^e \sum \sum^e \sum^e (afsscc + bfsscs) \\ & + \sum \sum^e \sum \sum^e \sum^e (afcssc + bfcsss) \\ & + \sum \sum^e \sum \sum^e \sum^e (afcscc + bfcscc) \quad (25) \end{aligned}$$

where the notation is best illustrated by writing the term

$$+ \sum \sum^e \sum \sum^e \sum^e afscce + bfscce$$

in full as:

$$\begin{aligned} & \sum_{h=0}^H \sum_{i=0}^{2I} \sum_{j=0}^J \sum_{k=1}^{2K+1} \sum_{l=0}^{2L} \{ [a_{hijkl} H^h \\ & \times \sin(i\omega) \cos(j2\theta) \cos(k\chi) \cos(l\varphi) \\ & + b_{hijkl} H^h \sin(i\omega) \cos(j2\theta) \cos(k\chi) \sin(l\varphi)] \}. \end{aligned}$$

The change in notation from a' and b' to a and b for the coefficients of the Fourier series is intentional. The a and b represent sum and differences of the a' and b' . Likewise all minus signs have been collected into the coefficients a and b .

Further restrictions on the functions represented by (25) are possible. Thus the discussion in § 2(b) shows that the coefficients C_{h0j00} (except C_{00000}) should always be zero, implying no variation of the Camel correction as a pure function of 2θ or intensity. Consider further the absorption correction measured for the incident X-ray beam. With $2\theta=0$, $\omega=0$ and φ fixed but arbitrary, the absorption correction should not vary as a function of χ since this represents a rotation of the crystal about the axis of the incident beam. Thus functions in $\cos(i\omega) \cos(j2\theta)$ should only have values of k (the χ index) equal to zero. Likewise $2\theta=0$, $\omega=\pi/2$, $\chi=\pi/2$ puts the φ axis along the incident beam and thus the absorption correction should not vary with φ . Hence functions in $\sin(i\omega) \cos(j2\theta) \sin(k\chi)$ must have $l=0$ only.

(h) *Spherical absorption and isotropic extinction*

The discussion § 2(b) shows that the experimental method of absorption-extinction correction is really only capable of taking care of *anisotropic* absorption and/or extinction. We thus complete the experimental correction by multiplying it by the absorption correc-

tion for a sphere of radius equivalent to the crystal under study. Methods of calculating this radius are given by Flack (1974). For extinction we have to refine an isotropic extinction parameter along with the structural parameters.

3. Experimental tests

We have tested the method on data from crystals available in this laboratory. The relevant crystal data are given in Table 1 and the measurements used to calculate the absorption-extinction correction are indicated in Table 2. As criteria for the success of the method two parameters are used. These are the weighted sum of squares S_2 (equation 20) and the weighted R obtained on least-squares refinement of structural parameters. It will be seen that in all cases significant reductions in both these parameters were obtained. This fact is important as Cromer (1976) has found that use of the previous Camel program (Flack, 1975) with insufficient data could produce a reduction in S_2 and an increase in R . With our crystals it was unfortunately not possible to calculate an absorption correction by a Gaussian grid integration or by the analytical method and to compare the results with the experimental procedure. For $\text{Cs}_3\text{Bi}_2\text{I}_9$, $\text{Cs}_3\text{Sb}_2\text{I}_9$, Ru_2Sn_3 and SmAu_6 it will be seen from the maximum value of the order of the intensity function that only an absorption correction was attempted whereas for $\text{Cr}_3\text{B}_7\text{O}_{13}$ and ScSi the possibility of extinction was also considered. In our tests a spherical absorption correction was applied whether or not the experimental method was being used. The X-RAY 76 system of programs (Stewart, 1976) was used.

$\text{Cs}_3\text{Bi}_2\text{I}_9$ and $\text{Cs}_3\text{Sb}_2\text{I}_9$ are isomorphous but the crystals have very different shapes. The azimuthal scan data of $\text{Cs}_3\text{Sb}_2\text{I}_9$ are of better quality than those of $\text{Cs}_3\text{Bi}_2\text{I}_9$. The platelet crystal of $\text{Cs}_3\text{Bi}_2\text{I}_9$ needed *ca* three times the number of trigonometric functions as the ellipsoidal crystal of $\text{Cs}_3\text{Sb}_2\text{I}_9$.

There are several interesting features in the application of the absorption-extinction method to the crystal of orthorhombic ScSi . This crystal is pseudo-spherical prepared by Vincent (1976) for accurate electron density measurements. The intensities consist of a complete sphere of reflexion out to $\sin \theta/\lambda = 0.63 \text{ \AA}^{-1}$ but there are no ψ scan measurements. Whereas the value of S_2 decreases from 1.90 to 1.55, the weighted R of structure refinement increases slightly from 0.022 to 0.024 upon application of the absorption-extinction correction. The reason for this is to be found in the method of treating the data. Before the least-squares structure refinement, all measurements of a form of reflexions are averaged together, regardless of whether an absorption-extinction correction has been carried out. With a whole sphere of data, this procedure is tantamount to an absorption correction excluding the spherical part. We are thus comparing two methods of making an absorption correction for a crystal which is in any case almost a sphere.

With the ScSi data the maximum permitted value of the order of the polynomial function in intensity was set to 3, hence allowing an extinction correction. However, no function with non-zero order in intensity was ever accepted, indicating that the crystal did not suffer from anisotropic extinction. This result is in agreement with those of Vincent (1976) who found that anisotropic extinction parameters for this crystal refined in the

Table 1. *Salient values used in the experimental*

Compound	Crystal specifications				CAMEL JOCKEY specifications			
	Laue symmetry	Cell dimensions (\AA)	Linear absorption μ (cm^{-1})	Spherical absorption μR	Crystal shape and dimensions (μm)	Camel function orders (1) Max tried (2) Max accepted <i>H I J K L</i>	Number of functions accepted (1) trigonometric (2) total	Sum of squares (1) before (2) after Camel
$\text{Cs}_3\text{Bi}_2\text{I}_9$	6/ <i>mmm</i>	<i>a</i> = 8.404 <i>c</i> = 21.169	245.0	~0.8	platelet 32 × 64 × 80	0 3 3 6 6 0 2 1 2 2	8 14	12.77 4.59
$\text{Cs}_3\text{Sb}_2\text{I}_9$	6/ <i>mmm</i>	<i>a</i> = 8.350 <i>c</i> = 20.936	177.6	~1.5	ellipsoid 190 × 128 × 128	0 3 3 6 6 0 2 0 0 2	3 13	44.47 31.96
ScSi	<i>mmm</i>	<i>a</i> = 3.988 <i>b</i> = 9.882 <i>c</i> = 3.659	52.03	~0.1	pseudo-sphere 49 (diameter)	3 0 6 6 6 0 0 3 0 2	2 46	1.904 1.553
Ru_2Sn_3	4/ <i>mmm</i>	<i>a</i> = 6.17 <i>c</i> = 9.91	270.0	~0.8	'spherical' 60 (10) diameter	0 6 2 6 6 0 6 1 4 5	28 34	2.161 0.472
$\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$	<i>m3m</i>	<i>a</i> = 12.132	41.32	~0.5	cuboid 325 × 200 × 150	4 6 3 6 6 1 4 0 3 4	7 25	59.4 48.7
SmAu_6	4/ <i>mmm</i>	<i>a</i> = 10.395 <i>c</i> = 9.706	1836.0	~5.9	parallelepiped 100 × 50 × 50	0 6 4 6 6 0 4 3 3 4	31 40	105.4 43.0

* With misalignment option (see text).

usual way were not significantly different from zero. It will be noticed from Table 1 that it was possible to reduce the weighted R from 0.022 to 0.019 with a misalignment option. In this option the variations amongst the intensity measurements of a form of reflexions are considered to be due to miscentring of the crystal, misalignment of the diffractometer or inhomogeneity of the incident beam, as well as to absorption-extinction. The implementation of this option is achieved by relaxing the symmetry of the diffractometer to only two positions (1 and 5) in (24) rather than to all eight positions.

The crystal of $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ was obtained from Dr H. Schmid of the Battelle Memorial Institute, Geneva, and is from the same batch as that used by Thornley & Nelmes (1974) in their study of highly anisotropic extinction. The two crystals show the same characteristics of large intensity variation due to extinction. As a result of the limited number of intensities measured, the structure refinement was carried out with variation of only a scale factor, an isotropic extinction parameter and four positional variables. The absorption-extinction correction method accepted three functions having non-zero order in intensity and produced a satisfactory reduction in the weighted R .

The experimental absorption correction of SmAu_6 has done little to reduce the R of the 721 reflexion. This may be due to the exceedingly large variation of intensity observed from this reflexion, the largest net intensity being 2402 and the smallest 36, a variation of 6700%.

4. Computer program

The absorption-extinction method described here has

been implemented as a computer program *CAMEL JOCKEY WITH THREE HUMPS* written in Fortran. The program is written in the style of the X-RAY 76 system (Stewart, 1976) in Pidgin Fortran and a one-dimensional array with dynamic storage allocation. The current program can use intensity data supplied from an intermediate file prepared by the program *DATCOS* of X-RAY 76; however the program is being changed to work directly on the X-RAY binary data file.

5. Conclusion

The experimental tests show that the absorption-extinction method described is effective in correcting for absorption and extinction. Furthermore, it may be useful in correcting for misalignment of the diffractometer or crystal. The technique is especially useful when the shape of the crystal cannot be conveniently defined or when the incident and diffracted beams pass through non-uniformly absorbing material.

We propose to make some further tests on the current experimental method. In particular it is desirable to examine a triclinic crystal, to compare the results of absorption correction for a crystal with well-defined faces by an analytical method and by the experimental technique, and to investigate an encapsulated crystalline specimen. Denner, Schulz & d'Amour (1977) are trying the technique for an opposed-anvil high-pressure cell.

The crystal structure data of the substances used in the experimental tests will be published elsewhere. This work was supported by the Swiss National Science Foundation under Project No. 2173-074.

tests of the absorption-extinction technique

Structure least-squares refinement specifications				Data source	
$\sin \theta/\lambda$ max (\AA^{-1})	Number of observations	Number of variables	Reflexions chosen	Weighted R ($\times 10^3$) (1) without Camel (2) with Camel	
0.71	768	19	$F > 3\sigma_F$	71	Chabot (1977)
				47	
0.71	727	19	$F > 3\sigma_F$	98	Chabot (1977)
				56	
0.63	104	10	$F > 3\sigma_F$	22	Vincent (1976)
				24 (19)*	
0.98	840	25	$F > 4\sigma_F$	73	Yvon (1976)
				60	
0.60	83	6	$F > 0\sigma_F$	73	Flack (1977)
				47	
0.71	544	18	$F > 2\sigma_F$	220	Flack & Moreau (1977)
				129	

Table 2. *Resumé of intensity data used in the experimental tests of the absorption-extinction technique*

ψ_i is the initial value of the azimuthal angle, $\Delta\psi$ is the step and ψ_f is the final value of azimuthal angle. $\psi = 0$ is the bisecting position. The mean intensity is given as a ratio of the largest intensity measured in the data collection. R_{before} and R_{after} are calculated from

$$R = \left[\frac{\sum \omega_i (I_i - \bar{I})^2}{\sum \omega_i I_i^2} \right]^{1/2}.$$

The mean intensity, R_{before} and R_{after} are all multiplied by 10^3 .

h	k	l	Number forms measured	ψ scan ($^\circ$)			Mean intensity	R_{before}	R_{after}
				ψ_i	$\Delta\psi$	ψ_f			
Cs₃Bi₂I₉									
2	0	3	12	0	15	180	314	140	55
1	2	4	24	0	15	180	12	172	90
2	0	9	12	0	15	180	212	149	55
2	4	9	24	0	15	180	28	136	70
3	4	9	24	0	15	180	4	199	171
4	2	21	24	0	15	180	4	115	99
Cs₃Sb₂I₉									
2	0	3	12	0	15	180	451	254	198
2	1	4	24	0	15	180	6	259	212
2	4	7	24	0	15	180	12	211	158
1	2	8	24	0	15	180	1	136	184
0	4	9	12	0	15	180	87	185	146
0	2	9	12	0	15	180	230	117	124
2	4	9	24	0	15	180	40	182	146
4	3	9	24	0	15	180	2	205	171
1	1	16	12	0	15	180	8	57	106
2	4	21	24	0	15	180	5	69	125
ScSi									
1	1	1	8	0	0	0	661	43	24
1	1	3	8	0	0	0	101	46	23
3	1	1	8	0	0	0	132	15	10
3	1	3	8	0	0	0	46	46	42
2	2	1	8	0	0	0	43	38	28
2	2	2	8	0	0	0	4	136	129
2	2	3	8	0	0	0	8	123	114
1	3	1	8	0	0	0	461	43	16
1	3	2	8	0	0	0	130	43	20
1	3	3	8	0	0	0	97	39	26
1	3	4	8	0	0	0	25	40	26
4	2	1	8	0	0	0	7	67	65
3	3	1	8	0	0	0	123	17	11
3	3	2	8	0	0	0	45	26	27
3	3	3	8	0	0	0	45	38	30
2	4	1	8	0	0	0	141	17	10
2	4	2	8	0	0	0	138	35	14
2	4	3	8	0	0	0	44	52	35
2	4	4	8	0	0	0	36	50	35
1	5	1	8	0	0	0	70	40	23
1	5	2	8	0	0	0	7	59	81
1	5	3	8	0	0	0	16	49	58
4	4	1	8	0	0	0	37	16	19
4	4	2	8	0	0	0	45	26	14
3	5	1	8	0	0	0	21	23	23
3	5	2	8	0	0	0	3	174	175
3	5	3	8	0	0	0	9	66	51
2	6	1	8	0	0	0	76	40	23
2	6	3	8	0	0	0	27	46	42
1	7	1	8	0	0	0	20	41	26
1	7	3	8	0	0	0	6	144	130
4	6	1	8	0	0	0	24	24	20
3	7	1	8	0	0	0	8	101	89
3	7	2	8	0	0	0	81	43	30
2	8	1	8	0	0	0	85	33	19
2	8	2	8	0	0	0	5	110	83
2	8	3	8	0	0	0	37	25	28

Table 2 (cont.)

h	k	l	Number of forms measured	ψ scan ($^\circ$)			Mean intensity	R_{before}	R_{after}
				ψ_i	$\Delta\psi$	ψ_f			
ScSi (cont.)									
1	9	1	8	0	0	0	5	51	47
1	9	3	8	0	0	0	3	126	119
3	9	1	8	0	0	0	3	155	143
2	10	1	8	0	0	0	49	41	39
2	10	2	8	0	0	0	7	97	75
1	11	1	8	0	0	0	12	60	60
1	11	2	8	0	0	0	53	38	34
Ru₂Sn₃									
1	2	2	16	-75	25	75	515	76	27
4	1	1	16	-75	25	75	104	67	24
1	5	4	16	-75	25	75	125	67	25
3	6	6	16	-75	25	75	69	67	37
5	7	4	16	-75	25	75	23	76	39
4	7	10	16	-75	25	75	12	62	42
Cr₃B₇O₁₃Cl									
4	0	0	6	-180	10	180	639	205	139
6	0	0	6	-180	10	180	66	109	73
8	0	0	6	-180	10	180	251	205	170
12	0	0	6	-180	10	180	192	217	192
14	0	0	6	-180	10	180	51	91	72
2	2	0	12	0	22.5	175	111	75	64
4	4	0	12	0	22.5	175	488	152	153
8	8	0	12	0	22.5	175	156	111	99
12	8	0	24	0	22.5	175	72	129	109
4	4	2	24	0	22.5	175	17	82	87
6	6	2	24	0	22.5	175	114	209	208
10	6	2	48	0	22.5	175	56	87	75
0	0	16	6	-180	10	180	42	93	76
12	12	0	12	0	22.5	175	66	116	98
16	16	0	12	0	22.5	175	9	113	94
16	8	8	24	0	22.5	175	33	73	73
20	8	4	48	0	22.5	175	11	76	75
12	4	20	28	0	22.5	175	11	76	75
SmAu₆									
4	1	2	16	0	10	175	155	499	197
6	0	0	4	0	10	175	61	399	205
7	2	1	16	0	10	175	68	476	467
3	3	1	8	0	10	175	137	651	340
6	6	0	4	0	10	175	58	502	297
4	3	5	16	0	10	175	39	220	154
8	1	6	16	0	10	175	27	186	154
9	5	6	16	0	10	175	24	163	208
6	0	12	8	0	10	175	29	230	128

APPENDIX

The Gram-Schmidt transformation

As the Gram-Schmidt transformation is not well known in crystallography, we present here some of its important properties. The subject matter is not original and the reader is referred to Lawson & Hanson (1974) and to Wind (1972) for fuller details.

The object of the calculation is to find the 'best' approximate solution of the equation

$$D \approx FC$$

where \mathbf{F} is an $N \times P$ matrix, an element of which is given by F_{np} , n labelling the N observations and p labelling the P functions ($N \geq P$), \mathbf{C} is a p -vector of coefficients to be determined and d_n are the known observational values. (In the least-squares refinement of structural parameters in crystallography \mathbf{D} corresponds to the vector of ΔF values, \mathbf{F} to the matrix of *observational* equations and \mathbf{C} to the vector of parameter shifts). The approximate solution sought is that of least-squares whereby \mathbf{C} is chosen such that $(\mathbf{D} - \mathbf{FC})^2$ is a minimum. This may be achieved by the Gram-Schmidt orthogonalizing process in which a matrix \mathbf{W} with columns \mathbf{W}_j is defined as

$$\begin{aligned} \mathbf{W}_1 &= \mathbf{F}_1 \\ \mathbf{W}_j &= \mathbf{F}_j - \sum_{k=1}^{j-1} (\mathbf{F}_j \cdot \mathbf{W}_k) \mathbf{W}_k / \mathbf{W}_k^2. \end{aligned} \quad (A1)$$

It can be shown that $\mathbf{W}_i \cdot \mathbf{W}_j = 0$ if $i \neq j$. We now replace the model \mathbf{FC} by a new model

$$\mathbf{WA},$$

and in this new model we wish to minimize

$$S \equiv (\mathbf{D} - \mathbf{WA})^2.$$

Differentiating with respect to a_j , we obtain

$$\begin{aligned} \mathbf{D} \cdot \mathbf{W}_j - a_j \mathbf{W}_j^2 &= 0 \\ \text{or} \\ a_j &= (\mathbf{D} \cdot \mathbf{W}_j) / \mathbf{W}_j^2. \end{aligned} \quad (A2)$$

In order to derive \mathbf{C} from \mathbf{A} , we first note that (A1) may be written as

$$\mathbf{F} = \mathbf{WB}$$

where

$$\begin{aligned} b_{ij} &= (\mathbf{F}_j \cdot \mathbf{W}_i) / \mathbf{W}_i^2 & \text{if } i < j \\ b_{ij} &= 1 & \text{if } i = j \\ b_{ij} &= 0 & \text{if } i > j. \end{aligned}$$

Clearly \mathbf{B} is an upper triangular matrix, which may easily be inverted. Thus

$$\mathbf{FB}^{-1} = \mathbf{W}$$

and the model \mathbf{WA} may be written as $(\mathbf{FB}^{-1})\mathbf{A}$ or $\mathbf{F}(\mathbf{B}^{-1}\mathbf{A})$. Comparing this model to the original we see that

$$\mathbf{C} = (\mathbf{B}^{-1}\mathbf{A}).$$

It is interesting to calculate the reduction in the sum of squares of residuals S upon introducing the j th coefficient into the model. This may be done *before* inverting the matrix \mathbf{B} . Let S_j be the sum of squares of residuals when taking j functions (coefficients c) into consideration. Then

$$S_j = (\mathbf{D} - \sum_{i=1}^j a_i \mathbf{W}_i)^2 = \mathbf{D}^2 - 2\mathbf{D} \sum_{i=1}^j a_i \mathbf{W}_i + \sum_{i=1}^j a_i^2 \mathbf{W}_i^2.$$

But from (A2),

$$(\mathbf{D} \cdot \mathbf{W}_i) = a_i \mathbf{W}_i^2$$

so that

$$S_j = \mathbf{D}^2 - 2 \sum_{i=1}^j a_i^2 \mathbf{W}_i^2 + \sum_{i=1}^j a_i^2 \mathbf{W}_i^2 = \mathbf{D}^2 - \sum_{i=1}^j a_i^2 \mathbf{W}_i^2.$$

Hence for each new function \mathbf{F}_j included in the model we will produce a reduction in the sum of squares of residuals of $a_j^2 \mathbf{W}_j^2$. This provides a convenient way of deciding whether a function \mathbf{F}_j should be included in the final model before the matrix inversion step.

(A1) may be written in a form suitable for programming as

$$\begin{aligned} \mathbf{W}_{j+1}^{(1)} &= \mathbf{F}_{j+1} \\ \mathbf{W}_{j+1}^{(k+1)} &= \mathbf{W}_{j+1}^{(k)} - (\mathbf{F}_{j+1} \cdot \mathbf{W}_k) \mathbf{W}_k / \mathbf{W}_k^2 \quad (k=1, 2, \dots, j) \\ \mathbf{W}_{j+1} &= \mathbf{W}_{j+1}^{(j+1)} \end{aligned}$$

where the superscripts in parentheses indicate the 'update' number of the vector in question. This algorithm may be rewritten in an alternative form which is less subject to machine rounding errors (Björk, 1967), the so-called modified Gram-Schmidt transformation (Rice, 1966):

$$\begin{aligned} \mathbf{W}_{j+1}^{(1)} &= \mathbf{F}_{j+1} \\ \mathbf{W}_{j+1}^{(k+1)} &= \mathbf{W}_{j+1}^{(k)} - (\mathbf{W}_{j+1}^{(k)} \cdot \mathbf{W}_k) \mathbf{W}_k / \mathbf{W}_k^2 \quad (k=1, 2, \dots, j) \\ \mathbf{W}_{j+1} &= \mathbf{W}_{j+1}^{(j+1)}. \end{aligned}$$

This analysis should demonstrate the advantage of the (modified) Gram-Schmidt transformation over repeated inversions of a normal-equations matrix in multivariate analysis of the kind used in Camel. Matrix inversion in the Gram-Schmidt calculation takes place only once.

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Lattice Energy Calculations for $(C_6H_5)_5M \cdot \frac{1}{2}C_6H_{12}$, $M = P, As,$ and Sb : Towards an Understanding of Crystal Packing in the Pentaphenyl Group V Compounds

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Semi-empirical calculations of the energy due to intermolecular interactions have been made for crystals of $(C_6H_5)_5M \cdot \frac{1}{2}C_6H_{12}$, $M = P, As,$ and Sb . This energy has been calculated as a pairwise sum over non-bonded atoms; energy minimizations have been performed with respect to the unit-cell parameters and molecular positions and orientations. Two sets of potential functions including repulsive and van der Waals terms have been employed; one of the sets also contains r^{-1} (Coulombic) contributions to the energy. The experimentally determined structures of the arsenic and antimony compounds have been well reproduced, as has the disorder observed for the solvent molecule in the former; it is suggested that this disorder is also present in the latter crystal. A comparison of the energies calculated for these solvates with those computed previously for unsolvated species predicts the stability of $(C_6H_5)_5P \cdot \frac{1}{2}C_6H_{12}$, for which no crystallographic data have been previously reported. Crystals of this compound have now been identified. These comparisons also show the relative lattice energies of the three possible crystal structures seen in this system (Cc , $P\bar{1}$, and the $P\bar{1}$ cyclohexane solvate considered here) to be the same for all three molecules, suggesting that the molecular packing is not greatly affected by a change in the central group V atom.

Introduction

The study of molecular packing in crystals is important if the influence of intermolecular nonbonded interactions on molecular geometry or conformation is to be understood. We have attacked this problem by considering the pentaphenyl compounds of phosphorus, arsenic, and antimony. Three different structures have been reported for these molecules (see Table 1). In one of these, that of the unsolvated pentaphenylantimony crystal, the molecule adopts anomalous square-pyramidal geometry; in the others, the expected trigonal-bipyramidal conformation is observed. In previous work (Brock & Ibers, 1976; Brock, 1977) we modeled the unsolvated $P\bar{1}$ and Cc structures with a semi-empirical force field describing intermolecular nonbonded interactions; those cell constants and molecular positions and orientations which had been found experimentally were well reproduced after energy minimization. Correlations were drawn between the relative magnitudes of the calculated energies

and the observed crystal form for the three compounds, and the observation of square-pyramidal geometry for unsolvated pentaphenylantimony was explained as a packing effect.

Table 1. *Crystal structures reported for $(C_6H_5)_5M$ compounds, $M = P, As,$ and Sb*

Cc :	$(C_6H_5)_5P^a$	$(C_6H_5)_5As^b$	$(C_6H_5)_5Sb^c$
$P\bar{1}$:			
$P\bar{1}$ (solvate):	$(C_6H_5)_5As \cdot \frac{1}{2}C_6H_{12}^d$	$(C_6H_5)_5Sb \cdot \frac{1}{2}C_6H_{12}^e$	

References: (a) Wheatley (1964). (b) Wheatley & Wittig (1962) (unit-cell data only). (c) Beauchamp, Bennett & Cotton (1968). (d) Brock & Webster (1976). (e) Brabant, Blanck & Beauchamp (1974).

In this work we have attempted to describe the cyclohexane solvated structure of these compounds in a similar fashion. In the pentaphenylarsenic solvate the cyclohexane molecule is disordered; in a successful model the two orientations of this species must have