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Extinction within the Limit of Validity of the Darwin Transfer Equations. II. Refinement of Extinction in Spherical Crystals of SrF_2 and LiF

BY PIERRE J. BECKER* AND PHILIP COPPENS

Chemistry Department, State University of New York at Buffalo, Acheson Hall, Buffalo, New York 14214, *U.S.A.*

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The extinction-correction formalisms derived in a previous article have been applied to two sets of diffraction data on spherical crystals. Application to the neutron data on SrF_2, collected by Cooper & Rouse at three different wavelengths, shows that the theory gives a slightly better fit than a special empirical formula used previously to allow for extinction in this data set. A simultaneous refinement on all the data varying both particle size and mosaic spread and allowing for primary extinction leads to physically reasonable results. It is found that Lorentzian or Fresnellian mosaic-spread distributions fit the data considerably better than a Gaussian model. A similar refinement on the two-wavelength data on LiF confirms Lawrence's original conclusions that the extinction is mainly of the primary type. However, the results are in sharp disagreement with a treatment of the same data by Killean and coworkers, in which only secondary extinction was considered. The physical upper limit for the particle size in the sample is found to be $1{\cdot}9\times10^{-4}$ cm.

Introduction

The theoretical aspects of the extinction correction in X-ray structure analysis have been discussed extensively in a previous article (Becker & Coppens, 1974*a*), here referred to as I. It was concluded that the theory for X-ray diffraction given by Zachariasen (1967) contains unjustifiable assumptions. A revised set of formalisms was developed, which gives a reasonable approximation to the extinction correction y, in the case of a spherical crystal. It will be shown in a forthcoming article (Becker & Coppens, 1974*b*), that the expressions for y are similar when more general shapes of crystals are considered or when extinction is anisotropic. The present article describes the use of the new formalism for extinction least-squares refinement. The necessary formulae are given in the Appendix. The theory is applied to the neutron data on SrF_2 (Cooper & Rouse, 1970, 1971) and to the X-ray data on LiF (Killean, Lawrence & Sharma, 1972). The notations are those of I [see the glossary of symbols (Appendix *E*) of I].

Summary of the theory

When applied to a perfect crystal, the equations (1–10) lead to the following expression for the primary extinction correction:

$$y_p=v^{-1}Q^{-1}\int_{-\infty}^{+\infty}\sigma(\varepsilon_1)\mathrm{d}\varepsilon_1\int \mathrm{d}v\mathscr{I}_0(2i\sigma(\varepsilon_1)/t_1t_n')\times\exp\left[-\sigma(\varepsilon_1)\,(t_1+t_2')\right]. \quad (1)$$

Comparison with calculations based on the dynamical theory shows that the solution given by (1) is a reasonable approximation in the case of a spherical crystal.

Use of a theory based on transfer of intensity, rather than interference between waves is better justified in the case of secondary extinction, where the lowering of intensity inside each crystallite is neglected. It is shown in I that absorption and extinction effects cannot be considered independently if $\mu\bar{T}>0{\cdot}50$. The general expression for the secondary extinction correction y_s is found to be:

$$y_s=v^{-1}Q^{-1}A^*(\mu)\int_{-\infty}^{+\infty}\bar{\sigma}(\varepsilon_1)\mathrm{d}\varepsilon_1\int_v \mathrm{d}v\times\exp\left[-(\bar{\sigma}+\mu)\,(T_1+T_2')\right]\mathscr{I}_0(2i\bar{\sigma}(\varepsilon_1)/T_1T_2'). \quad (2)$$

When the particle size is sufficiently large for primary extinction inside each perfect crystallite to be of importance, the overall extinction correction is taken in first approximation as:

$$y\sim y_py_s. \quad (3)$$

If the particle size and the mosaic distribution could be directly estimated, the absorption-extinction correction should be calculated numerically during data processing. Such measurements are generally impossible on crystals suitable for structure analysis, while $\sigma(\varepsilon_1)$ and $\bar{\sigma}(\varepsilon_1)$ depend on the kinematical structure factor which is only known after refinement.

In the case of spherical crystals, the numerical result of integration of (1) or (2) can be fitted by a function of the type:

$$y_i=\left\{1+c_ix_i+\frac{A_i(\theta)x_i^2}{1+B_i(\theta)x_i}\right\}^{-1/2} \quad (4)$$

* Permanent address: Centre de Mécanique Ondulatoire Appliquée, 23 rue du Maroc, 75019 Paris, France.

(with $i=p$ or s). The expressions for the primary and secondary extinction parameters x_p and x_s are given in the Appendix. The values for $A_i(\theta)$ and $B_i(\theta)$ have been discussed in I* [equations I–(38, 43, 43*a*, 44*a*); Tables 5, 6, 7, 8].

Zachariasen (1967) introduced two idealized crystal types (type I for extinction dominated by mosaic spread, type II for extinction dominated by particle size). It is shown in I that within the present theory (which introduces a factor sin 2θ in the particle-size dependence of x_i), this classification becomes less well defined when extinction is severe: even in a crystal which would have been previously classified as type I, particle-size effects may become dominant at small Bragg angles.

As a result, it may be necessary to consider simultaneously both the particle radius r and the mosaic distribution coefficient g in the least-squares refinement.

It should be noted that the first-order approximation introduced by Zachariasen (1967):

$$y_s=(1+2x_s)^{-1/2} \tag{5}$$

remains valid to within 2% when extinction is not severe ($y>0{\cdot}8$), provided that the factor sin 2θ is taken into account when extinction is particle-size dominated.

Extinction in a spherical crystal of strontium fluoride

The expressions (3) and (4) have been applied to the refinement of the neutron data collected by Cooper & Rouse (1970, 1971) on strontium fluoride. The structure is of fluorite type ($a_0=5{\cdot}794$ Å) and a sphere of radius 1·5 mm was used to measure the diffracted intensities for three wavelengths ($\lambda_1=0{\cdot}746$, $\lambda_2=0{\cdot}865$, $\lambda_3=1{\cdot}077$ Å). The absorption is small enough to be neglected in the analysis. The data have been corrected for isotropic thermal diffuse scattering (Cooper & Rouse, 1968). If I_0 is the true Bragg intensity and αI_0 the contribution from TDS, the measured intensity I is:

$$I=I_0\alpha+I_0y=I_0(\alpha+y) \tag{6}$$

where y is the extinction correction. The values for α are tabulated by Cooper & Rouse (1971).

A main point of interest in this analysis is the contribution from anharmonic thermal motion (Willis, 1970); if u_i stands for a displacement coordinate, the potential is:

$$V=V_0+\tfrac{1}{2}\alpha(u_1^2+u_2^2+u_3^2)+\beta u_1u_2u_3.$$

Since Sr occupies an octahedral site, only the fluorine ions are affected, with an effective temperature factor (when $h+k+l=2n+1$):

$$T_F(h,k,l)=\exp\left[-W_F(h,k,l)\right]\times\left\{1+i(k_BT)^2\left(\frac{2\pi}{a_0}\right)^3\frac{\beta_F}{\alpha_F^3}hkl\right\} \tag{7}$$

(W_F is the Debye–Waller factor).

Substituting the values given by Cooper & Rouse (1971), one obtains for the structure factor:

$$F=b_{Sr}\exp(-W_{Sr})+(-1)^n0{\cdot}32\times10^{-4}b_F\times\exp(-W_F)hkl \quad \text{for } h+k+l=2n+1. \tag{8}$$

In the present study, b_{Sr} and b_F, the coherent neutron scattering amplitudes, are taken from a compilation by Shull (1972):

$$b_{Sr}=0{\cdot}700\ (8)\times10^{-12}\text{ cm};\qquad b_F=0{\cdot}565\ (5)\times10^{-12}\text{ cm}.$$

The maximum effect of anharmonic contribution is 6% on the amplitude for the reflection 777 while all reflections with hkl larger than 50 are affected by more than 1%. This anharmonic contribution was allowed for in our calculations but the value for (β/α^3) was fixed in expression (8). (If this effect is neglected, only the strontium atoms contribute to the calculated structure factor when $h+k+l=2n+1$ and as a result, a highly biased value for the temperature parameter of Sr is obtained.) For the shortest wavelength λ_1, some intensities were affected by anomalous nuclear scattering and were therefore eliminated from the analysis (Cooper & Rouse, 1971).

The following extinction formalisms were tested,* varying the two temperature parameters, the scale factor and the extinction parameters $\varrho(=r/\lambda)$ and g† (only g or ϱ when the crystal was assumed to be respectively of type I or of type II):

1. Zachariasen formalism (1967) (Table 1). Only the results for type I are given as the agreement factor was

* $c_l=2$ except for a Gaussian mosaic spread for which $c_s=2{\cdot}12$.

* The number of observations is 28 for λ_1, 52 for λ_2, 36 for λ_3. All refinements described here are based on the minimization of $\sum w(F_o^2-k^2F_c^2)^2$.

† In the Tables, the particle radius $r(=\lambda\varrho)$ is given instead of ϱ.

Table 1. *Zachariasen formalism* (*type* I)

$$R=\frac{\sum F_o-k|F_c|}{\sum F_o}$$

$$R_w=\left\{\frac{\sum w(F_o-k|F_c|)^2}{\sum wF_o^2}\right\}^{1/2}$$

R_2 and R_{2w} corresponding agreement indices based on F^2.

	λ_1	λ_2	λ_3
U_{Sr}(Å^2)	0·00761 (43)	0·00684 (28)	0·00547 (50)
U_F	0·01060 (48)	0·01009 (34)	0·00939 (59)
$g\,.\,10^{-4}$	2·45 (34)	2·27 (27)	3·36 (72)
R	0·022	0·030	0·029
R_w	0·029	0·035	0·033
R_2	0·038	0·056	0·056
R_{2w}	0·058	0·070	0·068

very much higher in the type II refinement ($R \simeq 0{\cdot}06$ compared with $R \simeq 0{\cdot}03$ for type I).

2. The original study on SrF_2 did not include a simultaneous least-squares refinement on the scale, temperature and extinction parameters, needed here for comparison purposes. The formalism of Cooper & Rouse (1970, equation 29, see also I) was applied in this sense (Table 2).

3. The correction based on equations (3) and (4). The results for a Lorentzian mosaic distribution are given in Table 3. The results, using a Fresnellian distribution, were about equally satisfactory and are not reproduced here. The Gaussian distribution seems less appropriate as it gives a significantly higher value of the reliability index R.

Both the Cooper & Rouse formalism and expressions (3) and (4) give a significant improvement when compared with the Zachariasen correction, which considerably underestimates extinction for the most severely affected reflections (for the 022 reflection, $F_o^2 = 42$ after correction for extinction, $F_c^2 = 49{\cdot}2$). The type I refinements show a significant increase of g with λ. Extinction becomes more severe when λ is increased; and, as ϱ $(=r/\lambda)$ decreases, the influence of the particle size at low angles increases with λ. In the mixed-type crystal, one may, according to the formalisms, introduce the particle size r as a variable, though the very high correlation between ϱ and g in the refinement of single-wavelength data is not unexpected ($\sim 0{\cdot}99$ for λ_1, $0{\cdot}97$ for λ_2, $0{\cdot}92$ for λ_3). When refining simultaneously on r and g, the convergence could only be obtained for the data collected at 1·077 Å. From the results for λ_3, the introduction of the particle size in the refinement gives an improvement by a factor two in the agreement factors. Our formalism leads to a slightly better agreement than the Cooper & Rouse method. For both treatments, temperature parameters obtained at various wavelengths are in good agreement, which is not the case when the Zachariasen approximation is used. Primary extinction is not negligible (the smallest value of y_p is 0·9 for the 022 reflection, at $\lambda = 1{\cdot}077$ Å).

Correlation between r and g is reduced considerably when all data are refined simultaneously. The result

Table 2. *Results of the Cooper–Rouse formalism*

	Type I			Mixed type
	λ_1	λ_2	λ_3	λ_3
U_{Sr}(Å²)	0·00807 (25)	0·00752 (14)	0·00817 (40)	0·00742 (17)
U_F	0·01070 (26)	0·01078 (17)	0·01166 (45)	0·01078 (19)
r(microns)				9·5 (0·7)
$g \cdot 10^{-4}$	1·31 (07)	1·42 (06)	1·82 (18)	1·36 (14)
R	0·015	0·013	0·020	0·009
R_w	0·017	0·017	0·021	0·011
R_2	0·022	0·020	0·042	0·020
R_{2w}	0·035	0·035	0·043	0·021

Table 3. *Present theory*

	Type I			Mixed type
	λ_1	λ_2	λ_3	λ_3
U_{Sr}(Å²)	0·00803 (28)	0·00742 (16)	0·00763 (28)	0·00689 (13)
U_F	0·01075 (30)	0·01069 (19)	0·01122 (31)	0·01017 (15)
$r_{(microns)}$				9·6 (07)
$g \cdot 10^{-4}$	1·64 (11)	1·75 (09)	2·35 (18)	1·50 (16)
R	0·014	0·016	0·013	0·006
R_w	0·019	0·020	0·016	0·008
R_2	0·022	0·026	0·023	0·013
R_{2w}	0·038	0·040	0·031	0·017

Table 4. *Simultaneous refinements on all data sets*

	Cooper & Rouse correction	Lorentzian distribution	Fresnellian distribution	Gaussian distribution
U_{Sr}	0·00720 (11)	0·00698 (10)	0·00715 (10)	0·00690 (14)
U_F	0·01041 (13)	0·01016 (12)	0·01028 (11)	0·00998 (16)
$r_{(microns)}$	9·6 (8)	11·5 (7)	6·8 (7)	2·20 (15)
$g \cdot 10^{-4}$	1·33 (12)	1·31 (12)	1·17 (08)	0·87 (03)
R	0·012	0·011	0·011	0·015
R_w	0·016	0·016	0·016	0·022
R_2	0·023	0·020	0·019	0·029
R_{2w}	0·034	0·031	0·031	0·044

of such a calculation is given in Table 4, for the function of Cooper & Rouse with allowance for primary extinction, and the present method with Lorentzian, Gaussian and Fresnellian mosaic-spread distributions. The Gaussian mosaic-spread distribution can again be excluded. The Lorentzian and the Fresnellian distributions fit the data about equally, but, as may be expected from the properties of these distributions, g (Fresnel) is less than g (Lorentz). The correlation factor between ϱ and g decreased appreciably to 0·70. It is also worth mentioning that the Lorentzian distribution, the Fresnellian distribution and the Cooper & Rouse correction lead to the same values for the three scale factors.

The temperature parameters obtained by Cooper & Rouse (1971) were in good agreement with the values of Table 4:

$$U_{Sr}=0{\cdot}00715\ (15)\ \text{Å}^2 \qquad (9)$$
$$U_F=0{\cdot}01070\ (16)\ \text{Å}^2.$$

They were obtained from the reflections that are not much affected by extinction. From the comparison of (9) with the results of Tables 2, 3, 4, it is clear that the correlation between extinction and thermal motion is small in the case of SrF_2.

The general expression (3) for extinction gives a very consistent fit to the severely affected intensities ($y\sim0{\cdot}41$ for the high-order reflection 844 at $\lambda_3=1{\cdot}077$ Å) indicating that the formalism is physically realistic. The formalism of Cooper & Rouse gives a similar agreement for strong reflections, but it has been derived such as to give an optimal fit to the θ dependence of the extinction in the SrF_2 data sets. It is satisfying that the present theory which has been derived from first principles gives a somewhat better fit to extinction in the all-wavelength data refinement.

Extinction in a spherical crystal of lithium fluoride

Lawrence (1972) has recently studied extinction in a large single crystal of LiF (NaCl structure type, $a_0=4{\cdot}027$ Å) using Mo $K\alpha$ X-rays. As the measured intensities of symmetry-equivalent reflections are approximately the same, Lawrence concludes that the extinction is independent of the path length through the crystal and therefore mainly of primary type. From the published intensities of the symmetry-equivalent reflections {622} ($y=0{\cdot}85$), a mean intensity of 23·40 ($\pm0{\cdot}16$) is derived. The maximum deviation of the mean is >1, which seems significant. Unfortunately, the set {200} for which y is equal to 0·17 is not listed and no Friedel pairs were measured. It thus appears that a small contribution from particle anisotropy for low Bragg angles (where $\varrho\sin 2\theta/g$ is the smallest) cannot be ruled out. Using the Zachariasen formalism, Lawrence estimates the particle size to be $2{\cdot}8\times10^{-3}$ cm. A similar estimate is found with the formalism of our general theory, which gives values for r in the range ($2{\cdot}6\times10^{-3}$ cm–3×10^{-3} cm), except for the reflections 111 and 200.

From the same batch of material, Killean *et al.* (1972) ground a small sphere of radius 0·21 mm and collected sets of reflections with Mo $K\alpha$ radiation (52 reflections) and Cu $K\alpha$ (9 reflections, corrected for absorption since $\mu R=0{\cdot}68$). Four reflections from the Mo $K\alpha$ set are affected by extinction ($y\geq0{\cdot}95$), while all the 9 Cu $K\alpha$ reflections are affected ($y\geq0{\cdot}80$). Killean *et al.* assume the extinction to be of secondary type and get for the mean particle radius $1{\cdot}5\times10^{-6}$ cm. From comparison of this result with the value given by Lawrence, Killean *et al.*, conclude that 'the practice of including an extinction parameter in a least-squares analysis has little validity'. It seems obvious, however, that a secondary-extinction theory may not be valid for a sample in which extinction is almost exclusively of the primary type. Furthermore, the results are obtained by trial and error rather than by systematic least-squares refinement. To elucidate to what extent the present theory fits extinction in LiF, the two sets of data were refined, with allowance for the $\sin 2\theta$ dependence of the effective particle size. It was clear from the copper radiation set* that the extinction is dominated by the particle size ($R\sim0{\cdot}005$ for type II, $R=0{\cdot}011$ for type I). The particle size, assuming secondary extinction only, was $1{\cdot}8\times10^{-6}$ cm, a value similar to earlier results by Killean *et al.*

The primary extinction correction to be applied has the same mathematical form as a type II secondary extinction, except that rR ($=\frac{2}{3}r\bar{T}$) is replaced by r^2 in the expression for x. The results of a simultaneous refinement on both wavelength sets are given in Table 5. The particle radius r is found to be $1{\cdot}9\times10^{-4}$ cm, in much better agreement with conclusions based on the dislocation density (Killean *et al.*, 1972), especially if the grinding of the X-ray specimen is considered.

The real mean value of the particle radius cannot be larger since allowance for secondary extinction will reduce the primary extinction and therefore the effective radius. This value must be accepted as a physically realistic upper limit since it was shown in article I that the present theory agrees with dynamical calculations for a spherical crystal and small primary extinction.

Thus it follows that the conclusions drawn by Killean *et al.* (1972) are premature and that a modified extinction refinement allowing for the primary nature of extinction in the crystal of LiF is in reasonable agreement with information derived from the dislocation density in a different specimen of the same batch of material.

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* The absorption-weighted path length $\bar{T}_\mu$ was considered for each reflection of the copper set.

Table 5. *Refinement of* LiF *based on* Mo $K\alpha$ *and* Cu $K\alpha$ *sets of data*

	U_{Li} (Å^2)	U_F (Å^2)	r	R	R_w	R_2	R_{2w}
Present analysis	0·01159 (20)	0·00832 (7)	1·9 (2)μ	0·013	0·011	0·027	0·022
Killean *et al.* analysis	0·01220	0·00861	$1{\cdot}5\times10^{-6}$ cm				

APPENDIX

Expressions necessary to calculate the normal equations in a least-squares routine when extinction parameters are included

Let s be the scale factor, F_c the absolute value of the calculated structure factor, F_k the kinematical scaled structure factor and F the scaled extinction-affected structure factor:

$$F_k = sF_c$$
$$F^2 = s^2F_c^2y = F_k^2y. \qquad (A1)$$

A structural parameter will be represented by P. In the isotropic case, the two extinction parameters are g and ϱ $(=r/\lambda)$.

Let x_p and x_s be the appropriate values of x in case of primary and secondary extinction respectively:

$$X_p = K^2\gamma_pF_c^2\varrho^2 = K^2\xi_p$$
$$X_s = K^2\gamma_sF_c^2\psi = K^2\xi_s, \qquad (A2)$$

where ψ is either ψ_G or ψ_L, depending on the mosaic distribution,

$$\psi_G = \varrho\Big/\left\{1+\frac{\varrho^2\sin^2 2\theta}{g^2}\right\}^{1/2} \qquad (A3)$$

$$\psi_L = \varrho\Big/\left\{1+\varrho\frac{\sin 2\theta}{g}\right\}, \qquad (A4)$$

and with

$$\gamma_p = \tfrac{3}{2}\frac{\lambda^4}{V^2}a^2$$
$$\gamma_s = \frac{\lambda^3}{V^2}a^2\bar{T}_\mu, \qquad (A5)$$

in which $\bar{T}_\mu$ is the absorption-weighted path length given by

$$\bar{T}_\mu = v^{-1}A^*(\mu)\int_v (T_1+T_2')\exp[-\mu(T_1+T_2')]\mathrm{d}v.$$

In the neutron diffraction case,

$$y = y_p(\xi_p)y_s(\xi_s), \qquad (A6)$$

where

$$y_i(\xi_i) = \left\{1+c_i\xi_i+\frac{A_i\xi_i^2}{1+B_i\xi_i}\right\}^{-1/2} \quad \text{for } i=s,p. \qquad (A7)$$

c_p is equal to 2.

When primary extinction is neglected, ξ_p is put equal to zero. Let $z_i(\xi_i)$ be the function

$$z_i(\xi_i) = \frac{1}{y_i}\frac{\mathrm{d}y_i}{\mathrm{d}\xi_i} \qquad (A8a)$$

$$z_i(\xi_i) = -\tfrac{1}{2}y_i^2\left\{c_i+A_i\xi_i\frac{2-B_i\xi_i}{(1+B_i\xi_i)^2}\right\} \qquad (A8b)$$

(z_p is put equal to zero when primary extinction is neglected).

In the X-ray diffraction case, let v and v_0 be:

$$v = \cos^2 2\theta$$
$$v_0 = \cos^2 2\theta_M \qquad (A9)$$

where θ_M is the Bragg angle of the monochromator. If the beam is unpolarized, v_0 is equal to 1. y is then given by

$$y = \{v_0y_p(\xi_p)y_s(\xi_s)+vy_p(v\xi_p)y_s(v\xi_s)\}/(v_0+v)$$
$$= \{v_0y_0+vy_v\}/(v_0+v). \qquad (A10)$$

The derivatives are listed in Table 6, in which $\frac{\partial\psi}{\partial g}$ and $\frac{\partial\psi}{\partial\varrho}$ are given by:

1. crystal of type I $\frac{\partial\psi}{\partial g} = 1/\sin 2\theta$ (A11)

2. crystal of type II $\frac{\partial\psi}{\partial\varrho} = 1$ (A12)

3. General case

Table 6. *Table of derivatives*

Refinement on F^2	Refinement on F
$\frac{\partial F^2}{\partial s} = y\frac{\partial F_k^2}{\partial s}$	$\frac{\partial F}{\partial s} = y^{1/2}\frac{\partial F_k}{\partial s}$
$\frac{\partial F^2}{\partial P} = \Omega_1\frac{\partial F_k^2}{\partial P}$	$\frac{\partial F}{\partial P} = y^{1/2}\,\Omega_1\frac{\partial F_k}{\partial P}$
$\frac{\partial F^2}{\partial g} = s^2F_c^4\,\gamma_s\Omega_2\frac{\partial\psi}{\partial g}$	$\frac{\partial F}{\partial g} = \frac{1}{2}sF_c^3\,\gamma_sy^{-1/2}\,\Omega_2\frac{\partial\psi}{\partial g}$
$\frac{\partial F^2}{\partial\varrho} = s^2F_c^4\,\Omega_3$	$\frac{\partial F}{\partial\varrho} = \frac{1}{2}sF_c^3\,y^{-1/2}\,\Omega_3$

Neutron diffraction case

$$\Omega_1 = y\{1+\xi_pz_p(\xi_p)+\xi_sz_s(\xi_k)\}$$
$$\Omega_2 = yz_s(\xi_s)$$
$$\Omega_3 = y\left\{2\gamma_p\varrho z_\varrho(\xi_\varrho)+\gamma_sz_s(\xi_s)\frac{\partial\psi}{\partial\varrho}\right\}$$

X-ray diffraction case

$$\Omega_1 = \frac{1}{v_0+v}\{v_0y_0[1+\xi_pz_p(\xi_p)+\xi_sz_s(\xi_s)]+v^2y_v[1+\xi_pz_p(v\xi_p)+\xi_sz_s(v\xi_s)]\}$$

$$\Omega_2 = \frac{1}{v_0+v}\{v_0y_0z_s(\xi_s)+v^2y_vz_s(v\xi_s)\}$$

$$\Omega_3 = \frac{1}{v_0+v}\left\{2\gamma_p\varrho[v_0y_0z_p(\xi_p)+v^2y_vz_p(v\xi_p)]+\gamma_s\frac{\partial\psi}{\partial\varrho}[v_0y_0z_s(\xi_s)+v^2y_vz_s(v\xi_s)]\right\}$$

– Gaussian or Fresnellian distribution

$$\frac{\partial \psi_G}{\partial Q} = (\psi_G/Q)^3$$

$$\frac{\partial \psi_G}{\partial g} = (\psi_G/g)^3 \sin^2 2\theta \qquad (A13)$$

– Lorentzian distribution:

$$\frac{\partial \psi_L}{\partial Q} = (\psi_L/Q)^2$$

$$\frac{\partial \psi_L}{\partial g} = (\psi_L/g)^2 \sin 2\theta. \qquad (A14)$$

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Tchebycheff Extraction of the Periodic Vector Set from the Patterson Function

BY G. R. GOLDAK

College of Engineering, University of Saskatchewan at Saskatoon, Saskatoon, Saskatchewan, Canada

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The image-seeking method of Buerger and the procedure of Tokonami and Hosoya appear to be capable of dealing with complex crystal structures *via* the Patterson function, provided that the periodic vector set is accurately determined. Unfortunately, a general and powerful method for the location of peaks in the Patterson function has not yet been developed, and it is the lack of such a method which now prevents the formulation of a general Patterson method of structure analysis. This paper presents further results in the author's attempts to formulate a general method of vector-set extraction by representing the Patterson function as a linear generalized polynomial in a system of independent interatomic functions. This approach has the advantage in that the essentially non-linear problem of vector-set extraction is reduced to an apparently simple linear problem, namely that of determining the coefficients of the approximating polynomial. In the present paper, the Tchebycheff approximation norm is employed with coefficient determination by linear-programming procedures. Since linear-programming methods are flexible and extremely powerful, this Tchebycheff vector-set-extraction procedure is much more promising than the author's earlier published methods, which were based on interpolatory approximations.

Introduction

In order to formulate a general method of structure analysis, one would naturally think of working in terms of the Patterson function, since this function is not restricted to centrosymmetric structures. It is well known that the Patterson function may be regarded as a badly resolved representation of the weighted periodic vector set (Buerger, 1959). For a crystal containing N atoms per unit cell, the weighted periodic vector set consists of N periodic images of the crystal structure, and the phase problem is essentially the problem of separating the various points of the periodic vector set into these images. This separation can be accomplished by the image-seeking method of Buerger (1950) or the procedure of Tokomami & Hosoya (1965). Since neither of these methods has been widely used in practice, it might well be that their power is restricted in some ways which are not now apparent. At present, however, it appears that they could be successfully applied to extremely complex crystals, provided the weighted periodic vector set could be accurately determined.

In the past, the determination of the periodic vector set from the Patterson function has been attempted *via* various sharpening procedures (Patterson, 1934; Wunderlich, 1965). These sharpening methods depend to a large extent on the initial resolution of the Patterson function, and therefore they do not appear to be capable of dealing with complex structures which produce badly resolved Patterson functions. Certain other methods, which in effect locate individual peaks