

those given in the first paper, because the two types of transmission geometry become identical at zero scattering angle.

Discussion

The portions of the discussion in the first paper of this series that apply for transmission geometry also apply to the present case.

The type of transmission geometry described in this paper can often be used by only slight modification of a reflection geometry diffractometer. The sample holder is rotated by 90° so that the surface of the sample is normal to the incident X-ray beam at zero scattering angle. The slits of the diffractometer may have to be changed in some cases.

A comparison of the three forms of geometry considered in this and the first paper of the series is interesting. For very large scattering angles, reflection geometry often is superior from the standpoints of secondary scattering, primary scattering, and the magnitude of the absorption correction. For intermediate scattering angles, the type of transmission geometry described in this paper and reflection geometry often are both satisfactory. At small scattering angles, either type of transmission geometry is usually superior to reflection geometry. At extremely small angles, the usual transmission geometry described in the first paper is superior, because fewer moving parts are required in the diffractometer.

If a sample cannot be made thin enough to yield a small calculated ratio of secondary-to-primary intensity, the calculated secondary intensity can be used to obtain an approximation of primary coherent intensity, using the normalization procedure described in the first paper. An improved value of secondary intensity can then be calculated using the approximate coherent experimental intensity. However, this procedure would require a very large amount of work. Very careful design of the scattering experiment will usually allow such problems to be avoided.

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Application of Constraints to Derivatives in Least-Squares Refinement

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The effect of imposing constraints on the parameters of a least-squares refinement is considered, and a general equation is presented that relates the derivatives for the calculated, unconstrained parameters to those of the constrained parameters.

A problem which is frequently encountered in the least-squares refinement of positional and thermal parameters for crystal-structure analyses is the imposition

Nomenclature

A_j	Atomic weight of element j .
b, q	Parameters used to approximate scattering in $J = [\sum Z_j^2] [q + (1 - q)/(1 + b \sin^2 \theta)]$.
c	Velocity of light.
e	Electronic charge.
I_1	Total intensity of primary scattering.
I_2	Total intensity of secondary scattering.
J	Intensity of primary scattering in electron units.
m	Rest mass of electron.
N	Avogadro's number.
r	Vector from first to second scattering point in the case of secondary scattering.
t	Sample thickness.
V_1	Volume of sample illuminated by incident X-ray beam.
Z_j	Atomic number of element j .
2θ	Total scattering angle for primary scattering.
μ	Linear absorption coefficient at the wavelength of incident radiation.
μ'	Linear absorption coefficient at the wavelength of incoherent radiation as a function of scattering angle.
$\mu_j\{m\}$	Mass absorption coefficient of element j .

APPENDIX

Normalization can be done in the same manner as described in the appendix of the first paper of this series, if the expressions for \mathcal{F}_2 and \mathcal{F}_3 are used as given below.

$$\mathcal{F}_2 = [\mu t \exp(-\mu t \sec \theta)] / [\cos \theta \sum A_j \mu_j\{m\}]$$

$$\mathcal{F}_3 = \frac{\mu [\exp(-\mu t \sec \theta) - \exp(-\mu' t \sec \theta)]}{[\mu' - \mu] \sum A_j \mu_j\{m\}} \left(\frac{v'}{v} \right)^2$$

Reference

DWIGGINS, C. W. JR & PARK, D. A. (1971). *Acta Cryst.* A27, 264.

of constraints to account for the interdependence of such parameters. The constraints usually arise from the imposition of known symmetry or geometry for parts

of the structure, or from a proper treatment of the refinement in structures that exhibit disorder.

The constraints which are imposed on the positional and thermal parameters of an atom which lies at a point of crystallographic site symmetry are well-known and routinely applied (Levy, 1956). More recently, the solution of large structures which contain molecular fragments of known geometry has led to rigid-group refinement procedures (Scheringer, 1963; La Placa & Ibers, 1965), in which a geometry for part of the structure, such as a phenyl ring, is assumed to be known to a higher precision than can be determined in the structure being refined. The remaining variable parameters for the atoms within the group are only the origin and orientation of the group. The effect of a relaxation of the rigid-group assumption has recently been considered (Strouse, 1970); the constraints in this case arise only from an assumed molecular point symmetry for a fragment of the molecule. The molecular parameters for this fragment, such as bond lengths and angles, are free to vary, subject only to the point-symmetry requirements. Finally, appearance of disorder problems has increased with the size and precision of structure analyses. The presence of disorder and a known chemical composition always imply a constraint among atomic occupation factors. If assumptions are made regarding the geometries of two disordered molecular fragments, relative to one another, additional constraints are imposed (Ibers, 1971).

Each of the above types of constraint has been described in a manner specific to the problem considered. We have recently encountered several of these problems (Raymond & Wenk, 1971; Goldberg, Duesler & Raymond, 1971, 1972; Wenk & Raymond, 1972) and solved each in the same general way. All of these constraints have the same fundamental mathematical form. We present here a brief, but general, derivation of the equations which impose the proper constraints on the derivatives generated in the least-squares refinement. Only the specific method of application of these constraints will vary, depending on the type of problem and the particular least-squares program being used.

The fundamental problem lies in the construction of the design matrix for the least-squares refinement (Hamilton, 1964). This matrix is given by $\mathbf{D}^T\mathbf{D}$, where $D_{ij} = \partial F_i / \partial x_j$. Here, x_j represents the j th variable and F_i is the absolute value of the i th calculated structure factor (or structure factor squared if the refinement is based on that form of the observations); the superscript T represents the transpose operation. For a nonlinear, least-squares refinement with unit weights applied to the observations, the shifts in parameters, $\Delta\mathbf{x}$, are given by: $\Delta\mathbf{x} = (\mathbf{D}^T\mathbf{D})^{-1} \mathbf{D}^T \Delta\mathbf{F}$. The imposition of constraints lessens the number of independent variables and requires a suitable combination of the original derivatives in constructing a new design matrix for the smaller, independent set of variables.

Assume that there are n variables in the original set \mathbf{x}

(a column vector). Let m be the number of constraints imposed upon the variables \mathbf{x} . These constraints are represented by a set of m equations:

$$f_1(\mathbf{x}) = c_1 \dots f_i(\mathbf{x}) = c_i, \dots f_m(\mathbf{x}) = x_m.$$

Then,

$$df_i = \sum_{j=1}^m \left(\frac{\partial f_i(\mathbf{x})}{\partial x_j} \right) dx_j = 0, \quad (1)$$

which can be expressed in matrix form as

$$\mathbf{A}d\mathbf{x} = \mathbf{0}, \quad (2)$$

where $A_{ij} = \partial f_i(\mathbf{x}) / \partial x_j$ and $\mathbf{0}$ is a column vector of dimension m whose elements are all zero. The m by n matrix \mathbf{A} summarizes all constraints imposed on the problem.

With m constraints and n original variables there are $n-m$ linearly independent variables. Let $k = n-m$ and choose k independent variables, \mathbf{v} , such that:

$$\mathbf{B}\mathbf{x} = \mathbf{v} \text{ and } \mathbf{B}d\mathbf{x} = d\mathbf{v}. \quad (3)$$

It will usually be convenient to let \mathbf{v} be just the first k elements of \mathbf{x} , in which case $B_{ij} = 0$ if $i \neq j$ and $B_{ij} = 1$ for $i = j$; however, any other linearly independent set of new variables is also legitimate.

The two matrix equations (2) and (3) can be combined to give

$$\begin{pmatrix} \mathbf{B} \\ \mathbf{A} \end{pmatrix} d\mathbf{x} = \begin{pmatrix} d\mathbf{v} \\ \mathbf{0} \end{pmatrix}. \quad (4)$$

Let $\begin{pmatrix} \mathbf{B} \\ \mathbf{A} \end{pmatrix} = \mathbf{Q}$, where

$$\begin{aligned} Q_{ij} &= B_{ij} & i \leq k \\ Q_{ij} &= A_{ij} & i > k. \end{aligned}$$

The n by n square matrix, \mathbf{Q} , will be nonsingular if both the constraints and new variables are linearly independent. The reverse transformation then exists:

$$d\mathbf{x} = \mathbf{Q}^{-1} \begin{pmatrix} d\mathbf{v} \\ \mathbf{0} \end{pmatrix}. \quad (5)$$

Only the linear relation between $d\mathbf{x}$ and $d\mathbf{v}$ is of present interest:

$$d\mathbf{x} = \mathbf{J} d\mathbf{v}.$$

The n by k matrix, \mathbf{J} , is composed of just the first k columns of \mathbf{Q}^{-1} ; i.e. \mathbf{J} is defined by $J_{ij} = Q_{ij}^{-1}$, $j \leq k$.

We assume that the derivatives with respect to the original parameters \mathbf{x} , $dF/d\mathbf{x}$, have been calculated. However, the required derivatives are those for the new set of independent variables $dF/d\mathbf{v}$.

By the chain rule

$$\left(\frac{\partial F}{\partial v_j} \right) = \sum_{i=1}^n \left(\frac{\partial F}{\partial x_i} \right) \left(\frac{\partial x_i}{\partial v_j} \right) \quad (6)$$

Note that

$$\left(\frac{\partial x_i}{\partial v_j} \right) = J_{ij}. \quad (7)$$

This immediately gives the final relation between the original derivatives and the new, constrained set:

$$\frac{dF}{dv} = \mathbf{J}^T \frac{dF}{dx}. \quad (8)$$

Here, $\frac{dF}{dv}$ and $\frac{dF}{dx}$ are column vectors. In order to illustrate the application of these constraint equations, two typical examples follow.

Example 1

In an analysis of disorder in lunar minerals (Wenk & Raymond, 1972) the following constraints are applied to atom occupation factors x_1, x_2, x_3, x_4, x_5 and x_6 ; $x_4 = x_5, x_6 = 2x_4$, and

$$12 \cdot 2x_1 + 12 \cdot 2x_2 + 14x_3 + 8x_4 + 8x_5 + 8x_6 = \text{constant}.$$

Let $v_1 = x_1, v_2 = x_2, v_3 = x_3$,

then

$$\begin{pmatrix} dv_1 \\ dv_2 \\ dv_3 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 \cdot 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 \cdot 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 \cdot 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \cdot 0 & -1 \cdot 0 & 0 \\ 0 & 0 & 0 & 2 \cdot 0 & 0 & -1 \cdot 0 \\ 12 \cdot 2 & 12 \cdot 2 & 14 \cdot 0 & 8 \cdot 0 & 8 \cdot 0 & 8 \cdot 0 \end{pmatrix} \begin{pmatrix} dx_1 \\ dx_2 \\ dx_3 \\ dx_4 \\ dx_5 \\ dx_6 \end{pmatrix}$$

$dv \qquad \qquad \qquad \mathbf{Q} \qquad \qquad \qquad dx$

$$\mathbf{Q}^{-1} = \begin{pmatrix} 1 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 \\ 0 \cdot 0 & 1 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 \\ 0 \cdot 0 & 0 \cdot 0 & 1 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 \\ -0 \cdot 3812 & -0 \cdot 3812 & -0 \cdot 4375 & -0 \cdot 2500 & -0 \cdot 2500 & 0 \cdot 0312 \\ -0 \cdot 3812 & -0 \cdot 3812 & -0 \cdot 4875 & -0 \cdot 7500 & 0 \cdot 2500 & 0 \cdot 0312 \\ -0 \cdot 7625 & -0 \cdot 7625 & -0 \cdot 8750 & 0 \cdot 5000 & -0 \cdot 5000 & 0 \cdot 0625 \end{pmatrix}$$

and the result

$$\begin{pmatrix} \partial F / \partial v_1 \\ \partial F / \partial v_2 \\ \partial F / \partial v_3 \end{pmatrix} = \begin{pmatrix} 1 \cdot 0 & 0 \cdot 0 & 0 \cdot 0 & -0 \cdot 3812 & -0 \cdot 3812 & -0 \cdot 7625 \\ 0 \cdot 0 & 1 \cdot 0 & 0 \cdot 0 & -0 \cdot 3812 & -0 \cdot 3812 & -0 \cdot 7625 \\ 0 \cdot 0 & 0 \cdot 0 & 1 \cdot 0 & -0 \cdot 4375 & -0 \cdot 4375 & -0 \cdot 8750 \end{pmatrix} \begin{pmatrix} \partial F / \partial x_1 \\ \partial F / \partial x_2 \\ \partial F / \partial x_4 \\ \partial F / \partial x_5 \\ \partial F / \partial x_6 \end{pmatrix}$$

$dF/dv \qquad \qquad \qquad \mathbf{J}^T \qquad \qquad \qquad dF/dx$

follows.

Example 2

In a crystal, a bond length is held constant between two atoms whose coordinates are \mathbf{y} and \mathbf{x} . This constraint is applied to the coordinates of the second atom. If \mathbf{G} is the metric tensor and b is the bond length

$$f(\mathbf{x}) = b^2 = (\mathbf{x} - \mathbf{y})^T \mathbf{G} (\mathbf{x} - \mathbf{y})$$

$$\frac{df}{dx} = 2 \mathbf{G} (\mathbf{x} - \mathbf{y}), \quad df = \left(\frac{df}{dx} \right)^T dx = 0.$$

Let $v_1 = x_1, v_2 = x_2$,

then

$$\begin{pmatrix} dv_1 \\ dv_2 \\ 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} dx_1 \\ dx_2 \\ dx_3 \end{pmatrix},$$

where $\begin{pmatrix} a_{31} \\ a_{32} \\ a_{33} \end{pmatrix} = 2\mathbf{G} (\mathbf{x} - \mathbf{y})$. This gives

$$\begin{pmatrix} \frac{\partial F}{\partial v_1} \\ \frac{\partial F}{\partial v_2} \\ \frac{\partial F}{\partial v_2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & -a_{31} \\ 0 & 1 & -a_{32} \\ 0 & 1 & a_{33} \end{pmatrix} \begin{pmatrix} \frac{\partial F}{\partial x_1} \\ \frac{\partial F}{\partial x_2} \\ \frac{\partial F}{\partial x_3} \end{pmatrix}.$$

To summarize, all of the constraint problems which arise in least-squares refinement have the same fun-

damental structure. The equations which relate the derivatives for the constrained parameters are given by the matrix equation (8). The equations which have been previously given in discussions of particular types of constraints are all special forms of this fundamental equation.

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Debye–Waller B Values of Some NaCl-Type Structures and Interionic Interaction

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Debye–Waller B values of NaCl, KCl, MgO and AgCl are calculated from lattice dynamics based on a simple, rigid-ion type, interaction model. The parameters introduced in the model have intelligible significance. The present approach compares favourably with experimental evidence and previous physical calculations.

Introduction

The determination of Debye–Waller B values from X-ray and neutron-diffraction data is a problem not yet completely solved. Table 1 shows, chronologically, experimental room-temperature B values of NaCl. Large deviations, even between values determined most recently, indicate that these data are probably not the final ones. Various problems connected with experiment and data analysis have been amply discussed by several authors (Abrahams & Bernstein, 1965; Maslen, 1967; Göttlicher, 1968; Linkoaho, 1969). It seems that, at this moment, the most serious problem is evaluating the thermal diffuse scattering (TDS) contribution to observed intensities at the Bragg reflexions. Different authors use different simplified models to deduce the magnitude of the TDS corrections. The resulting change in average room-temperature NaCl Debye–Waller B values ranges from 0.04 to 0.20 Å² for single-crystal measurements and from 0.03 to 0.06 Å² for powder measurements, depending on experimental set-up and model used for calculations (Nilsson, 1957; Pryor, 1966; Suortti, 1967; Göttlicher, 1968).

Theoretical calculations of Debye–Waller B values for NaCl-type structures have been made for most of the interaction models in current use for lattice dynamical calculations. In the following, Debye–Waller B values of NaCl, KCl, MgO and AgCl are calculated from lattice dynamics employing a simple rigid-ion type

interaction model. The results compare favourably with experimental evidence and previous calculations based on more complicated interaction models.

Interaction model

The interaction model, used for the present calculations, is essentially Kellerman's (1940) rigid-ion model but extended with second nearest-neighbour short-range interactions. The lattice dynamical calculations have been done using the Born von Kármán theory as presented by Maradudin, Montroll & Weiss (1963).

Like other models, the model is semi-empirical in the sense that, lacking sufficient knowledge of interatomic forces, parameters need to be scaled with the aid of experimental information. The interaction is assumed to be pair-wise additive and is split into a long-range Coulomb part and a short-range part, not necessarily repulsive. The parameters of the model are:

1. The effective electric charge of the ions, se , where e is the elementary charge, determining the Coulomb interaction. Values of se , required for lattice dynamics, are closely comparable with Szigeti's (1950) effective charge used in his theory of dielectric constants.

2. First and second derivatives of the short-range pair-potentials, with respect to interionic distance, taken at equilibrium separation. Considering only first- and second-neighbour short-range interactions, then, for NaCl type structures, one is dealing with three different short-range interactions and, thus, six short-range parameters. These parameters, or force constants, are denoted by ϕ'_{++} , ϕ''_{++} , ϕ'_{+-} , ϕ''_{+-} , ϕ'_{--} , ϕ''_{--} , (ϕ'_{++} being the first derivative of the potential between

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