Finally we discuss the relation between the electrogyration and dielectric properties of the alums by considering the rule of Miller (1964), who defined a quantity Δ, applicable to non-linear optical properties and valid for all materials. In the case of the electrogyration of alums this magnitude is defined by (Miller, 1973)

$$\Delta^g_{123} = s_{123}/[4\pi\chi^2(\omega)\chi(0)] \ .$$

The susceptibility $\chi(\omega)$ at frequency ω is related to the index of refraction n by the relation

$$\chi(\omega) = (n^2-1)/4\pi \ ,$$

and the value of $\chi(0)$ is equal to $(\varepsilon-1)/4\pi$, where ε is the dielectric constant. The reduced constants Δ^g_{123} are listed in Table 2.

Contrary to the second-harmonic generation and the linear electro-optical effect of many materials, where Δ is nearly a constant, Miller's rule does not explain the differences in the electrogyration properties of the alums.

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Rigid-Body Constraints and the Least-Squares Refinement of Crystal Structures*

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To refine the orientation and location of a rigid group of atoms in a crystal it is not necessary to store the atom coordinates relative to a localized axial system. All atoms in the asymmetric unit are defined relative to a single orthonormal axial system. A local axial system is created by taking an atom in the rigid group as origin and defining the local axes as parallel to these orthonormal axes. The evaluation of the required derivatives is then very easy. The replacement of approximate atom positions by idealized atom positions is described.

Introduction

Rigid group refinement has previously been performed in a somewhat awkward manner (Scheringer, 1963; La Placa & Ibers, 1965; Doedens, 1970). The awkwardness occurs because the orientation of the rigid group of atoms is described by rotations about fixed axial directions whereas the atoms are described by fixed coordinates in a refineable local axial system.

There are two ways of simplifying the evaluation of an incremental change in orientation and location of a rigid group of atoms.

(i) If fixed local coordinates are used, rotate the rigid group about the initial directions of the refineable axial system.

(ii) If fixed rotation axial directions are used, redefine the local coordinates each cycle so that the initial axial directions of the local axial system are parallel to the rotation axes.

The first method requires the redefinition of the scattering vector relative to the local coordinate system for easy implementation (Rae, 1975). It has an advantage if the group is not truly rigid (symmetry constraints and equal object constrants). It also has an advantage for a linear rigid group in that rotation about the linear direction is easily omitted from the refinement. However, it does require the storage of both the local coordinates and the local axial system. For a strictly rigid, non-linear group the second method is more advantageous and is described in detail.

Theory

We can describe the position vector of the nth atom in the rigid group relative to standard orthonormal reference axes $\mathbf{A}_i$ as

$$\sum_i X^i_n \mathbf{A}_i = \sum_i X^i_o \mathbf{A}_i + \sum_{ij} V_{ij}(Y^j_n - Y^j_o)\mathbf{A}_j \qquad (1)$$

where the X^i_n are orthonormal crystal coordinates of the nth atom in the group and the X^i_o are orthonormal crystal coordinates of the local origin after refinement. The Y^j_n and Y^j_o are the corresponding values of these

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coordinates before refinement. For simplicity the first atom in the group is chosen as origin. The matrix **V** is chosen as the product of three matrices

$$\mathbf{V}=\begin{pmatrix} C_3 & S_3 & 0\\ -S_3 & C_3 & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix} C_2 & 0 & -S_2\\ 0 & 1 & 0\\ S_2 & 0 & C_2\end{pmatrix}\begin{pmatrix} 1 & 0 & 0\\ 0 & C_1 & S_1\\ 0 & -S_1 & C_1\end{pmatrix} \qquad (2)$$

where $C_i=\cos\psi_i$, $S_i=\sin\psi_i$ and ψ_i is the angle of rotation about the ith local axis direction which is parallel to $\mathbf{A}_i$. Initially the ψ_i are zero and **V** is the unit matrix.

Derivatives for least squares follow naturally. Thus

$$(\partial F/\partial\psi_1)_0=\sum_{i,n}(\partial F/\partial X_n^i)_0(\partial X_n^i/\partial\psi_1)_0$$

$$=\sum_n[(\partial F/\partial X_n^2)_0(Y_n^3-Y_o^3)-(\partial F/\partial X_n^3)_0(Y_n^2-Y_o^2)] \qquad (3)$$

$$(\partial F/\partial X_o^i)_0=\sum_n(\partial F/\partial X_n^i)_0\,. \qquad (4)$$

Derivatives with respect to ψ_2 and ψ_3 are obtained from (3) by cyclic permutation of indices.

The problem is non-linear since the values of the derivatives depend on the values of ψ_i and X_n^i. The subscript 0 outside the brackets in (3) and (4) implies evaluation from the initial parameter values (*i.e.* $C_i=1$, $S_i=0$, $i=1,3$). The use of orthonormal coordinates rather than fractional coordinates to evaluate $(\partial F/\partial X_n^i)_0$ is discussed by Rae (1975).

A single refinement cycle evaluates the matrix **V** and the local origin $\mathbf{X}_0$ and then replaces the coordinates Y_n^j by the coordinates X_n^i with the transformation (1). For the next cycle **V** is again initially the unit matrix.

If linearity is assumed the derivatives evaluated in (3) imply a non-unitary matrix

$$\begin{pmatrix} 1 & \psi_3 & -\psi_2\\ -\psi_3 & 1 & \psi_1\\ \psi_2 & -\psi_1 & 1\end{pmatrix}$$

for **V** and take no account of the multiplication sequence given in (2). Because of this non-linearity it is desirable to damp the change in orientation that results by evaluating the ψ_i and then the matrix **V** obtained from (2). A procedure with desirable characteristics follows. Evaluate the ψ_i and create the matrix

$$\mathbf{U}=\begin{pmatrix} 1 & S_3 & -S_2\\ -S_3 & 1 & S_1\\ S_2 & -S_1 & 1\end{pmatrix}.$$

A unitary approximation to **V** is then obtained by replacing column vectors

$$\mathbf{u}_1=\begin{pmatrix} 1\\ -S_3\\ S_2\end{pmatrix},\quad \mathbf{u}_2=\begin{pmatrix} S_3\\ 1\\ -S_1\end{pmatrix},\quad \mathbf{u}_3=\begin{pmatrix} -S_2\\ S_1\\ 1\end{pmatrix}$$

by $\mathbf{v}_1,\mathbf{v}_2,\mathbf{v}_3$ where $\mathbf{v}_2=\mathbf{u}_2/N_1$, $\mathbf{v}_3=\mathbf{u}_1\times\mathbf{v}_2/N_2$, $\mathbf{v}_1=\mathbf{v}_2\times\mathbf{v}_3$ and N_1 and N_2 are normalization constants.

The replacement of approximate atoms by idealized atoms

The recommended procedure is essentially that of Nyburg (1974) except that full-matrix rather than diagonal-matrix least-squares equations are solved. The transformation between two groups of atoms having a known 1 to 1 correspondence is best evaluated by minimizing $\sum_n w_n\Delta_n^2$ where Δ_n is the distance between the nth corresponding atoms when one group is superimposed on the other and w_n^{-1} is the variance of this distance.

The best least-squares solution causes the weighted centroids to coincide, but does not necessarily cause the directions of the principal axes of inertia to coincide unless one of the groups is linear.

The position of the nth atom relative to the coincident centroids is given as $\sum_i(Y_n^i-Y_o^i)\mathbf{B}_i$ for the replacement atom described relative to local orthonormal axes $\mathbf{B}_i$ and as $\sum_i(X_n^i-X_o^i)\mathbf{A}_i$ for the atom being replaced described relative to orthonormal crystal axes $\mathbf{A}_i$.

We say

$$\sum_i(X_n^i-X_o^i)\mathbf{A}_i=\sum_{ijk}V_{ij}W_{jk}(X_n^k-X_o^k)\mathbf{B}_i$$

and minimize $\sum_{in}w_n(\Delta_n^i)^2$, where the

$$\Delta_n^i=\sum_{jk}V_{ij}W_{jk}(X_n^k-X_o^k)-(Y_n^i-Y_o^i)$$

are components of the separation of the nth pair of corresponding atoms in the local axial system $\mathbf{B}_i$. The matrix **V** is of the form given in (2) and is refineable with the initial assumption that **V** is the unit matrix. The matrix **W** is not refined and is an initial estimate of the transformation matrix. The refinement is non-linear, but converges very rapidly with the approximation to **V** given earlier. The equations solved are

$$\sum_j M_{ij}\Delta\psi_j=N_i\,,\quad i=1,2,3 \qquad (5)$$

where

$$M_{11}=\sum_n w_n[(X_n^2-X_n^o)^2+(X_n^3-X_n^o)^2]$$

$$M_{12}=-\sum_n w_n(X_n^1-X_n^o)\,(X_n^2-X_n^o)$$

and

$$N_1=\sum_n w_n[(X_n^2-X_o^2)\,(\Delta_n^3)_0-(X_n^3-X_o^3)\,(\Delta_o^2)_0]\,,$$

where

$$(\Delta_n^i)_0=\sum_k W_{ik}(X_n^k-X_o^k)-(Y_n^i-Y_o^i)\,.$$

The other elements in (5) are obtained by cyclic permutation. (5) are ill-conditioned only if the inertia tensor M_{ij} has a zero eigenvalue, *i.e.* if the group of atoms being replaced is linear.

It is, of course, necessary to make a good approximation for the matrix $\mathbf{W}$. For the method described in this paper a meaningful approximation is only possible if the chiralities of the two groups agree. For a linear group the solution is complete if the direction of the principal axis of inertia of minimum value is found for the atoms being replaced. With the correct choice of sign this corresponds to the best estimate of the linear direction. For non-linear groups, the alignment of principal inertial axes is not to be recommended as the choice of sign question remains and accuracy is very doubtful whenever two principal inertial axes are almost equal. The matrix $\mathbf{W}$ transforms three uniquely defined orthonormal directions in one axial system into equivalently defined directions in the other axial system. A sensible choice of three non-collinear atoms is used. Vector $\mathbf{u}_1$ between atoms 1 and 2 and vector $\mathbf{u}_2$ between atoms 1 and 3 define orthonormal vectors $\mathbf{v}_2=\mathbf{u}_2/N_1$, $\mathbf{v}_3=\mathbf{u}_1\times\mathbf{v}_2/N_2$ and $\mathbf{v}_1=\mathbf{v}_2\times\mathbf{v}_3$, where N_1 and N_2 are normalization constants. We say that

$$\mathbf{v}_i=\sum_j U^A_{ij}\mathbf{A}_j=\sum_k U^B_{ik}\mathbf{B}_k\,,$$

so that

$$W_{jk}=\sum_i U^A_{ij}U^B_{ik}\,.$$

U^A_{ij} are direction cosines in the orthonormal axial system $\mathbf{A}_j$ defined by three of the atoms being replaced. U^B_{ik} are direction cosines in the axial system $\mathbf{B}_k$ defined by the corresponding three replacement atoms.

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Temperature Effect on the Breadth of Powder Pattern Reflections

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A general method is developed for calculating the temperature diffuse intensity for cubic powder patterns. The method is applied to the pattern of an f.c.c. crystal containing 10^{12} atoms. The effect of temperature vibration is a spreading out at the base of the peak. In terms of the integral breadth, there is an increase which may be of the order of several percent. But the main part of the peak is essentially unaltered, and the increase does not relate to what is generally measured as a breadth. The usual observation is better represented by the breadth at half maximum intensity, and for this quantity there is an increase of less than 0·07% for $2M=1{\cdot}0$ and less than 0·17% for $2M=2{\cdot}0$. It is concluded that a real temperature broadening of powder pattern peaks will always be too small to be of importance, or to be experimentally observable.

1. Introduction

For crystals containing only one kind of atom, the early Debye approximation, involving independent vibration of the atoms, predicted a reduction in the intensity of the Bragg reflections by the factor $\exp(-2M)$, and the appearance of a monotonic diffuse intensity equal to $I_eNf^2[1-\exp(-2M)]$. There was no broadening of a powder pattern reflection, only a reduction in height.

A better approximation represents the atomic vibrations in terms of a system of elastic waves. The first-order temperature diffuse intensity (TDS) for an f.c.c. powder pattern has been evaluated on the basis of the elastic wave model (Warren, 1953) and the contribution by second-order TDS has been given by Paskin (1958). It is found that the TDS averages closely to the old independent vibration result, but at the position of each of the Bragg reflections, the TDS rises sharply, and the Bragg reflections are superimposed on these peaks in the diffuse intensity. The elastic wave treatment predicts that the temperature vibration of the atoms should produce a broadening in the peaks occurring at the Bragg positions.

However the previous treatment is not satisfactory for predicting the magnitude of the broadening. At the position of each of the Bragg reflections, the TDS rises to infinite values. This unrealistic result came from an integration in the Brillouin zone over the elastic wave vectors $\mathbf{g}$, including all wave vectors down to $g=0$.