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The Application of External Forces to Computational Models of Crystals*

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Abstract

A computational model of a crystal consists of a description of the crystal structure, expressions for calculating the energy of the model in terms of this structure, and a way of minimizing this calculated energy with respect to the structural variables. External forces such as hydrostatic pressure, normal and shearing stresses, or electric fields can be simulated by adding a term to the energy which describes the external energy of the force-producing device. Minimizing the total energy produces a structure distorted by the external force. From the calculated distortion it is possible to obtain the complete elastic tensor and the dielectric and piezoelectric constants of the crystal. Some phase changes can be simulated, and it should be possible to induce ferroelastic or ferroelectric transitions in the model. The effect of these forces on the orientation and conformation of molecules in the crystal can also be computed.

Introduction

In recent years, computational models of crystal structures have been used extensively to interpret and predict the molecular or atomic arrangements and some properties of crystalline materials. Work on molecular crystals has been summarized by Timofeeva, Chernikova & Zorkii (1980). (See, for example, Warshel & Lifson, 1970; Kitaigorodsky, 1973; Momany, Carruthers & Scheraga, 1974; Gavezzotti & Simonetta, 1975; Williams & Starr, 1977; Taddei, Righini & Manzelli, 1977; Busing, 1982, 1983.) Examples of the application of these methods to inorganic crystals go back to Born & Mayer (1932) and include publications by Tosi & Fumi (1964), Slaughter (1966), Busing (1970, 1972*a*), Ohashi & Burnham (1972), Giese & Datta (1973), Catlow & Norgett (1973), Yuen, Murfitt & Collin (1974), Brown & Fenn (1979), Miyamoto & Takeda (1980), Matsui & Watanabé (1981), Matsui & Matsumoto (1982) and Catlow & Parker (1982).

Computer programs which are available for this kind of calculation include *PCK*5 and *PCK*6 (Williams, 1969, 1972, 1979), *QCFF/PI* and *MCA* (Warshel & Levitt, 1982; Huler, Sharon & Warshel, 1977; Warshel, 1977), *WMIN* (Busing, 1972*b*, 1981) and *PLUTO* and *METAPOCS* (Catlow & Mackrodt, 1982).

The purpose of this paper is to describe a simple way of simulating the application of external forces to a computational crystal model. Such forces could be hydrostatic pressure, normal or shearing stresses, electric fields, or any combination of these. By examining the way in which the model responds to these forces we can compute its elastic constants, static dielectric constants, and piezoelectric constants. The structure at high pressures can be simulated, as can certain kinds of phase changes and ferroelastic or ferroelectric transitions. The effect of external forces on the orientation and conformation of molecules in crystals can be predicted. Other ways of computing the elastic tensor and the piezoelectric and dielectric constants of a crystal have been described (see, for example, Weidner & Simmons, 1972; Catlow & Norgett, 1973; Catlow & Mackrodt, 1982), but these, in general, do not involve the application of finite forces or fields.

Computational models

A computational model of a crystal includes a description of the structure and a procedure for calculating the potential energy as a function of that structure. The description includes the lattice parameters, the coordinates of the atoms in one asymmetric unit, and the symmetry operations which can be used to generate the entire structure.

The energy calculation often uses the atom–atom approximation to calculate the nonbonded energy per formula unit as

$$W_{\text{non}} = \frac{1}{2Z} \sum_{i}^{\substack{\text{one}\\\text{cell}}} \sum_{j}^{\substack{\text{all}\\\text{cells}}} V(r_{ij}). \qquad (1)$$

Here j is restricted to select atoms not bonded to atom i, r_{ij} is the distance between these atoms, and Z is the number of formula units per cell. The factor of one half is needed because, in an infinite crystal,

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each distance would otherwise be included twice. The nonbonded potential $V(r_{ij})$ is often written

$$V(r_{ij}) = q_i q_j r_{ij}^{-1} - A r_{ij}^{-6} + B \exp(-C r_{ij}), \quad (2)$$

where the terms represent Coulomb, van der Waals and repulsion energy, respectively. The atomic charges q_i and the coefficients A, B and C, which depend on the kinds of atoms involved, are known as the nonbonded energy parameters.

When molecules are treated as flexible groups it is necessary to include terms representing the intramolecular energy in some form such as

$$V(r) = (k_r/2)(r - r_0)^2, \quad (3)$$

$$V(\alpha) = (k_\alpha/2)(\alpha - \alpha_0)^2, \quad (4)$$

$$V(\varphi) = (E_n/2)(1 \pm \cos n\varphi). \quad (5)$$

Here r is a bond distance, α is a bond angle, and φ is a torsion angle. The energy parameters include the force constants k_r and k_α, the unstrained values r_0 and α_0, and the n-fold barrier to torsion E_n. Some models may include additional energy terms, such as the internal energy of polarization for a shell model, for example.

The computational model is completed by adjusting the structural variables to minimize the calculated energy. This is therefore a static model in which the effects of thermal motion are absorbed in the form of the potential. Normal modes of vibration can be calculated for the structure, but the pseudorandom motion of individual atoms which can be obtained by molecular dynamics or Monte Carlo techniques does not appear.

The structural variables to be adjusted are just those which would be refined in a crystal-structure determination. They include from one to six lattice parameters, depending on the symmetry. There may be three coordinates per atom or fewer for atoms in special positions. Alternatively, molecules may be treated as rigid or segmented with up to three translations and three rotations per rigid group.

The starting values of these parameters are often taken as their experimental values. Alternatively, they may be chosen to represent a postulated arrangement. Usually only a local minimum in energy is sought, and there is no guarantee that there may not be other quite different structures with lower calculated energies.

When the starting structure is near the desired energy minimum, the Newton–Raphson method is an efficient adjustment technique. The equations to be solved are

$$\mathbf{D}\,\boldsymbol{\Delta}\mathbf{p} = -\mathbf{d}, \quad (6)$$

where p_i is a structural parameter, $d_i = \partial W/\partial p_i$, and $D_{ij} = \partial^2 W/\partial p_i\,\partial p_j$. Because the derivatives d_i are nonlinear in the p_i's, a few iterations are required to bring the structure to the point where the d_i's are zero. This may be the desired energy minimum, but, in fact, the Newton–Raphson method will converge to a maximum or a saddle point as readily as to a minimum. The answer can be checked, however, by examining the eigenvalues of $\mathbf{D}$; at a minimum these will all be positive.

If the trial structure is too far from the energy minimum, the Newton–Raphson method will fail, and it is necessary to use some other technique, such as the method of steepest descents, which requires only the first derivatives $\partial W/\partial p_i$, or search procedures, which require no derivatives. These include a method devised by Rosenbrock (1960) and the Simplex method of Nelder & Mead (1965). These techniques are slower than the Newton–Raphson method, but they invariably proceed to lower calculated energies.

Simulating hydrostatic pressure

Two ways of including the effects of hydrostatic pressure in the computational modeling of crystals have been reported. One method, used by Miyamoto & Takeda (1980) and also by Parker (1983), is simply to fix the lattice parameters at values determined experimentally at high pressures. The remaining structural parameters can then be computed from the model. The other method, reported by Hall & Williams (1975) and corrected by Hall, Starr, Williams & Wood (1980), adjusts the entire structural model, including the lattice parameters. Pressure is simulated by adjusting the structure until the derivatives of the energy with respect to the cell edges acquire specified negative values which are proportional to the applied pressure.

The procedure to be described here is equivalent to the latter method, but instead of requiring the derivatives to take non-zero values, we simply add an extra term, $W_{\rm ext}$, to the energy, where $W_{\rm ext}$ is the external energy of the force-producing device. Fig. 1 shows a schematic way of applying pressure to a crystal. The weight of mass m rests on a piston of area A which applies pressure to the crystal by means of an incompressible fluid. As the crystal contracts by an amount $\Delta v = A\,\Delta h$, the potential energy of the mass becomes less. The external energy change is

$$W'_{\rm ext} = mg\,\Delta h = (mg/A)A\,\Delta h = P\,\Delta v, \quad (7)$$

where P is the pressure. Note that both Δh and Δv are negative quantities. The external energy per formula unit is then

$$W_{\rm ext} = P\Delta V/Z, \quad (8)$$

where V is the cell volume and Z is the number of formula units per cell. The effect of pressure is introduced by minimizing $W_{\rm total}$, the energy of the entire system, crystal and force-producing device,

$$W_{\rm total} = W_{\rm cryst} + W_{\rm ext}. \quad (9)$$

The terms in (9) are illustrated in Fig. 2, where energy W is plotted against cell volume V. W_{cryst} is a typical potential curve at zero pressure with a minimum at the equilibrium cell volume, V_0. W_{ext} is a straight-line plot of (8) with a slope proportional to P. W_{total}, the sum of these two curves, is the energy of the system, and its minimum is at a new cell volume smaller than V_0 by ΔV. [A referee notes that the same procedure for simulating hydrostatic pressures was used by Muhlhausen & Gordon (1981).]

For example, to apply a pressure using program *WMIN* (Busing, 1981, p. 42) the user simply writes a subroutine to compute the external energy term

$$W_{\text{ext}} = CP(V - V_0)/Z. \tag{10}$$

Here P is the desired pressure, V is the current cell volume, V_0 is its value at zero pressure, and C is a constant to convert the result to the desired energy units. Minimizing the energy of the model then produces a result with smaller cell volume.

The calculated dilation is $\Delta V/V_0$, and the volume compressibility is $-(\Delta V/V_0)/P$. The bulk modulus, K, is the reciprocal of the compressibility (Nye, 1957, pp. 145–146):

$$K = -P/(\Delta V/V_0). \tag{11}$$

Simulating stresses on an orthogonal crystal

The application of normal or shearing stresses to an orthorhombic, tetragonal or cubic crystal will be considered first; and then a general method for use with any crystal will be developed.

To apply a normal tension σ_1 along the a axis of an orthorhombic crystal, we can imagine a weight of mass m hung so as to stretch the unit cell along a. The stretching force is applied to the area bc, so the energy change of the weight is

$$\begin{aligned} W'_{\text{ext}} &= -mg\,\Delta a = -(mg/bc)bc\,\Delta a \\ &= -\sigma_1 bc(a - a_0), \end{aligned} \tag{12}$$

where σ_1 has the dimensions of pressure. The external energy per formula unit is then

$$W_{\text{ext}} = -\sigma_1 bc(a - a_0)/Z. \tag{13}$$

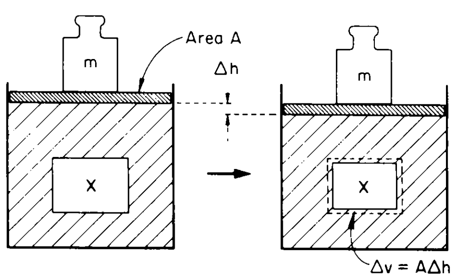

Fig. 1. The application of hydrostatic pressure to crystal X by means of an incompressible fluid. The external energy of the mass m changes by $W'_{\text{ext}} = P\Delta v$.

To apply this normal tension to a model, the external-energy term is calculated from the desired σ_1 and the current values of the lattice parameters. Minimizing the total energy produces a model with larger a and smaller b and c values. The computed strains are $\varepsilon_1 = (\Delta a/a)$, $\varepsilon_2 = (\Delta b/b)$ and $\varepsilon_3 = (\Delta c/c)$; and the elastic compliance constants, s_{ij}, can be calculated since $\varepsilon_1 = s_{11}\sigma_1$, $\varepsilon_2 = s_{12}\sigma_1$ and $\varepsilon_3 = s_{13}\sigma_1$. Other compliance constants can be obtained by applying stresses σ_2 and σ_3 along b and c, respectively.

A similar method can be used to apply a shear stress to an orthogonal crystal. The stress σ_4, for example, tends to reduce the cell angle α from its zero-stress value of 90°. This stress is simulated by adding the external energy term

$$W_{\text{ext}} = \sigma_4\,\Delta\alpha\,V/Z. \tag{14}$$

Relaxing the crystal symmetry to monoclinic (as described below) and minimizing the total energy produces a model with $\alpha < 90°$. The shear strain is $\varepsilon_4 = -\Delta\alpha$, and the shear compliance is $s_{44} = \varepsilon_4/\sigma_4$.

Applying stresses to a general crystal

By convention (IEEE, 1978; Nye, 1957, pp. 280–283), the physical properties of crystals are defined with respect to right-handed Cartesian axes with the z axis parallel to the crystal c axis and with the x axis lying in the ac plane. For a general crystal it is convenient to prepare a subroutine for applying stresses and computing strains in terms of this Cartesian system.

Consider a unit cube in the Cartesian system with corners defined by vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$ which form the columns of matrix $\mathbf{U}$

$$\mathbf{U} = (\mathbf{u}_1\mathbf{u}_2\mathbf{u}_3) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{15}$$

Let $\mathbf{C}$ be the matrix which converts coordinates from

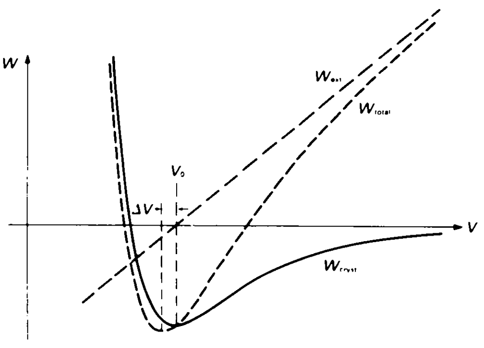

Fig. 2. The simulation of hydrostatic pressure. The energy W is plotted as a function of the unit-cell volume V. The external energy W_{ext} is added to the crystal energy W_{cryst} and the total energy W_{total} is minimized. The slope of the line for W_{ext} is proportional to the applied pressure.

the unstrained crystal system to the standard Cartesian system (see Appendix). Then

$$\mathbf{C}^{-1}\mathbf{U}=\mathbf{C}^{-1} \tag{16}$$

describes the unit cube in terms of the unstrained crystal axes. The crystal is then strained by changing its lattice parameters and the modified matrix, $\mathbf{C}'$, can be computed. Converting the unit cube back to the Cartesian system produces

$$\mathbf{U}'=\mathbf{C}'\mathbf{C}^{-1} \tag{17}$$

where $\mathbf{U}'$ describes the distorted unit cube. The strain matrix $\mathbf{E}$ is then

$$\mathbf{E}=\mathbf{U}'-\mathbf{U}=\mathbf{U}'-1. \tag{18}$$

Any rotational component of $\mathbf{E}$ should be removed by computing

$$\boldsymbol{\varepsilon}=(\mathbf{E}+\mathbf{E}^T)/2, \tag{19}$$

so that $\boldsymbol{\varepsilon}$ represents the symmetrical strain tensor with elements ε_{ij} (Nye, 1957, p. 97). These elements can be expressed in single-subscript form (Nye, 1957, p. 134):

$$\begin{pmatrix}\varepsilon_1 & \varepsilon_6 & \varepsilon_5\\ \varepsilon_6 & \varepsilon_2 & \varepsilon_4\\ \varepsilon_5 & \varepsilon_4 & \varepsilon_3\end{pmatrix}=\begin{pmatrix}\varepsilon_{11} & 2\varepsilon_{12} & 2\varepsilon_{13}\\ 2\varepsilon_{21} & \varepsilon_{22} & 2\varepsilon_{23}\\ 2\varepsilon_{31} & 2\varepsilon_{32} & \varepsilon_{33}\end{pmatrix}. \tag{20}$$

To simulate either a normal tension or a shear stress σ_i it is only necessary to compute an external energy term,

$$W_{\text{ext}}=-\sigma_i\varepsilon_i V/Z. \tag{21}$$

Here the factor V/Z is needed to convert from energy per unit cube to energy per formula unit. Minimizing W_{total} will again result in a crystal with modified lattice parameters reflected in the non-zero strain tensor $\boldsymbol{\varepsilon}$, and the elastic compliance constants can be computed as

$$s_{ij}=\varepsilon_j/\sigma_i. \tag{22}$$

In computing elastic constants from these static models the effects of thermal motion are being ignored, and the distinction between adiabatic and isothermal elastic constants is lost. For many materials the differences between these two kinds of constants can be expected to be less than 0·1% (Nye, 1957, pp. 187–188).

Simulating the effect of an electric field

The effect of an electric field $\mathbf{E}$ can be simulated by computing the change in polarization

$$\Delta\mathbf{P}=\sum_{i}^{\text{one cell}} q_i(\mathbf{r}_i-\mathbf{r}_{i0})/V \tag{23}$$

and setting the external energy to

$$W_{\text{ext}}=-\mathbf{E}\,.\,\Delta\mathbf{P}\;V/Z. \tag{24}$$

Here q_i is the Coulomb charge of an atom or ion with coordinates defined by $\mathbf{r}_i$. A field E_1 in the positive x direction will thus tend to increase the x coordinates of positively charged ions and reduce those of negative ones. As the energy is minimized under the influence of this field, other coordinates and lattice parameters may also change, subject to symmetry constraints, as described below.

Difficulties arise if the group of atoms included in the summation of (23) initially has a net electric moment. One way of avoiding this is to sum over the atoms which fall within the boundaries of one unit cell. Atoms on the cell faces, edges or corners are all included with the appropriate fractional charges. This method will work even for polar crystals if the arbitrary coordinates of the origin are chosen so that the cell boundaries pass through an atom. The charge on this atom is then divided among its translational equivalents so as to cancel any spontaneous net moment.

If a single component of field is applied, then the static dielectric susceptibility tensor elements χ_{ij} can be calculated from the equation

$$\Delta P_j=\kappa_0\chi_{ij}E_i, \tag{25}$$

and the dielectric constants are

$$K_{ij}=\delta_{ij}+\chi_{ij}. \tag{26}$$

Here κ_0 is the permittivity of a vacuum, and δ_{ij} is the Kronecker delta (Nye, 1957, pp. 68–69).

For noncentrosymmetric crystals the piezoelectric coefficients d_{ij} can be computed (Nye, 1957, pp. 115–116) from

$$\varepsilon_j=d_{ij}E_i. \tag{27}$$

Alternatively, the piezoelectric constants for a noncentrosymmetric crystal can be determined by simulating a stress σ_j and calculating the change in polarization. Then

$$\Delta P_i=d_{ij}\sigma_j. \tag{28}$$

If the crystal is originally centrosymmetric the lattice parameter changes and strain elements ε_j will be zero for small fields. For stronger fields, however, they could become appreciable as the model becomes noncentrosymmetric. This is the second-order effect known as electrostriction.

Interpolation for constants at zero stress

In order to get elastic constants free of round-off error to a precision of three or four significant figures, it is necessary to apply stresses at 0.2 to 0.5 GPa to soft crystals such as NaCl or at 2 to 5 GPa for hard materials such as the silicate minerals. Experimental elastic constants, on the other hand, are usually obtained by acoustic or dynamic methods in which the effective stresses approach zero. It has therefore been found useful to make the calculations at two or more values of the stress so that the constant at zero stress can be found by interpolation. If the effect is unsymmetric about zero, as for a normal stress (or for an electric field on a noncentrosymmetric crystal) then it may be sufficient to make the computation for two values of stress, one positive and one negative. The zero-stress result is then obtained by linear interpolation. For more precision the calculation can be made for four values of the stress, and cubic interpolation can be used.

If the effect is symmetric about zero, as for a shear stress on an orthorhombic crystal, then only two calculations need to be made, and parabolic interpolation will provide the zero-stress result.

Relaxing symmetry constraints

In computational modeling of crystals the original symmetry is usually maintained in order to keep the number of variables small and thus to reduce the requirements for computer time and memory size. The application of external forces to a crystal often reduces its symmetry, however, and it is necessary to consider how the symmetry constraints must be relaxed.

The application of hydrostatic pressure generally requires no change in the crystal symmetry. The application of a normal or shear stress, however, may require lowering of the symmetry consistent with the symmetry of the applied force. The point symmetry of a normal stress is $\infty/mmm - D_{\infty h}$ with the axis in the direction of the force. This requires the elimination of all mirrors or glide planes except those parallel or perpendicular to the force. It also requires elimination of all rotation and screw axes except those parallel to the force and 2 and 2_1 axes perpendicular to the force. Since mechanical stresses are centrosymmetric, any inversion center is permitted to remain.

The point symmetry of shearing stress $\sigma_4 = \sigma_{23}$ is $mmm - D_{2h}$ with twofold axes along x and bisecting y and z. The symmetries of σ_5 and σ_6 are analogous. This requires the elimination of all axes except 2 and 2_1 axes in these directions. It rules out all mirrors and glide planes except those perpendicular to these directions.

The point symmetry of an electric field is $\infty mm - C_{\infty v}$. This requires the elimination of all inversion centers and all rotation or screw axes not parallel to the field. Mirrors or glide planes not parallel to the field must also be omitted.

In deducing the space group of reduced symmetry it may be useful to consider first how the point group must change. Then a table of subgroups, such as those found in the *International Tables for Crystallography* (1983) or in the report by Neubüser & Wondratschek (1969), may be consulted.

Table 1. *Comparison of analytical* (I) *and numerical* (II) *elastic constants for the LKG model of* NaCl *referred to different axis systems*

Units are 10^{-14} Pa^{-1}. Note that the elastic tensor for these models of NaCl has more symmetry than is required for general monoclinic or rhombohedral crystals.

	Cubic		Monoclinic		Rhombohedral	
$\mathbf{a}'$	$\mathbf{a}$		$\mathbf{a}$		$(\mathbf{c}+\mathbf{a})/2$	
$\mathbf{b}'$	$\mathbf{b}$		$\mathbf{b}$		$(\mathbf{a}+\mathbf{b})/2$	
$\mathbf{c}'$	$\mathbf{c}$		$(\mathbf{c}-\mathbf{a})/2$		$(\mathbf{b}+\mathbf{c})/2$	
Z	4		2		1	
	I	II	I	II	I	II
s_{11}	2785	2783	2556	2555	2556	2555
s_{22}	2785	2783	2785	2783	2479	2479
s_{33}	2785	2783	2556	2555	2556	2555
s_{12}	−745	−744	−745	−744	−592	−592
S_{13}	−745	−744	−515	−515	−668	−668
S_{23}	−745	−744	−745	−744	−592	−592
S_{44}	6143	6141	6143	6141	6754	6750
S_{55}	6143	6141	7060	7055	6448	6446
s_{66}	6143	6141	6143	6141	6754	6750
s_{16}	0	0	0	0	216	215
s_{36}	0	0	0	0	−216	−216
s_{45}	0	0	0	0	−432	−431
Others	0	0	0	0	0	0

Tests of the method

Lincoln, Koliwad & Ghate (1966) (LKG) have published elastic constants which they calculated analytically for several well-defined models of the alkali halides. As a test of the numerical methods described above, we calculated the elastic constants for NaCl using the model of LKG which includes only Coulomb interactions and nearest-neighbor repulsions. Our calculations were made for NaCl referred to three different axial systems as described in Table 1. The computation in the usual cubic axis system produces three independent compliance constants. In the monoclinic system, six values were obtained, and for the rhombohedral description, eight independent constants were calculated. The computations were generally made at ±0.25 and ±0.5 GPa for interpolation as described above.

The analytical calculation of LKG was repeated for more precision, and values of $c_{11} = 44{\cdot}61$, $c_{12} = 16{\cdot}28$ and $c_{44} = 16{\cdot}28$ GPa were obtained for the three stiffness coefficients. These were converted to compliance constants s_{ij} in the cubic system, and the appropriate tensor transformations were made to express them in the monoclinic and rhombohedral systems. These analytical results are given in Table 1 together with the coefficients obtained numerically. The discrepancy is generally less than 0·1%, although for two of the smaller values in the rhombohedral system it increases to approach 0·3%. We regard this as confirmation that the numerical techniques described here are capable of producing the same calculated values of physical properties as the usual analytical methods, which could be cumbersome for complicated models.

Conclusions

Methods have been developed for simulating the effects of pressure, stress and electric fields on computational models of crystals. By minimizing the total energy of the system we can compute the effects of these external forces on the lattice parameters, atomic coordinates, interatomic distances and molecular geometry. It should be possible to simulate second-order phase transitions which occur under the influence of pressure. The same should be true of ferroelastic transitions, which may be induced by shearing stresses, or of ferroelectric transitions, which occur under the influence of an electric field. We can calculate the bulk modulus, elastic constants, limiting tensile strength, piezoelectric coefficients, and static dielectric constants. By applying more than one kind of force simultaneously we can obtain higher-order elastic constants or the pressure derivatives of the elastic or piezoelectric coefficients.

In forthcoming papers the authors will describe the application of these methods to the calculation of the elastic constants of the minerals forsterite (the olivine form of Mg_2SiO_4) and diopside (the pyroxene $CaMgSi_2O_6$).

APPENDIX

Matrix **C**, for the conversion of coordinates from a general crystal system to the IEEE (1978) standard Cartesian system, can be expressed in several ways. A simple form, analogous to that presented by Rollett (1965), is

$$\mathbf{C}=\begin{pmatrix} a\sin\beta & -b\sin\alpha\cos\gamma^* & 0\\ 0 & b\sin\alpha\sin\gamma^* & 0\\ a\cos\beta & b\cos\alpha & c\end{pmatrix}. \qquad (29)$$

With program *WMIN* we find it convenient to compute first the inverse matrix $\mathbf{C}^{-1}$ which, expressed in the tensor notation of Patterson (1959), is

$$\mathbf{C}^{-1}=\begin{pmatrix} (g_{33}/gg^{22})^{1/2} & g^{21}/(g^{22})^{1/2} & 0\\ 0 & (g^{22})^{1/2} & 0\\ -g_{13}/(gg^{22}g_{33})^{1/2} & g^{23}/(g^{22})^{1/2} & 1/(g_{33})^{1/2}\end{pmatrix}. \qquad (30)$$

Here g_{ij} is the direct metric tensor, which *WMIN* derives from the lattice parameters as

$$g_{ij}=a_ia_j\cos\alpha_k; \qquad (31)$$

g^{ij} is the reciprocal metric tensor, obtained by inverting g_{ij}; and g is the determinant of g_{ij}, so that $g^{1/2}=V$, the direct cell volume. Matrix **C** is then obtained by inverting $\mathbf{C}^{-1}$.

References

Born, M. & Mayer, J. E. (1932). *Z. Phys.* **75**, 1–18.
Brown, G. E. & Fenn, P. M. (1979). *Phys. Chem. Miner.* **4**, 83–100.
Busing, W. R. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 57–72.
Busing, W. R. (1972*a*). *J. Chem. Phys.* **57**, 3008–3010.
Busing, W. R. (1972*b*). *Acta Cryst.* **A28**, S252.
Busing, W. R. (1981). *WMIN.* Report ORNL–5747. Oak Ridge National Laboratory, Oak Ridge, TN.
Busing, W. R. (1982). *J. Am. Chem. Soc.* **104**, 4829–4836.
Busing, W. R. (1983). *Acta Cryst.* **A39**, 340–347.
Catlow, C. R. A. & Mackrodt, W. C. (1982). In *Computer Simulation of Solids*, edited by C. R. A. Catlow & W. C. Mackrodt, pp. 3–20. New York: Springer-Verlag.
Catlow, C. R. A. & Norgett, M. J. (1973). *J. Phys. C*, **6**, 1325–1339.
Catlow, C. R. A. & Parker, S. C. (1982). In *Computer Simulation of Solids*, edited by C. R. A. Catlow & W. C. Mackrodt, pp. 222–240. New York: Springer-Verlag.
Gavezzoti, A. & Simonetta, M. (1975). *Acta Cryst.* **A31**, 645–654.
Giese, R. F. Jr & Datta, P. (1973). *Am. Mineral.* **58**, 471–479.
Hall, D., Starr, T. H., Williams, D. E. & Wood, M. K. (1980). *Acta Cryst.* **A36**, 494.
Hall, D. & Williams, D. E. (1975). *Acta Cryst.* **A31**, 56–58.
Huler, E., Sharon, R. & Warshel, A. (1977). Quantum Chemistry Program Exchange, Vol. 11, program 325. Department of Chemistry, Indiana Univ.
IEEE (1978). Standard 176–1978. The Institute of Electrical and Electronic Engineers Inc., New York.
International Tables for Crystallography (1983). Vol. A. Dordrecht, Boston: Reidel.
Kitaigorodsky, A. I. (1973). *Molecular Crystals and Molecules.* New York: Academic Press.
Lincoln, R. C., Koliwad, K. M. & Ghate, P. B. (1966). *Phys. Status Solidi*, **18**, 265–277. (In Table 1 the values of the Pauling coefficients β_{++} and β_{--} should be interchanged.)
Matsui, M. & Matsumoto, T. (1982). *Acta Cryst.* **A38**, 513–515.
Matsui, M. & Watanabé, T. (1981). *Acta Cryst.* **A37**, 728–734.
Miyamoto, M. & Takeda, H. (1980). *Geochem. J.* **14**, 243–248.
Momany, F. A., Carruthers, L. M. & Scheraga, H. A. (1974). *J. Phys. Chem.* **78**, 1621–1630.
Muhlhausen, C. & Gordon, R. G. (1981). *Phys. Rev. B*, **23**, 900–923.
Nelder, J. A. & Mead, R. (1965). *Comput. J.* **7**, 308–313.
Neubüser, J. & Wondratschek, H. (1969). *Maximal Subgroups of the Space Groups.* Report. Karlsruhe.
Nye, J. F. (1957). *Physical Properties of Crystals.* Oxford: Clarendon.
Ohashi, Y. & Burnham, C. W. (1972). *J. Geophys. Res.* **77**, 5761–5766.
Parker, S. C. (1983). Thesis. TP968, AERE Harwell, Oxfordshire, England.
Patterson, A. L. (1959). In *International Tables for X-ray Crystallography*, Vol. II, pp. 56–61. Birmingham: Kynoch Press.
Rollett, J. S. (1965). *Computing Methods in Crystallography*, pp. 22–23. Oxford: Pergamon Press.
Rosenbrock, H. H. (1960). *Comput. J.* **3**, 175–184.
Slaughter, M. (1966). *Geochim. Cosmochim. Acta*, **30**, 315–322.
Taddei, G., Righini, R. & Manzelli, P. (1977). *Acta Cryst.* **A33**, 626–628.
Timofeeva, T. V., Chernikova, N. Yu. & Zorkii, P. M. (1980). *Usp. Khim.* **49**, 966–997; *Engl. trans*: *Russ. Chem. Rev.* **49**, 509–525.
Tosi, M. P. & Fumi, F. G. (1964). *J. Phys. Chem. Solids*, **25**, 45–52.

WARSHEL, A. (1977). *Comput. Chem.* **1**, 195–202.
WARSHEL, A. & LEVITT, M. (1982). Quantum Chemistry Program Exchange, Vol. 11, program 247. Department of Chemistry, Indiana Univ.
WARSHEL, A. & LIFSON, S. (1970). *J. Chem. Phys.* **53**, 582–594.
WEIDNER, D. J. & SIMMONS, G. (1972). *J. Geophys. Res.* **77**, 826–847.
WILLIAMS, D. E. (1969). *Acta Cryst.* **A25**, 464–470.
WILLIAMS, D. E. (1972). *Acta Cryst.* **A28**, 629–635.
WILLIAMS, D. E. (1979). Quantum Chemistry Program Exchange, Vol. 11, program 373. Department of Chemistry, Indiana Univ.
WILLIAMS, D. E. & STARR, T. L. (1977). *Comput. Chem.* **1**, 173–177.
YUEN, P. S., MURFITT, R. M. & COLLIN, R. L. (1974). *J. Chem. Phys.* **61**, 2383–2393.

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Intensity Profile of Debye–Scherrer Line from Small Crystallites

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Abstract

The exact intensity formula of the **h**-line profile from small crystallites has been obtained as the orientational average of the diffraction intensity of the **h** plane given by Ino & Minami [*Acta Cryst.* (1979), A35, 163–170]. While the formula is expressed as a triple integral including a sine Fourier integral, it can be expressed asymptotically with respect to the crystal size according to the theorem of asymptotic expansion of a Fourier integral. Hence the profile can be estimated by the sum of terms of single-integral type. The first term is of the same type as Wilson's formula but it has been shown that second and third terms improve considerably the accuracy of the asymptotic estimation especially for a very small crystal. The **h**-line profile can be successfully calculated for quite a small crystal of any shape and any crystal system by the asymptotic formula, which can be computed as easily as Wilson's formula.

1. Introduction

The diffraction from the **h** plane of a single-crystal sample is concentrated into a small region of reciprocal space **b** near the reciprocal-lattice point **h**. The intensity profile from a powdered polycrystalline sample is given by averaging the intensity distribution function $I_{\mathbf{h}}(\mathbf{b})$ over all directions of vector **b**:

$$I_{\mathbf{h}}(b)=\int I_{\mathbf{h}}(\mathbf{b})\,\mathrm{d}\Omega_b/4\pi, \tag{1}$$

where b is the magnitude of vector **b**.

The calculation of the profile was first treated by Laue (1926). He gave the intensity from a parallelepiped crystal having N_j unit cells along the $\mathbf{a}_j$ axis ($j=1,2,3$) as follows:

$$I(\mathbf{b})=|F(\mathbf{b})|^2G(\mathbf{b}), \tag{2}$$

with

$$G(\mathbf{b})=\prod_{j=1}^{3}\left\{\frac{\sin(\pi N_jb_j)}{\sin(\pi b_j)}\right\}^2, \tag{3}$$

where $F(\mathbf{b})$ is the structure factor and **b** is expressed as $\mathbf{b}=b_1\mathbf{a}_1^*+b_2\mathbf{a}_2^*+b_3\mathbf{a}_3^*$, $\mathbf{a}_j^*$ being the reciprocal-unit-cell vectors. As an approximate function of $I_{\mathbf{h}}(\mathbf{b})$ for a large crystal he adopted a Gaussian function:

$$I_{\mathbf{h}}(b)\simeq|F(\mathbf{h})|^2\prod_{j=1}^{3}N_j^2\exp\{-\pi N_j^2(b_j-h_j)^2\}, \tag{4}$$

where

$$\mathbf{h}=h_1\mathbf{a}_1^*+h_2\mathbf{a}_2^*+h_3\mathbf{a}_3^*\ (h_1,h_2,h_3\ \text{integers}). \tag{5}$$

Instead of attempting the evaluation of integral (1), he approximated it by an integral over the tangent plane to the sphere with radius b at the point $b\mathbf{h}/|\mathbf{h}|$:

$$I_{\mathbf{h}}(b)\simeq\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}I_{\mathbf{h}}(\mathbf{b})\,\mathrm{d}b_1'\,\mathrm{d}b_2'/(4\pi b^2), \tag{6}$$

where (b_1', b_2') are orthogonal coordinates on the tangent plane. Finally he derived the intensity profile formula as follows:

$$I_{\mathbf{h}}(b)\simeq|F(\mathbf{h})|^2N_1N_2N_3\times\exp\{-\pi(b-|\mathbf{h}|)^2/\eta^2\}/(4\pi b^2V_c\eta), \tag{7}$$

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