COCHRAN, W. (1963). *Rep. Prog. Phys.* **26**, 1-45.
COCHRAN, W. & PAWLEY, G. S. (1964). *Proc. R. Soc. London,* **280**, 1-22.
COPPENS, P. (Project Reporter) (1984). *Acta Cryst.* A40, 184-195.
CRIADO, A., CONDE, A. & MÁRQUEZ, R. (1985a). *Acta Cryst.* A41, 158-163.
CRIADO, A., CONDE, A. & MÁRQUEZ, R. (1985b). *Acta Cryst.* A41, 316-320.
DAM, J., HARKEMA, S. & FEIL, D. (1983). *Acta Cryst.* B39, 760-768.

HELMHOLDT, R. B. & VOS, A. (1977). *Acta Cryst.* A33, 38-45.
MARADUDIN, A. A., MONTROLL, E. W., WEISS, G. H. & IPATOVA, I. P. (1971). *Theory of Lattice Dynamics in the Harmonic Approximation.* New York: Academic Press.
RAMACHANDRAN, G. N. & WOOSTER, W. A. (1951). *Acta Cryst.* **4**, 335-344.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY* 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Calculation of Elastic Constants by the Method of Crystal Static Deformation*

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Abstract

The contribution of homogeneous lattice deformations (neglecting internal strains) to elastic properties of crystals with triclinic or higher symmetry is examined. The deformed lattice constants are expressed as functions of the components of the finite Lagrangian strain tensor, and their derivatives are calculated. Thus equations are obtained that relate the second-order elastic constants to first and second partial derivatives of the static crystal energy with respect to unit-cell parameters. With the assumption of a two-body Born-type interatomic potential, the energy derivatives were calculated analytically, and a rigid-body approximation was introduced to account for molecular groups in the crystal structure. Test computations of elastic constants were performed for MgF_2 (rutile-type), benzene and naphthalene, using literature potential parameters optimized on structural data; results are discussed with respect to adequacy of the potentials and of the approximations of the model used.

Introduction

The semi-empirical modelling of interatomic and intermolecular forces in crystals has been developed intensively in recent years, in order to reproduce and possibly predict various chemical-physical properties by computer simulations (Catlow & Mackrodt, 1982). In the past, this work was mainly performed by fitting the potential parameters to structural properties only, so that the least-energy atomic configuration approached the experimental one as closely as possible (Busing, 1970; Kitaigorodskii, 1973; Williams, 1981); such potentials were then proposed for determining unknown crystal structures by minimum-energy search. In attempts to extend the modelling to other physical properties of crystals, elastic behaviour and vibrational spectroscopic frequencies are usually considered, as they are related to the slope changes of the energy hypersurface (in the space of atomic position vectors) at its minimum point. However, vibrational properties are accounted for by dynamical methods only, whereas the crystal elasticity can be related both to lattice dynamics and to the statics of equilibrium atomic configuration. In the former case a microscopic crystal deformation changing with time is examined, through atomic oscillations during the propagation of an elastic wave (long-wavelength acoustic vibration mode); in the latter, a macroscopic static deformation of the crystal is assumed, implying atomic shifts from equilibrium positions that are constant with time. In both cases the elastic properties express the correlation between crystal strain and applied stress. The first full theory on the subject was developed by Born & Huang (1954).

A previous partial approach (Catti, 1981) is extended and the calculation of elastic constants by the method of crystal static deformation is considered here. The contribution of external strains will be taken into account by deriving equations that relate the elasticity tensor components to first and second partial derivatives of the crystal static energy with respect to lattice constants, calculated at zero strain, for tri-

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clinic or higher symmetry. This treatment is completely analytical, whereas other calculations (Busing & Matsui, 1984) are based on a numerical minimization of the energy simulating an external stress applied to the crystal structure. In principle the method is not restricted to two-body central potentials, and natural lattice coordinates without orthogonalization are used throughout, unlike the approach of Catlow & Mackrodt (1982) who follow Born & Huang's (1954) theory closely.

Reliable methods for calculating elastic constants seem to be attractive, as experimental determinations of these properties are not simple and need single crystals with adequate quality and dimensions. On the other hand, a knowledge of elastic behaviour of solids has noteworthy importance both in materials science and in geophysics. In crystallography, elasticity data are required to calculate the correction of Bragg diffraction intensities for thermal diffuse scattering, which cannot be neglected in accurate determinations of electron density. Models of the earth interior are based on observations of seismic waves, depending on elastic properties of crystalline phases present in the earth mantle.

Theory

Strain tensors

We consider a homogeneous deformation of the crystal lattice, which changes the unit-cell constants from the initial values $a, b, c, \alpha, \beta, \gamma = \{a_i\}_{i=1}^6$ to the final values $a', b', c', \alpha', \beta', \gamma' = \{a_i'\}_{i=1}^6$. Let O be a Cartesian basis, whose three orthonormal vectors have components with respect to the undeformed and deformed lattice bases forming the columns of the $\mathbf{R}$ and $\mathbf{R}'$ matrices, respectively; a representation of second-rank strain tensors in the O reference frame is searched, such that their components are explicit functions of old a_i and new a_i' lattice constants.

The fractional coordinates of a general point in space are left unchanged by a homogeneous deformation of the lattice; therefore, if $\mathbf{X}$ and $\mathbf{X}'$ are the Cartesian coordinates of that point before and after the deformation, the condition of equality of coordinates with respect to the unstrained and strained lattice bases is

$$\mathbf{R}'\mathbf{X}' = \mathbf{R}\mathbf{X}. \tag{1}$$

The strain tensor $\mathbf{e}$ (Nye, 1957) is defined by the relation $\mathbf{X}' - \mathbf{X} = \mathbf{e}\mathbf{X}$, so that using (1) we obtain $\mathbf{e} = \mathbf{R}'^{-1}\mathbf{R} - \mathbf{I}$ (where $\mathbf{I}$ is the identity matrix). However, the $\mathbf{e}$ tensor also expresses rigid rotations of the whole lattice, while the linear Lagrangian strain tensor $\boldsymbol{\varepsilon}$ and the finite Lagrangian strain tensor $\boldsymbol{\eta}$ do not have this disadvantage (Nye, 1957; Wallace, 1972). The following expressions are immediately obtained for $\boldsymbol{\varepsilon}$ and $\boldsymbol{\eta}$:

$$\boldsymbol{\varepsilon} \equiv \tfrac{1}{2}(\mathbf{e}+\mathbf{e}^T) = \tfrac{1}{2}[\mathbf{R}'^{-1}\mathbf{R}+(\mathbf{R}'^{-1}\mathbf{R})^T] - \mathbf{I}, \tag{2}$$

$$\boldsymbol{\eta} \equiv \tfrac{1}{2}(\mathbf{e}+\mathbf{e}^T+\mathbf{e}^T\mathbf{e}) = \tfrac{1}{2}[(\mathbf{R}'^{-1}\mathbf{R})^T(\mathbf{R}'^{-1}\mathbf{R})-\mathbf{I}]. \tag{3}$$

Similar relationships were derived previously in a lengthy way by Schlenker, Gibbs & Boisen (1978). As the elements of the $\mathbf{R}$ and $\mathbf{R}'$ matrices are functions of undeformed a_i and deformed a_i' lattice constants, these are the equations required.

The point is to decide which of the $\boldsymbol{\varepsilon}$ and $\boldsymbol{\eta}$ symmetrical tensors is better suited to representing the lattice change in the deformation. Born & Huang (1954) showed that $\boldsymbol{\eta}$ is appropriate for a strain of any magnitude, whereas $\boldsymbol{\varepsilon}$ is adequate either for an infinitesimal strain or for a finite strain to the first order of accuracy only. However, a different aspect will be analysed here. From (2) and (3), both tensors appear to depend on $\mathbf{R}$ and $\mathbf{R}'$. As the strain tensors are referred to the O basis, their dependence on $\mathbf{R}$, which expresses the orientation between the Cartesian and the undeformed lattice bases, is necessary; on the other hand, the apparent dependence on $\mathbf{R}'$ implies that there is a correlation between strained and unstrained lattice bases, which has no physical meaning. It can be shown that for $\boldsymbol{\varepsilon}$ this apparent dependence cannot be removed. The basic property of orthonormalization matrices, applied to $\mathbf{R}'$, gives $(\mathbf{R}'^{-1})^T\mathbf{R}'^{-1} = \mathbf{G}'$, where $\mathbf{G}'$ is the metric tensor of the deformed lattice. Substituting into (3) yields

$$\boldsymbol{\eta} = \tfrac{1}{2}(\mathbf{R}^T\mathbf{G}'\mathbf{R}-\mathbf{I}). \tag{4}$$

Thus the $\boldsymbol{\eta}$ tensor, unlike $\boldsymbol{\varepsilon}$, depends only on the metrics of the deformed lattice and not on its orientation with respect to the undeformed one.

The general case of a triclinic lattice deformed to a different geometry is examined. The standard orientation of the Cartesian basis with respect to the original triclinic cell is such that $\mathbf{i}_3 = \mathbf{c}/c$, $\mathbf{i}_1 = \mathbf{a}^*/a^*$, $\mathbf{i}_2 = \mathbf{i}_3 \times \mathbf{i}_1$ (Schlenker, Gibbs & Boisen, 1978); it follows that

$$\mathbf{R} = \begin{bmatrix} \dfrac{1}{a\sin\beta\sin\gamma^*} & 0 & 0 \\[2ex] \dfrac{\cos\gamma}{b\sin\alpha\sin\gamma^*} & \dfrac{1}{b\sin\alpha} & 0 \\[2ex] -\dfrac{1}{c\sin\gamma^*} & -\dfrac{\cos\alpha}{c\sin\alpha} & \dfrac{1}{c} \\[1ex] \times\left(\dfrac{\cos\alpha\cos\gamma^*}{\sin\alpha}+\dfrac{\cos\beta}{\sin\beta}\right) & & \end{bmatrix}. \tag{5}$$

The simplified Voigt notation (Nye, 1957) is adopted to transform the η_{ij} and G_{ij}' components into one-index terms: $\eta_i \equiv \eta_{ii}$ and $G_i' \equiv G_{ii}'$ for $i = 1, 2, 3$; $\eta_4 \equiv 2\eta_{23}$, $\eta_5 \equiv 2\eta_{13}$, $\eta_6 \equiv 2\eta_{12}$; $G_4' \equiv 2G_{23}'$, $G_5' \equiv 2G_{13}'$, $G_6' \equiv 2G_{12}'$, remembering that $G_{ij}' = a_i'a_j'\cos(\mathbf{a}_i', \mathbf{a}_j')$.

Now the symbols η and $\mathbf{G}'$ represent 6×1 linear instead of 3×3 square matrices; if the right-hand member of (4) is developed explicitly a linear form in the G'_i quantities is obtained, according to

$$\eta = \mathbf{Q}\mathbf{G}' - \mathbf{d}, \qquad (6)$$

where $\mathbf{Q}$ is a 6×6 square matrix whose components are bilinear terms in the R_{ij} elements, and $\mathbf{d} = [\frac{1}{2}\frac{1}{2}\frac{1}{2}0\,0\,0]$. If (6) is worked out in detail, explicit expressions can be obtained for the strain components η_i as functions of the deformed lattice constants a'_i; these, however, are not reported here because they are not strictly necessary for the following treatment. To calculate the expression of $\boldsymbol{\varepsilon}$ according to (2), the orientation of the deformed triclinic cell with respect to basis O must be specified through the $\mathbf{R}'$ matrix; for different choices of that orientation, different expressions of the $\boldsymbol{\varepsilon}$ tensor are obtained (*cf.* Appendix I).[†] Therefore, although several authors have treated lattice elasticity on the basis of $\boldsymbol{\varepsilon}$, the use of the finite Lagrangian strain tensor η is more correct.

Elastic equations

If the crystal deformation is carried out isothermally, the suitable thermodynamic potential to represent this process is the Helmholtz free energy F, and isothermal second-order elastic constants are defined (Wallace, 1972) as

$$c_{ijhk} \equiv (1/V)(\partial^2 F/\partial\eta_{ij}\,\partial\eta_{hk})_{\substack{T \\ \eta=0}}, \qquad (7)$$

being components of a fourth-rank tensor with symmetry properties $c_{ijhk} = c_{jihk} = c_{ijkh} = c_{hkij}$. As an extension of Hildebrand's equation of state (Tosi, 1964), where isotropic volume variations are considered, the changes of entropy and vibrational energy due to an isothermal static deformation are assumed to be very small compared with the change of lattice energy E and are neglected, so that

$$c_{ijhk} \simeq (1/V)(\partial^2 E/\partial\eta_{ij}\,\partial\eta_{hk})_0. \qquad (8)$$

This is equivalent to considering the frequencies of vibrational modes to be independent of volume and, more generally, of the crystal state of isothermal strain, which is exactly true in harmonic lattice dynamics and is a satisfactory approximation as far as anharmonic effects can be neglected (not very high temperatures). In the frame of this treatment, the variation of elastic constants with temperature depends only on the change of lattice energy due to thermal expansion: using unit-cell parameters and atomic coordinates measured at different tem-

peratures, in principle one can calculate the thermal dependence of E and then of c_{ijhk} by means of (8).

The above definition of elastic constants holds if no internal strains are caused inside the unit cell by the external lattice deformation, *i.e.* if the atomic displacements obey (1) (this must happen by symmetry reasons when atoms lie on inversion centres). If the atomic fractional coordinates do not remain constant, the total strain of the crystal structure is represented by the sum of the homogeneous lattice strain and of inner strain (Born & Huang, 1954). In this case the elastic constants defined by (8) make up just the contribution of the first strain term, to which that of the second term must be added to obtain the total values; the two contributions have been called partial and inner elastic constants, respectively, by Cousins (1978). In the present paper internal strains are not taken into account explicitly (*cf.* however the discussion of the rigid-body approximation below); the minor contribution of inner elastic constants will be considered in subsequent work.

According to the Voigt contraction of η_{ij} into η_i components, it follows from doubling of extra-diagonal terms that $\partial^2 E/\partial\eta_p\,\partial\eta_q = \partial^2 E/\partial\eta_{ij}\,\partial\eta_{hk}$, so that also elastic constants turn from four-index into two-index components: $c_{pq} = c_{ijhk}$. In order to relate energy derivatives with respect to strain components to energy derivatives with respect to lattice constants, the straightforward way is to use the general differentiation formula

$$(\partial^2 E/\partial\eta_p\partial\eta_q)_0 = \sum_{i,j}^{6} (\partial^2 E/\partial a'_i\,\partial a'_j)_0$$

$$\times (\partial a'_i/\partial\eta_p)_0(\partial a'_j/\partial\eta_q)_0$$

$$+ \sum_i^{6} (\partial E/\partial a'_i)_0(\partial^2 a'_i/\partial\eta_p\,\partial\eta_q)_0; \qquad (9)$$

all derivatives must be calculated at zero strain, *i.e.* for $\eta_i = 0$ and $a'_i = a_i$ ($i = 1, \ldots, 6$). For calculating the derivatives of lattice constants with respect to strain components, (6) is solved for $\mathbf{G}'$, obtaining $\mathbf{G}' = \mathbf{Q}^{-1}(\eta + \mathbf{d})$; then, by means of the differentiation formulae $\partial a'_i/\partial\eta_p = \sum_{h=1}^{6} (\partial a'_i/\partial G'_h)(\partial G'_h/\partial\eta_p)$ and $\partial^2 a'_i/\partial\eta_p\,\partial\eta_q = \sum_{h,k=1}^{6} (\partial^2 a'_i/\partial G'_h\,\partial G'_k)(\partial G'_h/\partial\eta_p)$ $\times (\partial G'_k/\partial\eta_q)$, the following expressions are derived:

$$(\partial a'_i/\partial\eta_p)_0 = \sum_h^{6} (\partial a'_i/\partial G'_h)_0(Q^{-1})_{hp},$$

$$(\partial^2 a'_i/\partial\eta_p\,\partial\eta_q)_0 = \sum_{h,k}^{6} (\partial^2 a'_i/\partial G'_h\,\partial G'_k)_0$$

$$\times (Q^{-1})_{hp}(Q^{-1})_{kq}. \qquad (10)$$

The matrix $\mathbf{Q}^{-1}$ corresponding to the $\mathbf{R}$ expression given in (5) was calculated and is as follows:

$$Q^{-1}=2\begin{bmatrix} a^2\sin^2\beta\sin^2\gamma^* & a^2\sin^2\beta\cos^2\gamma^* & a^2\cos^2\beta & -a^2\sin\beta\cos\beta\cos\gamma^* & a^2\sin\beta\cos\beta\sin\gamma^* & -a^2\sin^2\beta\sin\gamma^*\cos\gamma^* \\ 0 & b^2\sin^2\alpha & b^2\cos^2\alpha & b^2\sin\alpha\cos\alpha & 0 & 0 \\ 0 & 0 & c^2 & 0 & 0 & 0 \\ 0 & 0 & 2bc\cos\alpha & bc\sin\alpha & 0 & 0 \\ 0 & 0 & 2ac\cos\beta & -ac\sin\beta\cos\gamma^* & ac\sin\beta\sin\gamma^* & 0 \\ 0 & -2ab\sin\alpha\sin\beta & 2ab\cos\alpha\cos\beta & ab(\sin\alpha\cos\beta & ab\cos\alpha\sin\beta\sin\gamma^* & ab\sin\alpha\sin\beta\sin\gamma^* \\ & \times\cos\gamma^* & & -\cos\alpha\sin\beta\cos\gamma^*) & & \end{bmatrix};\quad (11)$$

of course, it depends on the orientation chosen for the Cartesian basis O with respect to the undeformed unit cell. The quantities $\partial a_i'/\partial G_h'$ and $\partial^2 a_i'/\partial G_h'\,\partial G_k'$ are obtained by straightforward differentiation; putting them into (10), the full set of derivatives of lattice constants with respect to strain components is worked out and is reported in Appendix II.† After substitution into (9), and with (8) taken into account, the formulae required, which relate the elastic constants to energy derivatives with respect to lattice parameters, are obtained. With $(\partial E/\partial a_i')_0$ and $(\partial^2 E/\partial a_i'\,\partial a_j')_0$ written as $\partial E/\partial a_i$ and $\partial^2 E/\partial a_i\,\partial a_j$ for shortness, the expression for c_{11} appears as follows:

$$c_{11}=(1/V)[\sin^4\beta\sin^4\gamma^*(a^2\,\partial^2 E/\partial a^2-a\,\partial E/\partial a)$$
$$+\sin^2\beta\cos^2\beta\sin^4\gamma^*\,\partial^2 E/\partial\beta^2$$
$$+\sin^2\gamma\cos^2\gamma\sin^4\beta^*\,\partial^2 E/\partial\gamma^2+2\sin\beta\cos\beta$$
$$\times\sin\gamma\cos\gamma\sin^2\beta^*\sin^2\gamma^*\,\partial^2 E/\partial\beta\,\partial\gamma$$
$$+2a\sin^3\beta\cos\beta\sin^4\gamma^*\,\partial^2 E/\partial a\,\partial\beta$$
$$+2a\sin^3\gamma\cos\gamma\sin^4\beta^*\,\partial^2 E/\partial a\,\partial\gamma$$
$$-\sin\beta\cos\beta(1+2\sin^2\beta)\sin^4\gamma^*\,\partial E/\partial\beta$$
$$-\sin\gamma\cos\gamma(1+2\sin^2\gamma)\sin^4\beta^*\,\partial E/\partial\gamma].\quad(12)$$

The expressions for the 20 triclinic elastic constants left are even longer than this one, and are not reported here; however, they can easily be derived from (9) and the tables of derivatives in Appendix II, as explained above. Instead we show below the special set of relationships for the 13 non-zero monoclinic elastic constants, which are much simpler:

$$c_{11}=(1/V)[\sin^4\beta(a^2\,\partial^2 E/\partial a^2-a\,\partial E/\partial a)$$
$$+\sin^2\beta\cos^2\beta\,\partial^2 E/\partial\beta^2$$
$$+2a\sin^3\beta\cos\beta\,\partial^2 E/\partial a\,\partial\beta$$
$$-\sin\beta\cos\beta(2\sin^2\beta+1)\,\partial E/\partial\beta]$$
$$c_{22}=(1/V)(b^2\,\partial^2 E/\partial b^2-b\,\partial E/\partial b)$$
$$c_{33}=(1/V)[c^2\,\partial^2 E/\partial c^2-c\,\partial E/\partial c$$
$$+\cos^4\beta(a^2\,\partial^2 E/\partial a^2-a\,\partial E/\partial a)$$
$$+2a\cos^2\beta\,\partial^2 E/\partial a\,\partial c+\sin^2\beta\cos^2\beta\,\partial^2 E/\partial\beta^2$$
$$-2a\sin\beta\cos^3\beta\,\partial^2 E/\partial a\,\partial\beta$$
$$-2c\sin\beta\cos\beta\,\partial^2 E/\partial c\,\partial\beta$$
$$+\sin\beta\cos\beta(2\cos^2\beta+1)\,\partial E/\partial\beta]$$

† See deposition footnote.

$$c_{12}=(1/V)(ab\sin^2\beta\,\partial^2 E/\partial a\,\partial b$$
$$+b\sin\beta\cos\beta\,\partial^2 E/\partial b\,\partial\beta)$$
$$c_{13}=(1/V)[ac\sin^2\beta\,\partial^2 E/\partial a\,\partial c$$
$$+\sin^2\beta\cos^2\beta(a^2\,\partial^2 E/\partial a^2-a\,\partial E/\partial a$$
$$-\partial^2 E/\partial\beta^2)+c\sin\beta\cos\beta\,\partial^2 E/\partial c\,\partial\beta$$
$$+\sin\beta\cos\beta(2\cos^2\beta-1)$$
$$\times(a\,\partial^2 E/\partial a\,\partial\beta-\partial E/\partial\beta)]$$
$$c_{23}=(1/V)(bc\,\partial^2 E/\partial b\,\partial c+ab\cos^2\beta\,\partial^2 E/\partial a\,\partial b$$
$$-b\sin\beta\cos\beta\,\partial^2 E/\partial b\,\partial\beta)$$
$$c_{44}=(1/V)(\partial^2 E/\partial\alpha^2+2\cos\beta\,\partial^2 E/\partial\alpha\,\partial\gamma$$
$$+\cos^2\beta\,\partial^2 E/\partial\gamma^2)$$
$$c_{55}=(1/V)[\sin^4\beta\,\partial^2 E/\partial\beta^2$$
$$+\sin^2\beta\cos^2\beta(a^2\,\partial^2 E/\partial a^2-a\,\partial E/\partial a)$$
$$-2a\sin^3\beta\cos\beta\,\partial^2 E/\partial a\,\partial\beta$$
$$+\sin\beta\cos\beta(2\sin^2\beta-1)\partial E/\partial\beta]$$
$$c_{66}=(1/V)\sin^2\beta\,\partial^2 E/\partial\gamma^2$$
$$c_{46}=(1/V)(\sin\beta\,\partial^2 E/\partial\alpha\,\partial\gamma+\sin\beta\cos\beta\,\partial^2 E/\partial\gamma^2)$$
$$c_{15}=(1/V)[\sin^3\beta\cos\beta(a^2\,\partial^2 E/\partial a^2$$
$$-a\,\partial E/\partial a-\partial^2 E/\partial\beta^2)$$
$$+\sin^2\beta(2\cos^2\beta-1)$$
$$\times(a\,\partial^2 E/\partial a\,\partial\beta-\partial E/\partial\beta)]$$
$$c_{25}=(1/V)(-b\sin^2\beta\,\partial^2 E/\partial b\,\partial\beta$$
$$+ab\sin\beta\cos\beta\,\partial^2 E/\partial a\,\partial b)$$
$$c_{35}=(1/V)[-c\sin^2\beta\,\partial^2 E/\partial c\,\partial\beta$$
$$+\sin\beta\cos^3\beta(a^2\,\partial^2 E/\partial a^2-a\,\partial E/\partial a)$$
$$+\sin^3\beta\cos\beta\,\partial^2 E/\partial\beta^2$$
$$-2a\sin^2\beta\cos^2\beta\,\partial^2 E/\partial a\,\partial\beta$$
$$+ac\sin\beta\cos\beta\,\partial^2 E/\partial a\,\partial c$$
$$+\sin^2\beta(2\cos^2\beta+1)\,\partial E/\partial\beta].\quad(13)$$

These equations (and also the corresponding ones for the general triclinic case) hold for the orientation of the Cartesian basis given by (5); if another $\mathbf{R}$ matrix is assumed, then different relationships are obtained. The alternative monoclinic orientation $\mathbf{i}_1=\mathbf{a}/a$, $\mathbf{i}_2=\mathbf{b}/b$, $\mathbf{i}_3=\mathbf{c}^*/c^*$ was considered, repeating the whole

analytical procedure until new equations replacing (13) were derived. These equations were also obtained from (13) by using the tensorial transformation rule

$$c'_{ijhk} = \sum_{m,n,p,q} c_{mnpq} T_{mi} T_{nj} T_{ph} T_{qk},\qquad(14)$$

where $\mathbf{T} = (\sin\beta\ 0\ -\cos\beta\ /\ 0\ 1\ 0\ /\ \cos\beta\ 0\ \sin\beta)$ is the transformation matrix of Cartesian axes from the former to the latter orientation, and c_{mnpq} and c'_{ijhk} are the elastic constants in general tensorial notation referred to such orientations, respectively (the contracted Voigt convention cannot be used for transformations of axes). To obtain the same result by two different ways is a good check for the correctness of calculations. Further, for the sake of comparison with experimental values, it is important to choose the set of equations corresponding to the orientation of Cartesian axes used in the measurements.

Method of calculation

Equations (13) hold quite generally for any type of interatomic forces. To perform actual calculations, however, a particular energy model has to be specified; the following simple two-body potential is the most widely used for semiempirical computations in complicated structures:

$$V(r_{ij}) = e^2 z_i z_j / r_{ij} - d_i d_j / r_{ij}^6 - q_i q_j / r_{ij}^8$$
$$+ b_i b_j \exp(-r_{ij}/\rho_{ij});\qquad(15)$$

e is the electron charge, and r_{ij}, ρ_{ij}, z_i, d_i, q_i, b_i are the distance between atoms i and j, the hardness parameter of ij repulsion, the atomic charge (in e units), the dipole–dipole dispersive, the dipole–quadrupole dispersive and repulsive constants, respectively. This potential accounts reasonably for both ionic (dominant electrostatic term) and molecular (dominant dispersive term) crystals; in the former case it is known as a Born–Mayer (Tosi, 1964), in the latter as a Buckingham (Williams, 1981) potential. A substantial fraction of bond covalency can also be taken into account by letting the moduli of atomic charges z_i take smaller values than those required by pure ionicity.

An important class of solids is characterized by the presence of molecular groups, containing covalent

interatomic bonds. Then only the intermolecular energy can be expressed by (15), while intramolecular interactions should be accounted for either by an appropriate covalent force field, e.g. the Morse potential (Williams, 1981; Price & Parker, 1984), or by a rigid-body approximation, implying that the molecular groups are quite undeformable under stress (Catti, 1982; Matsui & Busing, 1984). In the former case internal strains must be taken into account explicitly in a deformed crystal, as chemical bonds governed by different kinds of potentials will respond to stress inhomogeneously; in the latter, on the other hand, a pure external deformation of the crystal structure is quite conceivable, since the centre-of-mass position vectors of molecular units can be deformed homogeneously. However, a rigid-body external-strain approximation requires also that the molecular orientation with respect to the lattice is not changed during the deformation process; this may be accomplished in the simplest way by causing the α, β, γ cell angles to strain symmetrically with respect to the initial configuration. A bidimensional example of this process is shown in Fig. 1, and in Appendix III* the transformation matrix from a monoclinic to a triclinic lattice deformed symmetrically is derived.

According to the previously developed formalism (Catti, 1978, 1981), by summing the terms (15) over all atomic pairs an expression for E is obtained that is an explicit bilinear function of the potential parameters z_i, b_i, d_i, q_i. This bilinear dependence is also preserved in derivatives of the energy with respect to lattice constants:

$$\begin{aligned}(\partial^2 E/\partial a'_i\,\partial a'_j)_0 = \sum_{r=1}^{n}\sum_{s=r}^{n}&\ [z_r z_s(\partial^2 C^{el}_{rs}/\partial a'_i\,\partial a'_j)_0\\&+ d_r d_s(\partial^2 C^{DD}_{rs}/\partial a'_i\,\partial a'_j)_0\\&+ q_r q_s(\partial^2 C^{DQ}_{rs}/\partial a'_i\,\partial a'_j)_0\\&+ b_r b_s(\partial^2 C^{R}_{rs}/\partial a'_i\,\partial a'_j)_0];\qquad(16)\end{aligned}$$

an analogous formula holds for first derivatives, too. The C_{rs} coefficients depend only on lattice constants and on atomic fractional coordinates, except for C^R_{rs} depending on the ρ_{ij} parameters as well; their explicit expressions are reported in our previous papers (the C^{el}_{rs} quantities contain the rapidly converging Ewald double series). All derivatives of these coefficients were calculated analytically for a monoclinic unit cell deformed to triclinic; explicit formulas are available from the author on request. Particular care has to be taken when the rigid-body approximation is considered, as in that case the atomic fractional coordinates have non-zero derivatives with respect to lattice constants. A general interatomic vector inside the rigid molecular group is not affected by a lattice deformation, which then can be interpreted as a
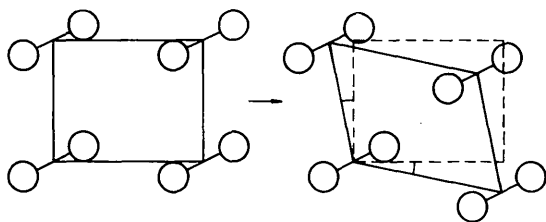

Fig. 1. Symmetrical angular strain of a bidimensional unit cell, keeping the orientation of the molecular unit constant with respect to the crystallographic axes.

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* See deposition footnote.

Table 1. Calculated elastic constants (GPa) (neglecting internal strains) for three crystalline compounds, compared to experimental adiabatic values (literature data)

References to crystal structure data and potential parameters used are given in the text.

MgF$_2$	$a = 4{\cdot}628$ Å		c_{11}	c_{33}	c_{12}	c_{13}	c_{44}	c_{66}		
(rutile-type)	$c = 3{\cdot}045$ Å	exp	137	199	87	61·5	56·4	95·5		($T = 293$ K)
$P4_2/mnm$		calc	138	252	90	59·2	59·1	90·1		

C$_6$H$_6$	$a = 7{\cdot}44$ Å		c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}	c_{44}	c_{55}	c_{66}	
benzene	$b = 9{\cdot}55$ Å	exp	6·1	6·6	5·8	3·5	4·0	3·9	2·0	3·8	1·5	(250 K)
$Pbca$	$c = 6{\cdot}92$ Å	calc	9·8	9·2	8·3	3·0	6·1	3·5	1·6	1·8	1·5	

C$_{10}$H$_8$	$a = 8{\cdot}266$ Å		c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}	c_{44}	c_{55}	c_{66}	c_{15}	c_{25}	c_{35}	c_{46}	
naphthalene	$b = 5{\cdot}968$ Å	exp	8·2	10·0	12·4	5·6	3·2	3·5	3·4	2·3	4·4	0·2	1·9	−2·9	0·7	(293 K)
$P2_1/a$	$c = 8{\cdot}669$ Å	calc	13·1	9·8	18·4	5·7	2·0	4·6	1·7	5·6	2·9	−0·3	1·6	−1·0	0·9	

simple change of crystallographic reference frame to express the components of that vector. If $\mathbf{D}$ is the matrix whose columns represent the vector components of the undeformed monoclinic basis I with respect to the deformed triclinic basis I', we have $\mathbf{x}(I') = \mathbf{D}\mathbf{x}(I)$, where $\mathbf{x}(I')$ and $\mathbf{x}(I)$ are the components of an interatomic vector $\mathbf{x}$ of the molecular unit with respect to basis I' and I, respectively. Therefore,

$$[\partial^2\mathbf{x}(I')/\partial a_i' \, \partial a_j']_0 = (\partial^2\mathbf{D}/\partial a_i' \, \partial a_j')_0\mathbf{x}(I). \quad (17)$$

By this formula the energy derivatives (16) were calculated also in the rigid-body approximation; the $\mathbf{D}$ matrix corresponding to a symmetrical deformation was used (cf. Appendix III), so that such derivatives can be considered to correspond to 'constant orientation' of the rigid molecular group. A computer program in Fortran was written to perform the calculations.

Discussion

Elastic constants were calculated for three compounds: a typical ionic solid, MgF$_2$ (rutile-type structure), and two molecular crystals for which the rigid-body approximation was used, benzene C$_6$H$_6$ and naphthalene C$_{10}$H$_8$. In all three cases measured values of elastic constants, experimental structural data and parameters of potentials of type (15) fitted to structural properties are available in the literature. The potentials optimized so as to reproduce only the equilibrium atomic arrangement are known to give a not too good agreement with elastic properties; thus these calculations are just a simple check of the method, and cannot discriminate surely between inadequacy of the approximations and inadequacy of the potential to explain the differences between calculated and observed elasticity data.

Structural parameters from neutron diffraction refinements were used for tetragonal MgF$_2$ (Vidal-Valat, Vidal, Zeyen & Kurki-Suonio, 1979), ortho-rhombic benzene (Bacon, Curry & Wilson, 1964) and monoclinic naphthalene (Pawley & Yeats, 1969). The potential parameters for the ionic compound were

determined by Yuen, Murfitt & Collin (1974) by the WMIN program (Busing, 1970). For both molecular crystals Williams's (1974) parameters, fitted to the structural configurations of 18 solid hydrocarbons (half aromatic and half aliphatic), were used; it should be remarked that the ρ_{ij} values had not been optimized but kept fixed to those derived from the graphite structure (C–C), from the quantum-mechanical repulsion of two H$_2$ molecules (H–H), and simply from their average value (C–H). Besides, following the same author, the positions of the H atoms were fixed so as to have C–H bonds 1·027 Å long, on the basis of the assumption that attractive or repulsive centres correspond to bonding electrons and so are closer to C atoms than H nuclei are. The calculated elastic constants are reported in Table 1 and compared to experimental values (Haussühl, 1968; Heseltine, Elliott & Wilson, 1964; Afanas'eva, 1968) for all three compounds.

The agreement appears to be good for MgF$_2$, whereas for benzene and naphthalene it is less good, but not unreasonable. The worst results are shown by the diagonal constants c_{11}, c_{22}, c_{33} of the two organic compounds, tending to give calculated values systematically larger than the measured ones. This might be due to neglect of thermal effects, which are much more important for molecular than for ionic crystals; however, this explanation was discarded after repeating all calculations for naphthalene with structural data determined at liquid N$_2$ temperature (Brock & Dunitz, 1982) and comparing results with elastic constants measured at the same temperature (Afanas'eva, 1968): both calculated and experimental values were larger than the corresponding room-temperature constants by about 50%, but their discrepancy did not change appreciably. Thus, if the observed disagreement is to be ascribed to approximations inherent in the model used, a more effective reason would probably be the neglect of contribution of internal strains, which would increase the stiffness of the crystal structure artificially to make up for missing molecular rearrangements inside the unit cell. However, we believe that the fitting of potential parameters of benzene and naphthalene was really too rough for this kind of calculation, so that it masks

the possible insufficiency of model approximations. In this respect, too, the results obtained seem to be encouraging; much work is needed to improve the potentials, if very accurate computations of elastic constants are wanted.

References

AFANAS'EVA, G. K. (1968). *Kristallografiya*, **13**, 1024-1027.
BACON, G. E., CURRY, N. A. & WILSON, S. A. (1964). *Proc. R. Soc. London Ser. A*, **279**, 98-110.
BORN, M. & HUANG, K. (1954). *Dynamical Theory of Crystal Lattices*. Oxford: Clarendon Press.
BROCK, C. P. & DUNITZ, J. D. (1982). *Acta Cryst.* B**38**, 2218-2228.
BUSING, W. R. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 57-72.
BUSING, W. R. & MATSUI, M. (1984). *Acta Cryst.* A**40**, 532-538.
CATLOW, C. R. A. & MACKRODT, W. C. (1982). *Computer Simulations of Solids. Lecture Notes in Physics*, Vol. 166. Berlin: Springer.
CATTI, M. (1978). *Acta Cryst.* A**34**, 974-979.
CATTI, M. (1981). *Acta Cryst.* A**37**, 72-76.
CATTI, M. (1982). *J. Phys. Chem. Solids*, **43**, 1111-1118.
CATTI, M. (1984). *Acta Cryst.* A**40**, C146.
COUSINS, C. S. G. (1978). *J. Phys. C*, **11**, 4867-4879.
HAUSSÜHL, S. (1968). *Phys. Status Solidi*, **28**, 127-134.
HESELTINE, J. C. W., ELLIOTT, D. W. & WILSON, O. B. (1964). *J. Chem. Phys.* **40**, 2584-2589.
KITAIGORODSKII, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
MATSUI, M. & BUSING, W. R. (1984). *Phys. Chem. Miner.* **11**, 55-59.
NYE, J. F. (1957). *Physical Properties of Crystals*. Oxford: Clarendon Press.
PAWLEY, G. S. & YEATS, E. A. (1969). *Acta Cryst.* B**25**, 2009-2013.
PRICE, G. D. & PARKER, S. C. (1984). *Phys. Chem. Miner.* **10**, 209-216.
SCHLENKER, J. L., GIBBS, G. V. & BOISEN, M. B. JR (1978). *Acta Cryst.* A**34**, 52-54.
TOSI, M. P. (1964). *Solid State Phys.* **16**, 1-120.
VIDAL-VALAT, G., VIDAL, J. P., ZEYEN, C. M. E. & KURKI-SUONIO, K. (1979). *Acta Cryst.* B**35**, 1584-1590.
WALLACE, D. C. (1972). *Thermodynamics of Crystals*. New York: Wiley.
WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71-77.
WILLIAMS, D. E. (1981). *Crystal Cohesion and Conformational Energies*, edited by R. M. METZGER, pp. 3-40. *Topics in Current Physics*, Vol. 26. Berlin: Springer.
YUEN, P. S., MURFITT, R. M. & COLLIN, R. L. (1974). *J. Chem. Phys.* **61**, 2383-2393.

Least-Squares Absolute-Structure Refinement.
Practical Experience and Ancillary Calculations

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Abstract

The least-squares refinement of non-centrosymmetric crystal structures as inversion twins is presented. It is shown that the absolute-structure (twin) parameter x may be used to define the chirality or polarity of untwinned crystals. The method has been applied to 20 compounds. The least-squares refinement of the absolute-structure parameter is rapid and stable. The value of x generally falls within three e.s.d.'s of the physically meaningful range $0 \le x \le 1$ and the e.s.d.'s increase as f'' becomes smaller. New residual and goodness-of-fit values are defined to judge the efficiency of the method. The estimated standard deviation of x, taken with a pseudo Durbin-Watson d statistic, provides an excellent criterion for the reliability of the absolute-structure determination. Refinements on data sets including very accurately measured Friedel pairs of reflections have also been tested. The determination of the free direction(s) of origin-free space groups and an efficient algorithm for the inversion of a crystal structure that refines to $x \simeq 1$ are given in detail. The data and procedural structures necessary for an efficient computer implementation of absolute-structure refinement are also considered. The formulae giving the correction for the effects of anomalous dispersion on $|F_{obs}|$ from an inversion-twinned crystal are given. These corrected $|F_{obs}|$ are the ones to be used in an electron-density calculation. The correlation of residuals following least-squares refinement is quantified by using a pseudo Durbin-Watson d statistic. The causes of the correlation, its effect on the value of x and its e.s.d., and ways of avoiding the correlation are considered. It is shown that in using x it is more suitable to refine on $|F|^2$ than $|F|$. A weighting scheme is presented and tested that increases the sensitivity of a refinement to absolute structure.