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Crystal Elasticity and Inner Strain: a Computational Model

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Abstract

The internal strain induced in a crystal structure by lattice deformation was considered. A suitable rotationally invariant representation was introduced and the corresponding contribution to the elastic constants was calculated. The method is based on the use of crystallographic rather than Cartesian atomic coordinates as variables of energy derivatives, with full exploitation of space-group symmetry and no constraint on the lattice geometry. A two-body Born interatomic potential was assumed, for both ionic and molecular crystals; energy derivatives of electrostatic lattice sums were calculated with the Ewald series. Molecular groups are treated within a rigid-body scheme based on Eulerian angles and translations as inner strain variables. Results of computations of Mg_2SiO_4 (forsterite) are reported, and the importance of optimizing the potential parameters against experimental data is discussed.

Introduction

Static models of crystals account for the response of the atomic structure to physical agents independent of temperature, such as mechanical stress and electric field. Being simpler than dynamic models, they provide an easier linkage between crystal properties and interatomic or intermolecular forces, by which the latter can be investigated. The property considered here is elasticity, following previous work (Catti, 1985) where the method of crystal static deformation to calculate elastic constants was outlined.

It is well known that when a crystal is stressed elastically, the induced deformation preserves the translational symmetry and can be considered the superposition of a pure lattice (external) strain and of an internal strain (Born & Huang, 1954). The former keeps the atomic fractional coordinates constant, changing just the unit-cell geometry, while the latter does the opposite. In the previous paper the contribution of external strain to crystal elasticity was considered explicitly, whereas here attention is focused onto inner strain. This is actually a relaxation of the crystal structure responding to a forced lattice change; by taking it into account, not only are more reliable values of elastic constants calculated, but also the structure changes caused by an applied anisotropic stress can be predicted.

Recently, the subject of internal strain in crystal structures has drawn considerable attention. A general thermodynamic theory was developed, where inner strain is considered as an independent physical variable on the same footing as macroscopic thermodynamic quantities (Barron, Gibbons & Munn, 1971). Besides, a number of experiments on uniaxially stressed crystals have produced energy-level shifts related to atomic displacements, which can be detected through the study of Jahn-Teller effect, spin-lattice coupling in electron paramagnetic resonance (EPR), stress-induced linear dichroism and other methods (Cousins, 1981; Devine, 1983). The most direct experimental technique to probe internal deformations in crystals relies of course on the strain dependence of the intensity of elastic scattering of X-rays or neutrons (Segmüller, 1964). Computational methods are particularly valuable in this respect, owing to the difficulty of experiments on anisotropically stressed crystals and to the need of interpretation of results when these are available.

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The method of calculation presented here is based on a natural choice for the variables representing the inner strain, and on the straightforward use of crystallographic atomic coordinates in the analytical computation of energy derivatives; the lattice strain is accounted for according to the previously developed model (Catti, 1985). A long-range Born potential was assumed for interatomic forces, holding for both ionic and molecular crystals. The presence of molecular groups in the structure was taken into account by introducing an explicit rigid-body model, which provides a test for the 'symmetrical strain' approximation formerly used.

Theory

Crystal deformation

Let the crystal structure be defined by the lattice constants $\{a_k\}_{k=1}^{6}$ ($\equiv a, b, c, \alpha, \beta, \gamma$) and by the coordinates referred to the lattice basis $\{\mathbf{x}_t\}_{t=1}^{N}$ of the N atoms in the unit cell. Alternatively, atomic positions can be specified by the coordinates $\{\mathbf{X}_t\}_{t=1}^{N}$ referred to a Cartesian basis; its three orthonormal vectors have components with respect to the lattice basis which form the columns of the square matrix $\mathbf{R}$, so that $\mathbf{X}_t = \mathbf{R}^{-1}\mathbf{x}_t$ holds. An external strain varies the unit-cell geometry only, and can be represented in the lattice reference frame by the metric tensor change $\mathbf{G}' - \mathbf{G}$; for every atom we also have that $\mathbf{x}'_t - \mathbf{x}_t = 0$, and $\mathbf{X}'_t - \mathbf{X}_t = \mathbf{e}\mathbf{X}_t$, where $\mathbf{e}$ is the strain tensor. Further on in this section all quantities with a prime are meant to be affected by an external strain. The most appropriate representation of a lattice deformation in the Cartesian reference frame was proved to be the finite Lagrangian strain tensor $\boldsymbol{\eta}$, as it is independent of the relative orientation of undeformed and deformed lattices (Catti, 1985). From a partial elaboration of equation (4) of the quoted paper, the relation between $\boldsymbol{\eta}$ and $\mathbf{G}' - \mathbf{G}$ is obtained:

$$\boldsymbol{\eta} = \tfrac{1}{2}\mathbf{R}^T(\mathbf{G}' - \mathbf{G})\mathbf{R}; \qquad (1)$$

the T superscript means matrix transposition. A pure inner strain leaves the lattice unvaried, so as to be represented naturally in crystallographic terms by the changes of fractional coordinates $\mathbf{x}_t^+ - \mathbf{x}_t$ for all atoms involved, while evidently $\mathbf{G}^+ - \mathbf{G} = 0$. All quantities with a + superscript are affected by internal strain. However, as the traditional theory of crystal elasticity is based on tensors, which are defined with respect to Cartesian bases, inner strain must be given a Cartesian representation as well.

The internal deformation is often expressed (*cf.* Catlow & Mackrodt, 1982) by the set of atomic displacements in Cartesian components occurring *after* the pure lattice strain (Fig. 1):

$$\mathbf{u}'_t \equiv \mathbf{X}'^{+}_t - \mathbf{X}'_t = \mathbf{R}'^{-1}(\mathbf{x}_t^+ - \mathbf{x}_t). \qquad (2)$$

Nevertheless the atomic shift $\mathbf{u}'_t$ is shown by the above equation to depend on the relative orientation between deformed and undeformed lattices through the matrix $\mathbf{R}'$, so that it lacks the rotational invariance required to represent the inner strain satisfactorily. An alternative Cartesian expression of atomic displacements due to internal deformation (Born & Huang, 1954; Cousins, 1978) is the following:

$$\begin{aligned}\mathbf{U}'_t &\equiv (\mathbf{e}+\mathbf{I})^T\mathbf{u}'_t = (2\boldsymbol{\eta}+\mathbf{I})\mathbf{R}^{-1}(\mathbf{x}_t^+ - \mathbf{x}_t)\\ &= \mathbf{R}^T\mathbf{G}'(\mathbf{x}_t^+ - \mathbf{x}_t).\end{aligned} \qquad (3)$$

This quantity is indeed rotationally invariant, but has a less-simple geometrical meaning than $\mathbf{u}'_t$. Besides, it is shown by (3) to depend explicitly on $\boldsymbol{\eta}$ or $\mathbf{G}'$: this would cause complications in transforming mixed energy derivatives $\partial^2 E/\partial x_{ti}\,\partial\eta_k$ into $\partial^2 E/\partial U'_{ti}\,\partial\eta_k$, because $\mathbf{U}'_t$ is a function of both $\mathbf{x}_t$ and $\boldsymbol{\eta}$ [*cf.* (12) below and the relevant discussion].

The use of a third variable is proposed here to represent the inner strain in Cartesian terms, following a previous hint (Barron, Gibbons & Munn, 1971):

$$\mathbf{u}_t \equiv \mathbf{X}_t^+ - \mathbf{X}_t = \mathbf{R}^{-1}(\mathbf{x}_t^+ - \mathbf{x}_t). \qquad (4)$$

A simple physical meaning can be associated with $\mathbf{u}_t$: it represents the Cartesian atomic shift which must occur *before* the lattice strain, so as to attain the same final atomic position as that produced by applying the $\mathbf{u}'_t$ shift (2) after the lattice strain (Fig. 1). The $\mathbf{u}_t$ displacement is rotationally invariant, and is related to $\mathbf{x}_t^+ - \mathbf{x}_t$ by (4) with no explicit dependence on $\boldsymbol{\eta}$; it is thus the natural Cartesian representation of the former quantity, analogously as is $\boldsymbol{\eta}$ for $\mathbf{G}' - \mathbf{G}$ in the case of lattice strain.

Elastic constants

A general deformation of the crystal structure is the sum of an external and an internal component, and is therefore represented by the $\boldsymbol{\eta}$ and $\mathbf{u}$ quantities. Adopting the Voigt notation, let $\boldsymbol{\eta}$ now mean a 6×1 linear instead of a 3×3 square matrix, while $\mathbf{u}$ is a $3N\times 1$ linear matrix containing the Cartesian components of inner strain (4) for every atom in the unit cell. Barron, Gibbons & Munn (1971) have distinguished a hypothetical case where all η_k ($k = 1, \ldots, 6$) and u_q ($q = 1, \ldots, 3N$) components are independent variables of the energy E (general regime), from the

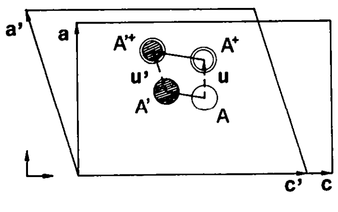

Fig. 1. Lattice and inner strains on the (010) plane, and corresponding shifts of atom A. See the text for the meaning of superscripts.

physically ordinary situation where only the η_k's are (macroscopic regime). In the latter case the u_q quantities are functions of the η_k's, and are determined by a condition of minimum for the energy (Born & Huang, 1954; Catlow & Mackrodt, 1982). A second-order approximation of the elastic energy gives

$$E = \tfrac{1}{2}\boldsymbol{\eta}^T\mathbf{V}_{\eta\eta}\boldsymbol{\eta} + \tfrac{1}{2}\mathbf{u}^T\mathbf{V}_{uu}\mathbf{u} + \boldsymbol{\eta}^T\mathbf{V}_{\eta u}\mathbf{u};$$

$$(\mathbf{V}_{\eta\eta})_{hk} \equiv \left(\frac{\partial^2 E}{\partial\eta_h\,\partial\eta_k}\right)_0, \quad (\mathbf{V}_{uu})_{pq} \equiv \left(\frac{\partial^2 E}{\partial u_p\,\partial u_q}\right)_0, \qquad (5)$$

$$(\mathbf{V}_{\eta u})_{kq} \equiv \left(\frac{\partial^2 E}{\partial\eta_k\,\partial u_q}\right)_0.$$

The quantities $\mathbf{V}_{\eta\eta}$ and $\mathbf{V}_{uu}$ are 6×6 and $3N\times 3N$ square matrices, respectively, while $\mathbf{V}_{\eta u}$ is a $6\times 3N$ rectangular matrix. All energy derivatives are calculated at the equilibrium structural configuration, as indicated by the zero subscript.

The condition of minimum $\partial E/\partial u_q = 0$ (for $q = 1,\ldots,3N$) leads to the equation

$$\mathbf{u} = -\mathbf{V}_{uu}^{-1}\mathbf{V}_{u\eta}\boldsymbol{\eta}, \qquad (6)$$

which can also be written as $\mathbf{u} = \mathbf{T}_{u\eta}\boldsymbol{\eta}$; $\mathbf{T}_{u\eta} \equiv -\mathbf{V}_{uu}^{-1}\mathbf{V}_{u\eta}$ is a representation of the internal strain tensor (Cousins, 1978), and gives a linear approximation of the dependence of inner strain on lattice strain. With this relationship structural changes induced by anisotropic stress can be calculated (Catti, 1987). By substituting (6) into (5), the expression of energy as a function of lattice strain only is obtained:

$$E = \tfrac{1}{2}\boldsymbol{\eta}^T(\mathbf{V}_{\eta\eta} - \mathbf{V}_{\eta u}\mathbf{V}_{uu}^{-1}\mathbf{V}_{u\eta})\boldsymbol{\eta}. \qquad (7)$$

In the frame of the static approximation (Catti, 1985) the elastic constants are $c_{hk} = (\partial^2 E/\partial\eta_h\,\partial\eta_k)_0/V$, and the 6×6 matrix $\mathbf{C}$ of which they are components is derived from (7):

$$\mathbf{C} = (1/V)(\mathbf{V}_{\eta\eta} - \mathbf{V}_{\eta u}\mathbf{V}_{uu}^{-1}\mathbf{V}_{u\eta}), \qquad (8)$$

where V is the volume of the crystal of energy E. Thus the elastic constants are expressed by the sum of a contribution from pure lattice strain, $\mathbf{V}_{\eta\eta}/V$, plus a contribution from pure inner strain, $-\mathbf{V}_{\eta u}\mathbf{V}_{uu}^{-1}\mathbf{V}_{u\eta}/V$, which are called partial and inner elastic constants, respectively (Cousins, 1978).

Computational method

Energy derivatives

As a thorough account of partial elastic constants was given previously (Catti, 1985), the calculation of inner elastic constants and of energy derivatives forming the $\mathbf{V}_{uu}$ and $\mathbf{V}_{u\eta}$ matrices will be examined here. The usual two-body interatomic potential of Born-Mayer type (electrostatic+dispersive+repulsive) is assumed, and the crystal static energy E is expressed by formulas given in previous papers (Catti, 1978, 1981). For simplicity, only the electrostatic term of the energy $E_{\rm el}$ will be considered, but quite analogous results hold for the two terms left as well. If the symbol $F(\mathbf{x})$ represents the Ewald double series calculated for an interatomic vector $\mathbf{x}$ within the unit cell [equation (3) of Catti (1978)], and $\mathcal{N}$, e, Z, z_r indicate Avogadro's number, the electron charge, the number of formula units in the unit cell and the electric charge on the rth atom in the asymmetric unit, respectively, then the following expression can be derived for the energy derivatives:

$$\frac{\partial^2 E_{\rm el}}{\partial x_{ri}\,\partial x_{smj}} = -\frac{\mathcal{N}e^2}{Z} z_r z_s \left[\frac{\partial^2 F(\mathbf{x})}{\partial x_i\,\partial x_j}\right]_{\mathbf{x}=\mathbf{x}_{sm}-\mathbf{x}_r}$$
$$(\text{excluding } s=r,\ m=1). \qquad (9)$$

x_{ri} means the ith fractional coordinate ($i = 1, 2, 3$) of atom r in the asymmetric unit ($m = 1$ is understood), while x_{smj} is the jth coordinate of atom s in the mth equivalent position within the unit cell. This formula does not hold when the two atoms coincide ($s = r$, $m = 1$); in this case the correct expression can be derived by the condition that the elastic energy of a rigid translation of the whole crystal be zero:

$$\frac{\partial^2 E_{\rm el}}{\partial x_{ri}\,\partial x_{rj}} = \frac{\mathcal{N}e^2}{Z} z_r \sum_{s=1}^{n} z_s \sum_{m=1}^{p_s} \left[\frac{\partial^2 F(\mathbf{x})}{\partial x_i\,\partial x_j}\right]_{\mathbf{x}=\mathbf{x}_{sm}-\mathbf{x}_r}, \qquad (10)$$

where the sums exclude the case $s = r$, $m = 1$; n and p_s indicate the number of atoms in the asymmetric unit and the symmetry multiplicity of the sth atom. Mixed derivatives with respect to atomic coordinates and lattice constants are given by a similar relation:

$$\frac{\partial^2 E_{\rm el}}{\partial x_{ri}\,\partial a_k} = -\frac{\mathcal{N}e^2}{Z} z_r \sum_{s=1}^{n} z_s \sum_{m=1}^{p_s} \left[\frac{\partial^2 F(\mathbf{x})}{\partial x_i\,\partial a_k}\right]_{\mathbf{x}=\mathbf{x}_{sm}-\mathbf{x}_r}; \qquad (11)$$

again the case $s = r$, $m = 1$ is excluded. The derivatives of repulsive E_R and dispersive E_{DD}, E_{DQ} terms of the energy are given by analogous formulas, where $F(\mathbf{x})$ is substituted simply by the corresponding quantities $F_R(\mathbf{x})$, $F_{DD}(\mathbf{x})$ and $F_{DQ}(\mathbf{x})$ (Catti, 1981). By straightforward differentiation of all lattice sums F, detailed analytical expressions were obtained for the whole set of energy derivatives, which are not reported here for the sake of brevity. It should be stressed that differentiation was performed with respect to crystallographic and not Cartesian atomic coordinates, thus preserving the lattice representation of the crystal structure and obtaining simpler formulas than in other treatments (Born & Huang, 1954; Catlow & Mackrodt, 1982).

The required components of matrices $\mathbf{V}_{uu}$ and $\mathbf{V}_{u\eta}$ given in (5) are calculated, taking into account the relation (4) between atomic fractional coordinates and inner strain variables:

$$\begin{aligned} \frac{\partial^2 E}{\partial u_{ri}\,\partial u_{smj}} &= \sum_{i',j'}^{3}\!{}_{1}\, \frac{\partial^2 E}{\partial x_{ri'}\,\partial x_{smj'}} R_{i'i} R_{j'j}, \\ \frac{\partial^2 E}{\partial u_{ri}\,\partial \eta_k} &= \sum_{1}^{3}{}_{i'} \frac{\partial^2 E}{\partial x_{ri'}\,\partial \eta_k} R_{i'i} \\ &= \sum_{1}^{3}{}_{i'} \sum_{1}^{6}{}_{h} \frac{\partial^2 E}{\partial x_{ri'}\,\partial a_h} \frac{\partial a_h}{\partial \eta_k} R_{i'i}, \end{aligned} \tag{12}$$

where the quantities $\partial a_h/\partial \eta_k$ were derived previously (Catti, 1985). It can be noticed that if the quantities (3) instead of (4) had been used as inner strain variables, then because of their explicit dependence on $\boldsymbol{\eta}$ the calculation of $\partial^2 E/\partial u_{ri}\,\partial \eta_k$ derivatives would have been much more complicated.

By the above formulas the $(\mathbf{V}_{uu})_{pq}$ and $(\mathbf{V}_{\eta u})_{kq}$ matrix components which are not symmetry related can be computed. They concern energy derivatives with respect to at least an atom belonging to the asymmetric unit. All other components are symmetry related to the previous ones through the equations

$$\begin{aligned} \frac{\partial^2 E}{\partial x_{rmi}\,\partial x_{sn'j}} &= \sum_{1}^{3}{}_{i',j'} \frac{\partial^2 E}{\partial x_{ri'}\,\partial x_{snj'}} (\mathbf{S}_m^{-1})_{i'i} (\mathbf{S}_m^{-1})_{j'j}, \\ \frac{\partial^2 E}{\partial x_{rmi}\,\partial a_k} &= \sum_{1}^{3}{}_{i'} \frac{\partial^2 E}{\partial x_{ri'}\,\partial a_k} (\mathbf{S}_m^{-1})_{i'i}; \end{aligned} \tag{13}$$

the $\mathbf{S}_m$ matrix represents the rotational part of the mth symmetry operation of the space group, so that the relation $\mathbf{x}_{sn'} = S_m \mathbf{x}_{sn}$ holds.

Rigid-body model

A large number of crystal structures contain molecular groups, either neutral or electrically charged, which are characterized by prevalently covalent interatomic bonds. Spectroscopic studies and structure determinations at high pressure or temperature have shown that intramolecular deformations are usually very small with respect to intermolecular ones, so as to justify the use of a rigid-body approximation (Catti, 1982). In this case the inner strain $\mathbf{u}$ is simply expressed by three Euler rotation angles φ_1, φ_2, φ_3 and three Cartesian displacements u_{01}, u_{02}, u_{03} of the molecular group considered as a rigid unit. If we introduce an internal Cartesian reference frame denoted by the I subscript, the crystallographic coordinates of atoms belonging to the rigid group can be related to inner strain coordinates by the relation

$$\mathbf{x}_r = \mathbf{RPX}_{Ir} + \mathbf{x}_0, \tag{14}$$

where $\mathbf{P}(\varphi_1, \varphi_2, \varphi_3)$ is the Euler matrix whose columns contain the vector components of basis I with respect to the crystal Cartesian basis, so that $\mathbf{PX}_{Ir} = \mathbf{X}_r$.

The components of matrices $\mathbf{V}_{uu}$ and $\mathbf{V}_{u\eta}$ defined in (5) are now energy derivatives with respect to orientation angles (or rigid translations) of the molecular group, and to lattice strain components; they can be calculated straightforwardly by the differentiation formula

$$\begin{aligned} \frac{\partial^2 E}{\partial \varphi_i\,\partial \varphi_j} &= \sum_{1}^{n}{}_{r,s} \sum_{1}^{3}{}_{i',j'} \frac{\partial^2 E}{\partial x_{ri'}\,\partial x_{sj'}} \frac{\partial x_{ri'}}{\partial \varphi_i} \frac{\partial x_{sj'}}{\partial \varphi_j} \\ &\quad + \sum_{1}^{n}{}_{r} \sum_{1}^{3}{}_{i'} \frac{\partial E}{\partial x_{ri'}} \frac{\partial^2 x_{ri'}}{\partial \varphi_i\,\partial \varphi_j}, \end{aligned} \tag{15}$$

where for simplicity the molecular group was assumed to coincide with the asymmetric unit, and the derivatives $\partial x_{ri'}/\partial \varphi_i$ and $\partial^2 x_{ri'}/\partial \varphi_i\,\partial \varphi_j$ are evaluated through (14) and the knowledge of $P(\varphi_1, \varphi_2, \varphi_3)$. As for derivatives with respect to φ_i and a_k we have

$$\begin{aligned} \frac{\partial^2 E}{\partial \varphi_i\,\partial a_k} &= \sum_{1}^{n}{}_{r,s} \sum_{1}^{3}{}_{i',j'} \sum_{1}^{p_s}{}_{m} \frac{\partial^2 E}{\partial x_{ri'}\,\partial x_{smj'}} \frac{\partial x_{ri'}}{\partial \varphi_i} \frac{\partial x_{smj'}}{\partial a_k} \\ &\quad + \sum_{1}^{n}{}_{r} \sum_{1}^{3}{}_{i'} \left(\frac{\partial^2 E}{\partial x_{ri'}\,\partial a_k} \frac{\partial x_{ri'}}{\partial \varphi_i} + \frac{\partial E}{\partial x_{ri'}} \frac{\partial^2 x_{ri'}}{\partial \varphi_i\,\partial a_k} \right); \end{aligned} \tag{16}$$

the quantities $\partial x_{smj'}/\partial a_k$ and $\partial^2 x_{ri'}/\partial \varphi_i\,\partial a_k$ can be calculated from (14) or similar relations for symmetrical coordinates, taking into account the dependence of $\mathbf{R}$ on lattice constants a_k.

If there are two or more symmetry-related molecular groups in the unit cell, then the mth rigid group is characterized by the orientation matrix $\mathbf{P}_m = \mathbf{S}_m\mathbf{P}$. As $\mathbf{P}_m$ is a function of φ_{1m}, φ_{2m}, φ_{3m}, the previous equation can be solved to give the relations $\varphi_{im}(\varphi_i)$ between Euler angles of the mth symmetrical group and those of the group chosen as asymmetric unit. In the independent energy derivatives of type (15) and (16) at least one differentiation angle belongs to the asymmetric unit group; all other derivatives can be related to the previous ones as follows:

$$\frac{\partial^2 E}{\partial \varphi_{im}\,\partial \varphi_{jn'}} = \frac{\mathrm{d}\varphi_i}{\mathrm{d}\varphi_{im}} \frac{\mathrm{d}\varphi_j}{\mathrm{d}\varphi_{jm}} \frac{\partial^2 E}{\partial \varphi_i\,\partial \varphi_{jn}},$$

where $\mathbf{S}_m\mathbf{S}_n = \mathbf{S}_{n'}$.

In a general case, the crystal structure may contain molecular groups and single atoms or ions together; then the linear matrix $\mathbf{u}$ characterizing the internal strain would have as components both rigid-body rotations and translations and Cartesian displacements of isolated atoms.

Symmetry considerations

The components of matrices $\mathbf{V}_{uu}$ and $\mathbf{V}_{u\eta}$ are energy derivatives calculated at zero strain: therefore they must obey the full space-group symmetry of the equilibrium crystal structure, as implied by (13). It follows that if symmetry-related atoms or molecular groups are treated formally as independent, then the corresponding computed deformations in the $\mathbf{u}$ vector of (6) are symmetrical as well. As the inner deformations must be consistent with the structural symmetry, that can be broken by the lattice strain only: for instance, a fourfold axis is destroyed by a uniaxial strain along a different lattice direction, or a mirror plane is broken by a shear strain on a different lattice plane. If an atom or rigid group lies on a symmetry element which cannot be destroyed by the lattice strain, then the symmetry-constrained coordinates undergo a zero inner deformation. In particular, the centrosymmetry of a structure can never be broken by a static elastic strain within this model, because any lattice strain is consistent with the symmetry centre.

Thus in the treatment of internal deformation the simplest scheme is to consider the degrees of freedom of atoms or molecular groups belonging to the asymmetric unit only as independent variables; however, energy derivatives must now include the shifts of symmetry-related atoms or groups. These symmetry-constrained derivatives are given by the formulas

$$\begin{aligned}\left(\frac{\partial^2 E}{\partial x_{ri}\,\partial x_{sj}}\right)_S &= p_r \sum_{1}^{p_s}{}_m \sum_{1}^{3}{}_{i'} \frac{\partial^2 E}{\partial x_{ri}\,\partial x_{smi'}} (\mathbf{S}_m)_{i'j},\\ \left(\frac{\partial^2 E}{\partial x_{ri}\,\partial a_k}\right)_S &= p_r \frac{\partial^2 E}{\partial x_{ri}\,\partial a_k}.\end{aligned} \tag{17}$$

By substituting into (12), the corresponding values of the $(\mathbf{V}_{uu})_{pq}$ and $(\mathbf{V}_{\eta u})_{kq}$ components can be derived, if we take into account that the **u** vector now contains atomic shifts within the asymmetric unit instead of the whole unit cell.

A computer program was written in Fortran to calculate the contribution of inner strain to elastic constants on the basis of the above method. It is made up of two modules: the first computes the energy derivatives (10) and (11) and writes them onto a disk file; these are read and worked out by the second module, according to the rigid-body scheme if required.

Discussion

Calculations of crystal elastic properties by static methods are usually based on an extension of Hildebrand's approximation (Tosi, 1964), implying that changes of entropy and vibrational energy due to an isothermal static deformation are very small compared with the change of static energy E and can be neglected. This is summarized by the relation

$$c_{hk} = (\partial^2 F/\partial \eta_h\, \partial \eta_k)_0/V \simeq (\partial^2 E/\partial \eta_h\, \partial \eta_k)_0/V,$$

where F is the Helmholtz free energy (Catti, 1985). Neglecting the effect of thermal vibrations on crystal elasticity should not introduce appreciable errors in the results, so long as the temperature is much lower than the melting point. The validity of this procedure is confirmed when semiempirical parameters of the interatomic potential are fitted by the static method, and then the optimized potential is used to calculate vibrational properties (*e.g.* spectroscopic frequencies or heat capacity, entropy) which compare well with experimental data. This was accomplished recently for the polymorphs of Mg_2SiO_4, whose lattice-dynamical and thermodynamical properties were reproduced successfully with a potential fitted to data of binary oxides (Price, Parker & Leslie, 1987).

In order to evaluate the importance of the inner-strain contribution to elastic constants, and to test the method of calculation proposed, a full calculation was performed for forsterite, α-Mg_2SiO_4, whose orthorhombic structure (Hazen, 1976) has a great crystal-chemical and mineralogical importance. Its main feature is the presence of SiO_4 tetrahedra with Si–O bonds much stiffer than Mg-O bonds in MgO_6 coordination octahedra, so that a rigid-body model for SiO_4 groups is advisable. In a previous calculation (Catti, 1982) only the lattice strain was taken into account and the parameters of the Born potential were fitted to some structural variables and to six elastic constants (excluding shear components c_{44}, c_{55}, c_{66}). With these parameters all elastic constants were recalculated according to the present method which includes the inner strain contribution, obtaining a slightly worse agreement with experimental values than before; in particular the diagonal components c_{11}, c_{22}, c_{33} were substantially lower.

Therefore, a full optimization of energy parameters was carried out in the new model; the expression of two-body potential terms is

$$\begin{aligned}E_{ij} = e^2 z_i z_j / r_{ij} + \beta_{ij} \exp\,[(r_i + r_j - r_{ij})/(\rho_i + \rho_j)]\\ - d_i d_j / r_{ij}^6 - q_i q_j / r_{ij}^8,\end{aligned}$$

where r_{ij} is the interatomic distance. The dispersive coefficients d_i and q_i used are the same as in the previous work (Catti, 1982), and come from experimental refractive data of MgO; the β_{ij} values are the Pauling coefficients. Six parameters were optimized: the charges z_O, z_{Mg}, the repulsive radii r_O, r_{Mg} and the hardness parameters ρ_O, ρ_{Mg} of oxygen and magnesium atoms. The Si charge is given by the electroneutrality condition $z_{Si} = -4z_O - 2z_{Mg}$, while the repulsive and dispersive interactions of Si are neglected because very small. The fitting process was based upon 21 equations involving nine elastic constants and twelve structural variables [cell edges, orientation angles and translations of the SiO_4 rigid group, coordinates of the Mg(2) atom]. All details will be reported and discussed in a separate paper (Catti, in preparation). The following best values of parameters were obtained: $z_O = -1\cdot20$, $z_{Mg} = 1\cdot59$ e, $r_O = 1\cdot25$, $r_{Mg} = 0\cdot81$, $\rho_O = 0\cdot135$, $\rho_{Mg} = 0\cdot125$ Å. It should be noticed that they correspond to a larger ionicity and larger repulsion than previous values (Catti, 1982). This stiffer potential is consistent with the structural relaxation under stress which is implied in the inner strain model.

Table 1. *Elastic constants* (GPa) *of forsterite,* Mg_2SiO_4

Experimental (Suzuki *et al.*, 1983), calculated (partial, inner, total) values and total/experimental ratios are reported. For shear components, partial and inner values are given for a non-symmetrical and a symmetrical lattice deformation.

	Experimental	Partial	Inner	Total	
c_{11}	329	351	22	329	1·000
c_{22}	200	213	15	198	0·990
c_{33}	236	243	8	235	0·996
c_{12}	67	61	−7	68	1·015
c_{13}	68	62	3	59	0·868
c_{23}	73	68	−8	76	1·041
c_{44}	67	97 84	28 16	68	1·015
c_{55}	81	131 96	42 7	89	1·099
c_{66}	81	101 91	20 10	81	1·000

The optimized parameters were used to compute the elastic constants reported in Table 1, where they are compared with experimental values (Suzuki, Anderson & Sumino, 1983). Contributions due to pure lattice strain and to pure inner strain, as well as total values, are shown distinctly. Besides, for shear constants c_{44}, c_{55}, c_{66} the values corresponding to a symmetrical and to a non-symmetrical lattice deformation (Catti, 1985) are given. In the former case the unit-cell angles α, β, γ change symmetrically with respect to the undeformed configuration, whereas in the latter the convention leaving the deformed $\mathbf{c}'$ vector parallel to $\mathbf{c}$ and $\mathbf{b}^{*\prime}$ parallel to $\mathbf{b}^*$ is assumed. The symmetrical deformation was introduced as a reasonable model for calculating the shear elastic constants when the contribution of inner strain is neglected in the frame of a rigid-body scheme. If inner strain is taken into account, the total value of each elastic constant is obviously independent of the kind of lattice deformation assumed. The data of Table 1 confirm that the model of symmetrical strain gives a better agreement between calculated partial elastic constants and experimental ones.

In a comparison of the total calculated values with those measured, a very good overall agreement is observed, with an average relative deviation of 3·5%. The largest deviations are found for the c_{13} and c_{55} components, which are smaller and larger by 13 and 10%, respectively, than the corresponding experimental values; for all other constants, the average relative deviation of 1·2% obtained is really excellent and practically within the experimental error. It should be remarked that both the c_{13} and c_{55} components refer to a stress-strain effect on the (010) plane; this contains the [001] direction of chains of MgO_6 octahedra sharing edges, while along [100] such chains are linked *via* SiO_4 tetrahedra sharing corners with them. Thus a strong crystal-chemical anisotropy characterizes the bonds on this plane (rigid packing inside the chains, and flexible connection between them), so that a two-body central-force model for Mg–O and O–O interactions may not be fully adequate for the present case.

Two other previous calculations of elastic constants of forsterite, including the effect of inner strain, gave average relative deviations from experimental values of 12·7% (Matsui & Busing, 1984) and 8·9% [(Price & Parker, 1984): best result from potential *P*5]. In both cases the dispersive energy was not taken into account. In the first paper the elastic properties were computed indirectly by a numerical procedure, and the z_{Mg} charge was kept fixed at the ideal value +2 without optimization. A subsequent refinement (Matsui & Matsumoto, 1985), where the z_{Mg} charge was relaxed and bond-distance-stretching (Si–O) and bond-angle-bending (O–Si–O) energy terms were introduced, gave an average relative deviation of 11·9%. In the second paper, the computation followed the method of Catlow & Mackrodt (1982), using a Morse potential to account for Si–O interactions instead of the rigid-body model. The improved results obtained in the present work are probably related to the inclusion of a dispersive energy term (not fitted, but calculated from measured data), and to details of the optimization process which will be discussed elsewhere (Catti, in preparation).

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