A Generalized Born–Mayer Parametrization of the Lattice Energy in Orthorhombic Ionic Crystals

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Abstract

Equations relating the first and second partial derivatives of the lattice energy (with respect to the unit-cell constants) to the components of the elastic stiffness tensor have been obtained for orthorhombic crystals. By assuming a Born–Mayer model for the lattice energy, and using Ewald's method for calculating the electrostatic term, formulas are derived for the computation of the lattice-energy derivatives. In these expressions, the repulsive coefficients and the atomic charges appear as unknown parameters which can be determined by solving the above equations, provided that experimental data about elasticity and thermal-expansion tensors are available.

Introduction

According to the most widely used model for ionic solids (Born & Mayer, 1932; Tosi, 1964), three terms (electrostatic, repulsive and dispersive) contribute to the lattice energy of a unit cell; each one of them in its turn is the sum of two-body contributions:

$$\mathscr{E}_L = \mathscr{E}_{el} + \mathscr{E}_R + \mathscr{E}_D = \tfrac{1}{2} e^2 \sum_{i,j}^{N} {}_1 z_i z_j \sum_{-\infty}^{+\infty} {}_1 |\mathbf{x}_{ij} + \mathbf{1}|^{-1}$$

$$+ \tfrac{1}{2} \sum_{i,j}^{N} {}_1 b_{ij} \sum_{-\infty}^{+\infty} {}_1 \exp\left(-|\mathbf{x}_{ij} + \mathbf{1}|/p\right)$$

$$- (\tfrac{1}{2} \sum_{i,j}^{N} {}_1 d_{ij} \sum_{-\infty}^{+\infty} {}_1 |\mathbf{x}_{ij} + \mathbf{1}|^{-6}$$

$$+ \tfrac{1}{2} \sum_{i,j}^{N} {}_1 q_{ij} \sum_{-\infty}^{+\infty} {}_1 |\mathbf{x}_{ij} + \mathbf{1}|^{-8}) \quad \text{(if } i = j, \mathbf{1} \neq 0). \quad (1)$$

e is the electron charge, N is the number of ions in the cell, z_i is an ionic charge referred to the electron charge, $\mathbf{x}_{ij}$ is an interatomic vector between the ith and jth ions contained in the unit cell, $\mathbf{1}$ is a vector of the direct lattice; d_{ij} and q_{ij} are the dipole–dipole and dipole–quadrupole coefficients of the van der Waals energy, and can be calculated by the London and Mayer

formulas, respectively, provided that ion polarizabilities and average excitation energies are known (Tosi, 1964). If a fully ionized model is assumed, the electrostatic and dispersive terms can be computed *ab initio*. This is not the case, however, for the repulsive term, since the repulsion coefficients b_{ij} and the 'hardness parameter' p cannot be calculated directly from any experimental quantities; they must then be considered as unknown parameters of the energy and are determined by a semi-empirical fitting to the elastic properties of the crystal. In the classic Born–Mayer approach, only cubic crystals are considered, so that the energetics of the elastic behaviour is accounted for satisfactorily by the derivatives of the molar internal energy E with respect to the molar volume v:

$$\left(\frac{\partial E}{\partial v}\right)_T = -p + T\frac{\alpha}{\beta}, \quad (2)$$

$$\left(\frac{\partial^2 E}{\partial v^2}\right)_T = \frac{1}{v\beta} \left\{ 1 + T\left[\frac{1}{\beta}\left(\frac{\partial \beta}{\partial T}\right)_p + \frac{\alpha}{\beta^2}\left(\frac{\partial \beta}{\partial p}\right)_T\right]\right\}, \quad (3)$$

where α is the volume thermal expansivity, β is the isothermal compressibility, p and T are pressure and temperature. In the Hildebrand approximation, derivatives of the internal energy and of the lattice energy are equal; it is then simple to differentiate (1) with respect to the volume (or to the cell constant), to substitute the results into (2) and (3) and to solve the two equations which are obtained with respect to the unknown repulsive parameters. The real problem is to get a sufficient number of equations, from different crystals, for a given number of ion–ion parameters which must be determined (Catti, 1979).

However, if crystals with symmetry lower than cubic are considered, the anisotropic character of their elastic properties must be taken into account, so that (2) and (3) are no more adequate. This may be an advantage in some respects because more unknown parameters (*e.g.* the ionic charges) can be introduced into (1), provided that a higher number of equations is available. The

objective of this work is to propose an extension of the Born–Mayer parametrization of the lattice energy to low-symmetry crystals, developing detailed calculations for the orthorhombic case.

Internal energy and elastic properties

In the general case of a triclinic crystal on which an anisotropic stress is applied, the internal energy change caused by the induced strain is expressed by the following equation (Nye, 1960; Wallace, 1972):

$$\left(\frac{\partial E}{\partial \varepsilon_{ij}}\right)_{T,\varepsilon'} = v\tau_{ij} - vT\left(\frac{\partial \tau_{ij}}{\partial T}\right)_{\varepsilon} \simeq vT \sum_{p=1}^{3} \sum_{q=1}^{3} c_{ijpq}\, \alpha_{pq}, \quad (4)$$

where ε_{ij}, τ_{ij}, α_{pq} are components of the symmetrical second rank tensors of linear Lagrangian strain, of stress and of thermal expansion, respectively. ε' means all tensor components different from those under the differential sign; $c_{ijpq} = (\partial \tau_{ij}/\partial \varepsilon_{pq})_{T,\varepsilon'}$ is a component of the fourth-rank tensor of the isothermal elastic stiffness. For pressures which are not very high, $v\tau_{ij}$ can be neglected with respect to $vT(\partial \tau_{ij}/\partial T)_{\varepsilon}$. To obtain the second partial derivatives of the energy, let us differentiate (4) with respect to ε_{rs}:

$$\left(\frac{\partial^2 E}{\partial \varepsilon_{ij}\, \partial \varepsilon_{rs}}\right)_{T,\varepsilon'} = vc_{ijrs} - vT\left(\frac{\partial c_{ijrs}}{\partial T}\right)_{\varepsilon}$$

$$= vc_{ijrs} - vT\left[\left(\frac{\partial c_{ijrs}}{\partial T}\right)_{\tau}\right.$$

$$+ \sum_{k=1}^{3} \sum_{m=1}^{3} \left(\frac{\partial c_{ijrs}}{\partial \tau_{km}}\right)_{T,\tau'}\left(\frac{\partial \tau_{km}}{\partial T}\right)_{\varepsilon}\right]$$

$$= vc_{ijrs} - vT\left[\left(\frac{\partial c_{ijrs}}{\partial T}\right)_{\tau}\right.$$

$$\left. - \sum_{k=1}^{3} \sum_{m=1}^{3} \left(\sum_{p=1}^{3} \sum_{q=1}^{3} c_{kmpq}\, \alpha_{pq}\right)\left(\frac{\partial c_{ijrs}}{\partial \tau_{km}}\right)_{T,\tau'}\right].$$

$$(5)$$

Since there are six independent strain-tensor components ε_{ij}, there are also six equations of type (4) for the first derivatives of the energy, and 21 equations of type (5) for the second derivatives. These equations are the generalization of (2) and (3).

It is not simple, however, to express explicitly the dependence of the lattice energy (1) on the strain-tensor components; the derivatives of the lattice energy with respect to the cell constants can be calculated much

more easily, so that their relationships with the derivatives in (4) and (5) must be considered:

$$\left(\frac{\partial E}{\partial a_k}\right)_{a'} = \sum_{i=1}^{3} \sum_{j=1}^{3} \left(\frac{\partial E}{\partial \varepsilon_{ij}}\right)_{T,\varepsilon'}\left(\frac{\partial \varepsilon_{ij}}{\partial a_k}\right)_{a'}, \quad (6)$$

$$\left(\frac{\partial^2 E}{\partial a_k\, \partial a_m}\right)_{a'}$$

$$= \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{r=1}^{3} \sum_{s=1}^{3} \left(\frac{\partial^2 E}{\partial \varepsilon_{ij}\, \partial \varepsilon_{rs}}\right)_{T,\varepsilon'}\left(\frac{\partial \varepsilon_{ij}}{\partial a_k}\right)_{a'}\left(\frac{\partial \varepsilon_{rs}}{\partial a_m}\right)_{a'}$$

$$+ \sum_{i=1}^{3} \sum_{j=1}^{3} \left(\frac{\partial E}{\partial \varepsilon_{ij}}\right)_{T,\varepsilon'}\left(\frac{\partial^2 \varepsilon_{ij}}{\partial a_k\, \partial a_m}\right)_{a'}. \quad (7)$$

Expressions relating the strain-tensor components ε_{ij} to the cell constants a_k ($k = 1, \ldots, 6$) have been worked out for monoclinic symmetry (Morimoto & Tokonami, 1969) and for the general case of triclinic symmetry (Ohashi & Burnham, 1973; Schlenker, Gibbs & Boisen, 1978). In the orthorhombic case $\varepsilon_{ij} = (a_i/a_{0,i} - 1)\, \delta_{ij}$, where δ_{ij} is the Kronecker symbol and $a_{0,i}$ is the equilibrium ith cell constant ($a_{0,1} = a$, $a_{0,2} = b$, $a_{0,3} = c$); by differentiating, we have $\partial \varepsilon_{ii}/\partial a_k = a_{0,k}^{-1}\, \delta_{ik}$, and all second derivatives are equal to zero. Since the derivatives in (6) and (7) must be calculated for $a_k = a_{0,k}$, for simplicity the symbol a_k will be used to mean the equilibrium value $a_{0,k}$ of the cell constant at temperature T. By substituting the derivatives of the strain-tensor components and the derivatives of the energy (4) and (5) into (6) and (7), and taking into account that $\alpha_{pq} = \alpha_{qq}\, \delta_{pq}$, a set of nine independent equations is obtained:

$$\left(\frac{\partial E}{\partial a_k}\right)_{a'} = \frac{vT}{a_k} \sum_{q=1}^{3} c_{kkqq}\, \alpha_{qq}; \quad (8)$$

$$\left(\frac{\partial^2 E}{\partial a_k\, \partial a_m}\right)_{a'} = \frac{v}{a_k a_m}\left[c_{kkmm} - T\left(\frac{\partial c_{kkmm}}{\partial T}\right)_{\varepsilon}\right], \quad (9)$$

where

$$\left(\frac{\partial c_{kkmm}}{\partial T}\right)_{\varepsilon} = \left(\frac{\partial c_{kkmm}}{\partial T}\right)_{\tau}$$

$$- \sum_{i=1}^{3} \sum_{j=1}^{3} \left(\sum_{q=1}^{3} c_{ijqq}\alpha_{qq}\right)\left(\frac{\partial c_{kkmm}}{\partial \tau_{ij}}\right)_{T,\tau'}. \quad (10)$$

By extending the Hildebrand approximation (Tosi, 1964) to the case of anisotropic strain, the vibrational part of the internal energy can be assumed not to be affected by the isothermal strain, so that $(\partial E/\partial \varepsilon_{ij})_{T,\varepsilon'} = (\partial E_L/\partial \varepsilon_{ij})_{T,\varepsilon'}$, and the internal energy E can be substituted by the lattice energy E_L in all the foregoing derivatives. Then the nine equations (8) and (9) relate derivatives which can be calculated from the theoretical

expression (1) to experimental quantities. Since adiabatic rather than isothermal elastic constants are usually reported in the literature, the relative conversion must be performed using the equation (Wallace, 1972)

$$s_{ijkm} = s_{ijkm}^{S} + \alpha_{ij}\,\alpha_{km}\,\frac{vT}{C_p},\qquad(11)$$

where s_{ijkm} and s_{ijkm}^{S} are the isothermal and adiabatic elastic compliances, which are related to the corresponding stiffnesses by expressions such as

$$\sum_{r=1}^{3}\sum_{q=1}^{3} s_{ijrq}\,c_{rqkm} = \tfrac{1}{2}(\delta_{ik}\,\delta_{jm} + \delta_{im}\,\delta_{jk});$$

C_p is the heat capacity at constant pressure. The term $T(\partial c_{kkmm}/\partial T)_{\varepsilon}$ which appears in (9) is very small with respect to c_{kkmm}; neglecting it would cause a small but appreciable error. To calculate that term, (10) must be used: however, the derivatives $(\partial c_{kkmm}/\partial \tau_{ij})_{T,\tau'}$ are usually not known, while the value of $(\partial c_{kkmm}/\partial p)_{T}$, measured by applying an isotropic pressure, is generally available. Then, by taking into account the relation

$$\left(\frac{\partial c_{kkmm}}{\partial p}\right)_{T} = -\sum_{r=1}^{3}\left(\frac{\partial c_{kkmm}}{\partial \tau_{rr}}\right)_{T,\tau'},\qquad(12)$$

the following approximation can be introduced:

$$\left(\frac{\partial c_{kkmm}}{\partial \tau_{ij}}\right)_{T,\tau'} \simeq -\frac{1}{3}\left(\frac{\partial c_{kkmm}}{\partial p}\right)_{T}\delta_{ij};\qquad(13)$$

then (10) is substituted by the approximate expression:

$$\left(\frac{\partial c_{kkmm}}{\partial T}\right)_{\varepsilon} \simeq \left(\frac{\partial c_{kkmm}}{\partial T}\right)_{p}$$
$$+\frac{1}{3}\left(\frac{\partial c_{kkmm}}{\partial p}\right)_{T}\sum_{l=1}^{3}\left(\sum_{q=1}^{3} c_{llqq}\,\alpha_{qq}\right),\quad(14)$$

which is to be inserted into (9). The right-hand members of (8) and (9) can then be calculated, provided that the single-crystal thermal-expansion coefficients, the elastic constants and their temperature and pressure derivatives are available.

The lattice energy derivatives

Following the same demonstration used in a previous paper (Catti, 1978) for the electrostatic term, it is easy

to show that the lattice energy of a mole of crystalline substance can be written as:

$$E_L = E_{el} + E_R + E_D = \sum_{r=1}^{n}\sum_{s=r}^{n} z_r z_s\,C_{rs}^{el}$$
$$+\sum_{r=1}^{n}\sum_{s=r}^{n} b_{rs}\,C_{rs}^{R} + \sum_{r=1}^{n}\sum_{s=r}^{n} d_{rs}\,C_{rs}^{DD}$$
$$+\sum_{r=1}^{n}\sum_{s=r}^{n} q_{rs}\,C_{rs}^{DQ},\qquad(15)$$

where n is the number of ions in the asymmetric unit. The coefficients C_{rs}^{R}, C_{rs}^{DD}, C_{rs}^{DQ} are expressed by the same formulas [(9) and (10) in Catti's (1978) paper] which hold for C_{rs}^{el}, provided that the factor e^2 is omitted; the functions $F(x)$ in the three cases are, respectively,

$$F_R(x) = \sum_{-\infty}^{+\infty}{}_1\exp\left(-|x+1|/\rho\right),$$

$$F_{DD}(x) = -\sum_{-\infty}^{+\infty}{}_1|x+1|^{-6}$$

and

$$F_{DQ}(x) = -\sum_{-\infty}^{+\infty}{}_1|x+1|^{-8}.$$

In (15) the only quantities which depend on the unit-cell constants are the coefficients C_{rs}^{el}, C_{rs}^{R}, C_{rs}^{DD}, C_{rs}^{DQ}, so that the first derivatives of the lattice energy are expressed as follows:

$$\left(\frac{\partial E_L}{\partial a_k}\right)_{a'} = \sum_{r=1}^{n}\sum_{s=r}^{n} z_r z_s\left(\frac{\partial C_{rs}^{el}}{\partial a_k}\right)_{a'} + \sum_{r=1}^{n}\sum_{s=r}^{n} b_{rs}\left(\frac{\partial C_{rs}^{R}}{\partial a_k}\right)_{a'}$$
$$+\sum_{r=1}^{n}\sum_{s=r}^{n} d_{rs}\left(\frac{\partial C_{rs}^{DD}}{\partial a_k}\right)_{a'} + \sum_{r=1}^{n}\sum_{s=r}^{n} q_{rs}\left(\frac{\partial C_{rs}^{DQ}}{\partial a_k}\right)_{a'};\quad(16)$$

analogous expressions hold for the second derivatives. In order to calculate the derivatives of the C_{rs} coefficients, the four functions $F(x)$ must be differentiated with respect to the cell constants; these derivatives will be reported for crystals with orthorhombic symmetry.

In the case of the electrostatic term, the function $F(x)$ is expressed by Ewald series as reported by equation (3) of Catti (1978); its derivatives are

$$\left(\frac{\partial F_{el}}{\partial a_k}\right)_{a'} = \frac{2}{\pi V a_k} \sum_{-\infty}^{+\infty}{}'_{\mathbf{h}} \left[\frac{2h_k^2}{a_k^2}\left(\frac{1}{h^2}+\frac{\pi^2}{A^2}\right) - 1 \right]\frac{1}{h^2}$$
$$\times \exp\left(-\frac{\pi^2 h^2}{A^2}\right)\cos(2\pi\mathbf{h}.\mathbf{x})$$
$$- a_k \sum_{-\infty}^{+\infty}{}_{\mathbf{l}} \frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^2}\left[\frac{\mathrm{erfc}(A|\mathbf{x}+\mathbf{l}|)}{|\mathbf{x}+\mathbf{l}|} \right.$$
$$\left. + \frac{2A}{\sqrt{\pi}}\exp(-A^2|\mathbf{x}+\mathbf{l}|^2) \right]; \qquad (17)$$

$$\left(\frac{\partial^2 F_{el}}{\partial a_k^2}\right)_{a'} = \frac{4}{\pi V a_k^2}\sum_{-\infty}^{+\infty}{}'_{\mathbf{h}}\left[\frac{2h_k^4}{a_k^4}\left(\frac{1}{h^2}+\frac{\pi^2}{A^2}\right)^2 \right.$$
$$\left. - \frac{5h_k^2}{a_k^2}\left(\frac{1}{h^2}+\frac{\pi^2}{A^2}\right) + \frac{2h_k^4}{a_k^4}\frac{1}{h^4} + 1 \right]\frac{1}{h^2}$$
$$\times \exp\left(-\frac{\pi^2 h^2}{A^2}\right)\cos(2\pi\mathbf{h}.\mathbf{x})$$
$$+ a_k^2 \sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^2}\left\{ \left[\frac{3(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^2} - \frac{1}{a_k^2}\right] \right.$$
$$\times \frac{\mathrm{erfc}(A|\mathbf{x}+\mathbf{l}|)}{|\mathbf{x}+\mathbf{l}|} + \frac{2A}{\sqrt{\pi}}\left[\frac{3(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^2} \right.$$
$$\left.\left. + 2A^2(x_k+l_k)^2 - \frac{1}{a_k^2}\right] \right.$$
$$\left. \times \exp(-A^2|\mathbf{x}+\mathbf{l}|^2) \right\}; \qquad (18)$$

$$\left(\frac{\partial^2 F_{el}}{\partial a_k\,\partial a_m}\right)_{a'} = \frac{2}{\pi V a_k a_m}\sum_{-\infty}^{+\infty}{}'_{\mathbf{h}}\left[\frac{4h_k^2 h_m^2}{a_k^2 a_m^2}\left(\frac{1}{h^2}+\frac{\pi^2}{A^2}\right)^2 \right.$$
$$- \left(\frac{2h_k^2}{a_k^2}+\frac{2h_m^2}{a_m^2}\right)\left(\frac{1}{h^2}+\frac{\pi^2}{A^2}\right)$$
$$\left. + \frac{4h_k^2 h_m^2}{a_k^2 a_m^2}\frac{1}{h^4} + 1 \right]\frac{1}{h^2}\exp\left(-\frac{\pi^2 h^2}{A^2}\right)$$
$$\times \cos(2\pi\mathbf{h}.\mathbf{x})$$
$$+ a_k a_m \sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2(x_m+l_m)^2}{|\mathbf{x}+\mathbf{l}|^4}$$
$$\times \left[\frac{3\,\mathrm{erfc}(A|\mathbf{x}+\mathbf{l}|)}{|\mathbf{x}+\mathbf{l}|} \right.$$
$$\left. + \frac{2A}{\sqrt{\pi}}(2A^2|\mathbf{x}+\mathbf{l}|^2+3) \right.$$
$$\left. \times \exp(-A^2|\mathbf{x}+\mathbf{l}|^2) \right]. \qquad (19)$$

V is the volume of a unit cell, $\mathbf{h}$ is a vector of the reciprocal lattice, $\mathrm{erfc}(y) = 2/\sqrt{\pi}\int_y^{+\infty}\exp(-t^2)\,dt$ is the complementary error function, $\sum'$ is a sum over noncentrosymmetric lattice vectors only, excluding the zero vector; A is the arbitrary parameter which conditions the relative convergence rates of the two partial series (Catti, 1978).

The partial derivatives of the functions $F_R(\mathbf{x})$, $F_{DD}(\mathbf{x})$ and $F_{DQ}(\mathbf{x})$ with respect to the cell parameters are

$$\left(\frac{\partial F_R}{\partial a_k}\right)_{a'} = -\frac{a_k}{\rho}\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|}\exp\left(-\frac{|\mathbf{x}+\mathbf{l}|}{\rho}\right); \qquad (20)$$

$$\left(\frac{\partial^2 F_R}{\partial a_k^2}\right)_{a'} = \frac{a_k^2}{\rho}\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^2}\left[\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|} \right.$$
$$\left. + \frac{(x_k+l_k)^2}{\rho} - \frac{|\mathbf{x}+\mathbf{l}|}{a_k^2} \right]$$
$$\times \exp\left(-\frac{|\mathbf{x}+\mathbf{l}|}{\rho}\right); \qquad (21)$$

$$\left(\frac{\partial^2 F_R}{\partial a_k\,\partial a_m}\right)_{a'} = \frac{a_k a_m}{\rho}\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2(x_m+l_m)^2}{|\mathbf{x}+\mathbf{l}|^2}$$
$$\times \left(\frac{1}{|\mathbf{x}+\mathbf{l}|}+\frac{1}{\rho}\right)\exp\left(-\frac{|\mathbf{x}+\mathbf{l}|}{\rho}\right). \qquad (22)$$

$$\left(\frac{\partial F_{DD}}{\partial a_k}\right)_{a'} = -6a_k\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^8}; \qquad (23)$$

$$\left(\frac{\partial^2 F_{DD}}{\partial a_k^2}\right)_{a'} = 48a_k^2\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^{10}}$$
$$\times \left[(x_k+l_k)^2 - \frac{|\mathbf{x}+\mathbf{l}|^2}{8a_k^2} \right]; \qquad (24)$$

$$\left(\frac{\partial^2 F_{DD}}{\partial a_k\,\partial a_m}\right)_{a'} = 48a_k a_m\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2(x_m+l_m)^2}{|\mathbf{x}+\mathbf{l}|^{10}}. \qquad (25)$$

$$\left(\frac{\partial F_{DQ}}{\partial a_k}\right)_{a'} = -8a_k\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^{10}}; \qquad (26)$$

$$\left(\frac{\partial^2 F_{DQ}}{\partial a_k^2}\right)_{a'} = 80a_k^2\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2}{|\mathbf{x}+\mathbf{l}|^{12}}\left[(x_k+l_k)^2 \right.$$
$$\left. - \frac{|\mathbf{x}+\mathbf{l}|^2}{10a_k^2} \right]; \qquad (27)$$

$$\left(\frac{\partial^2 F_{DQ}}{\partial a_k\,\partial a_m}\right)_{a'} = 80a_k a_m\sum_{-\infty}^{+\infty}{}_{\mathbf{l}}\frac{(x_k+l_k)^2(x_m+l_m)^2}{|\mathbf{x}+\mathbf{l}|^{12}}. \qquad (28)$$

Conclusions

In the case of an orthorhombic crystal, the first and second partial derivatives of the lattice energy with respect to the cell parameters can be calculated by expressions like (16), where the repulsive coefficients b_{rs} and some of the charges z_r are considered as unknown parameters. By substituting the results into (8) and (9) a set of nine equations is obtained, which can be solved to determine up to nine wanted parameters.

A computer program (in Fortran IV) has been written to perform the calculations of the lattice-energy derivatives, using formulas (16)–(28): the computing scheme follows that of *MADEWA*, a program which calculates the electrostatic term of the lattice energy by Ewald series (Catti, 1978). The method developed here has been applied to forsterite, Mg_2SiO_4, assuming as unknown parameters in the lattice-energy expression three repulsive coefficients plus the electric charge on the oxygen atom (Catti, 1981): the overdetermined system of nine equations has been solved by a numeric procedure of minimization of the sum of squared deviations. The convergence rates of the series (17)–(28) have proved to be comparable with those of the corresponding integral series $F(x)$: as for the derivatives of the Ewald double sum, satisfactory results have been obtained using the same values of the parameter A which optimize the convergence of the Ewald series itself.

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Calculation of Even Moments of the Trigonometric Structure Factor. Methods and Results

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Abstract

Two algorithms for the evaluation of even moments of the trigonometric structure factor are described. The first algorithm is based on conventional structure-factor algebra in the complex notation and is applicable to any space group with multiplicity of general positions not exceeding 24. The second algorithm, capable of dealing with all space groups, involves an interpretation of trigonometrical expressions input in a symbolic form and a programmed execution of algebraic and analytic operations. The results obtained in this study include the fourth and sixth moments of the trigonometric structure factor for all 230 space groups. It is assumed that all the atoms occupy general positions. All the subsets of *hkl* indices giving rise to different forms of the trigonometric structure factor (except those for zones and rows) are considered.

Introduction

Probability density functions of the structure amplitude $|F|$, which depend explicitly on the space-group symmetry and on the atomic composition of the asymmetric unit, were given by Karle & Hauptman (1953) and by Hauptman & Karle (1953) for centrosymmetric and non-centrosymmetric crystals respectively. Possible applications of these functions, which are asymptotic expansions in terms of the Wilson (1949) limiting distributions, to direct methods of phase determination have been discussed (Bertaut, 1955; Klug, 1958) and their application to intensity statistics investigated (Shmueli, 1979; Shmueli & Wilson, 1981). An obstacle that hindered an extensive application of these asymptotic expansions was, until recently, the necessity of obtaining the moments of the trigonometric structure factor for each space group considered. These