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Applications of the Ewald Method. II. Homogeneous Strain Derivatives of Dipole Lattice Sums

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The first and second homogeneous strain derivatives of the Lorentz-factor dipole-tensor lattice sum are expressed in terms of wave-vector derivatives of modulated higher multipole-tensor sums. Such derivatives can be calculated rapidly by the Ewald method, for which computationally convenient expressions are given. The first strain derivatives are highly symmetrical, but the symmetry of the second derivatives is lower and more complicated. The method is illustrated by calculations for anthracene and tetragonal hydrogen cyanide; it appears to be superior to more direct methods of calculation.

Introduction

Strain produces both quantitative and qualitative changes in crystal properties. For example, an isotropic pressure will change the positions of lines in a crystal spectrum, while stresses which lower the crystal symmetry may lift degeneracies and so change the number of spectral lines. Under the usual experimental condition of constant stress, changes of temperature also produce strains which may dominate the consequent change in some crystal properties. For properties dependent on lattice multipole sums, quantitative interpretation of these useful and important strain effects depends on a knowledge of the dependence of multipole sums on strain.

In part I of this series (Cummins, Dunmur, Munn & Newham, 1976) we discussed methods for calculating lattice multipole sums. Such methods may of course be used to calculate strain derivatives from multipole sums in different strained configurations, but such a procedure has marked disadvantages. One is that large strains may be required in order to produce significant changes in a multipole sum. Another disadvantage is that multipole sums are conveniently calculated directly from crystallographic data, whereas strains are usually specified by their Cartesian components, so that strains in the two systems have to be related separately. Finally, to obtain some strain derivatives it is necessary to treat lattices of lower symmetry than the equilibrium symmetry.

In the present paper we show how the Ewald method for calculating lattice multipole sums can be used to obtain strain derivatives without the above disadvantages. We derive expressions for the first and second derivatives of the Lorentz-factor dipole tensor sum (Dunmur, 1972) with respect to homogeneous strain. These derivatives, like the Lorentz factor itself, are only slowly convergent when summed over the direct lattice, but can be expressed in terms of multipole sums to which the rapid Ewald method is applicable. We illustrate the use of these expressions by numerical calculations for tetragonal hydrogen cyanide and for anthracene.

Method: the first and second homogeneous strain derivatives

We consider a lattice of points specified by vectors $\mathbf{r}(l,k)$ where l denotes the unit cell and k the sublattice. For dipoles of amplitude $\mathbf{p}(k)$ modulated in space by a wave of wave vector $\mathbf{y}$, the field at a point on sublattice k due to the dipoles on sublattice k' is

$$F_\alpha(kk';\mathbf{y})=(1/4\pi\varepsilon_0)\sum_l T_{\alpha\beta}[\mathbf{r}(l,kk')]p_\beta(k') \times \exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l,k')\,, \quad (1)$$

where $T_{\alpha\beta}(\mathbf{r})$ is the dipole tensor $\partial^2 r^{-1}/\partial r_\alpha \partial r_\beta$, and $\mathbf{r}(l,kk')$ is the distance between a point on sublattice k' in cell l and one on sublattice k in the origin cell, given by $\mathbf{r}(l,k')-\mathbf{r}(0,k)$. The field $\mathbf{F}$ is irregular as $\mathbf{y}\to 0$, and so it is convenient to define a new tensor, the Lorentz-factor tensor, as

$$L_{\alpha\beta}(kk';\mathbf{y})=(v/4\pi)\sum_l T_{\alpha\beta}[\mathbf{r}(l,kk')] \times \exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l,kk')+y_\alpha y_\beta/|\mathbf{y}|^2\,. \quad (2)$$

The second term in this equation cancels the irregular part of the dipole lattice sum in equation (1) as $\mathbf{y}\to 0$, making L a regular function of $\mathbf{y}$. (The definition of L includes the unit cell volume v to make L dimensionless.) By the Ewald method (Born & Huang, 1954) the irregularity in the dipole lattice sum may be shown to arise from the contribution to the transformed sum

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from the origin in reciprocal space, and to be proportional to the macroscopic field in the crystal. The field $\mathbf{F}(kk';\mathbf{y})$ can then be written as

$$F_\alpha(kk';\mathbf{y})=\exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(0,k)[E_\alpha + L_{\alpha\beta}(kk';\mathbf{y})p_\beta(k')/\varepsilon_0 v]\,, \quad (3)$$

where E_α is the amplitude of the macroscopic field. Here the leading exponential factor occurs because equation (2) is chosen to define $\mathsf{L}(kk';\mathbf{y})$ as symmetric in k and k', and independent of the choice of origin. We shall be concerned principally with the limit $\mathbf{y}\to 0$.

Under a static homogeneous deformation in which all sublattices suffer the same displacements, a lattice vector $\mathbf{r}$ in the unstrained lattice is transformed into a vector $\mathbf{r}'$ given by

$$\mathbf{r}'=(\mathsf{I}+\mathsf{u})\,.\,\mathbf{r}\,, \quad (4)$$

where the components of u are called displacement gradients. The dependence of the Lorentz-factor tensor on strain may be described by the tensor

$$U_{\alpha\beta,\,\gamma\delta}(kk';\mathbf{y})=\partial L_{\alpha\beta}(kk';\mathbf{y})/\partial u_{\gamma\delta}\,, \quad (5)$$

where the derivative is evaluated for the unstrained lattice, *i.e.* for $\mathsf{u}=0$. Since $L_{\alpha\beta}$ is a regular function of $\mathbf{y}$ in any lattice, $U_{\alpha\beta,\,\gamma\delta}$ is also a regular function of $\mathbf{y}$. Note that although the macroscopic field is strain dependent, the factor v introduced in the definition of $L_{\alpha\beta}$ cancels out this strain dependence in the second term on the right-hand side of equation (2). All the strain dependence originates in the first term, whose strain derivatives must therefore be regular functions of $\mathbf{y}$.

Substitution of equation (4) into equation (2) followed by differentiation with respect to $u_{\gamma\delta}$ yields in the limit $\mathsf{u}\to 0$

$$\begin{aligned}U_{\alpha\beta,\,\gamma\delta}(kk';\mathbf{y})=(v/4\pi)\sum_l \exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l,kk')\\ \times\{T_{\alpha\beta}[\mathbf{r}(l,kk')]\partial\ln v/\partial u_{\gamma\delta}\\ +2\pi i T_{\alpha\beta}[\mathbf{r}(l,kk')]y_\gamma r_\delta(l,kk')\\ +T_{\alpha\beta\gamma}[\mathbf{r}(l,kk')]r_\delta(l,kk')\}\,. \quad (6)\end{aligned}$$

Here the first derivative of $\ln v$ is just $\delta_{\gamma\delta}$ (see Appendix). The second and third terms on the right-hand side of equation (6) involve lattice sums of a multipole tensor multiplied by the lattice vector. Such sums cannot be evaluated by the Ewald method directly, but can be obtained indirectly as wave vector derivatives of the ordinary multipole lattice sums. If we define

$$S_{\alpha\beta}\ldots(kk';\mathbf{y})=(v/4\pi)\sum_l T_{\alpha\beta}\ldots[\mathbf{r}(l,kk')] \times\exp 2\pi i\mathbf{y}\,.\,\mathbf{r}(l,kk')\,, \quad (7)$$

and use ∇_δ for $\partial/\partial y_\delta$, then we can express equation (6) as

$$\begin{aligned}U_{\alpha\beta,\,\gamma\delta}(kk';\mathbf{y})=S_{\alpha\beta}(kk';\mathbf{y})\delta_{\gamma\delta}+y_\gamma\nabla_\delta S_{\alpha\beta}(kk';\mathbf{y})\\ +(1/2\pi i)\nabla_\delta S_{\alpha\beta\gamma}(kk';\mathbf{y})\,. \quad (8)\end{aligned}$$

The sums $S_{\alpha\beta\ldots}$ can now be evaluated by the Ewald method as usual.

In the limit as $\mathbf{y}\to 0$ each of the terms on the right-hand side of equation (8) has a non-regular part, although these must cancel since the U tensor is regular in this limit. In the Ewald method, the non-regular term in $S_{\alpha\beta}$ arises from a term proportional to

$$f_{\alpha\beta}(\mathbf{y})=(y_\alpha y_\beta/|\mathbf{y}|^2)\exp(-\pi^2|\mathbf{y}|^2/C^2) \quad (9)$$

(where C governs the division into direct and reciprocal lattice sums), while that in $S_{\alpha\beta\gamma}$ arises from a term having the same proportionality to $-2\pi i y_\gamma f_{\alpha\beta}(\mathbf{y})$. Together, the non-regular parts of equation (8) are thus proportional to

$$(\delta_{\gamma\delta}+y_\gamma\nabla_\delta-\nabla_\delta y_\gamma)f_{\alpha\beta}(\mathbf{y})\,,$$

which is zero by the operator identity

$$\nabla_\delta y_\gamma-y_\gamma\nabla_\delta=\delta_{\gamma\delta}\,. \quad (10)$$

Omitting the non-regular parts from equation (7) leaves in the limit $\mathbf{y}\to 0$

$$\begin{aligned}U_{\alpha\beta,\,\gamma\delta}(kk')=L_{\alpha\beta}(kk')\delta_{\gamma\delta}\\ +(1/2\pi i)\nabla_\delta S'_{\alpha\beta\gamma}(kk';\mathbf{y})|_{\mathbf{y}\to 0} \quad (11)\end{aligned}$$

where the prime on the quadrupole sum $S_{\alpha\beta\gamma}$ indicates that the first term in the Ewald sum over the reciprocal lattice is to be omitted. The Lorentz-factor tensor $L_{\alpha\beta}$ is just the regular part of $S_{\alpha\beta}$, and enters $U_{\alpha\beta,\,\gamma\delta}$ through the strain derivative of the volume in equation (2). The last term in equation (11) can be written as

$$(1/2\pi)\nabla_\delta J_{\alpha\beta\gamma}(kk';\mathbf{y})|_{\mathbf{y}\to 0}$$

where in a form suitable for computation

$$\begin{aligned}J_{\alpha\beta\gamma}(kk';\mathbf{y})=H^0_{\alpha\beta\gamma}(kk')\sin 2\mathbf{Q}\,.\,\mathbf{R}_{kk'}(0)\\ +\sum_l{}'\{H_{\alpha\beta\gamma}[\mathbf{R}_{kk'}(l)]\sin 2\mathbf{Q}\,.\,R_{kk'}(l)\\ +G_{\alpha\beta\gamma}[\mathbf{Q}(l)+\mathbf{Q}]\cos 2\mathbf{Q}(l)\,.\,\mathbf{R}_{kk'}(0)\}\,. \quad (12)\end{aligned}$$

The quantities in this equation are defined in Part I (Cummins *et al.*, 1976), except for the reduced wave vector $\mathbf{Q}=\pi^{1/2}v^{1/3}\mathbf{y}$.

The matrix u is not symmetric, and does not in general describe a pure strain. An infinitesimal pure strain is however described by the symmetric part of u:

$$\mathsf{e}=\tfrac{1}{2}(\mathsf{u}+\tilde{\mathsf{u}})\,, \quad (13)$$

where the superposed tilde denotes the transpose. The corresponding strain derivative is

$$\tilde{U}_{\alpha\beta,\,\gamma\delta}(kk')=\partial L_{\alpha\beta}(kk')/\partial e_{\gamma\delta} \quad (14)$$

$$=\tfrac{1}{2}[U_{\alpha\beta,\,\gamma\delta}(kk')+U_{\alpha\beta,\,\delta\gamma}(kk')]\,. \quad (15)$$

This quantity is symmetric in α and β, from the symmetry of $T_{\alpha\beta}$, and in γ and δ from the definition (15).

It may also be shown to be symmetric under interchange of $\alpha\beta$ with $\gamma\delta$, by writing a typical term in the sum as

$$T_{\alpha\beta}\delta_{\gamma\delta}+\tfrac{1}{2}(T_{\alpha\beta\gamma}r_\delta+T_{\alpha\beta\delta}r_\gamma)$$

and using the expressions for $T_{\alpha\beta}$ and $T_{\alpha\beta\gamma}$ in terms of the components r_α *etc.* Hence $\bar{U}_{\alpha\beta,\gamma\delta}$ has the symmetry of the second-order elastic constants. The number of independent components $\bar{U}_{\alpha\beta,\gamma\delta}$ is reduced because the trace $L_{\alpha\alpha}$ is unity for any strain, so that

$$\bar{U}_{\alpha\alpha,\gamma\delta}=0\,. \tag{16}$$

The Lorentz-factor tensor is also unchanged for uniform strains which preserve the unit-cell angles and axial ratios. Such strains correspond to $e_{\alpha\beta}=e\delta_{\alpha\beta}$, whence

$$\bar{U}_{\alpha\beta,\gamma\gamma}=0\,. \tag{17}$$

However, because of the symmetry of $\bar{U}_{\alpha\beta,\gamma\gamma}$ to interchange of pairs of suffixes, the condition (17) is equivalent to (16). These conditions provide useful checks on calculations because they are satisfied only to the extent that the summation in equation (12) has converged.

Calculation of the second strain derivative of $L_{\alpha\beta}(kk')$ proceeds similarly to that of the first. Defining

$$V_{\alpha\beta,\gamma\delta,\varepsilon\zeta}(kk';\mathbf{y})=\partial^2L_{\alpha\beta}(kk';\mathbf{y})/\partial u_{\gamma\delta}\partial u_{\varepsilon\zeta}\,, \tag{18}$$

we obtain from equations (2) and (4)

$$\begin{aligned}V_{\alpha\beta,\gamma\delta,\varepsilon\zeta}(kk')&=U_{\alpha\beta,\gamma\delta}(kk')\delta_{\varepsilon\zeta}+U_{\alpha\beta,\varepsilon\zeta}(kk')\delta_{\gamma\delta}\\&\quad-L_{\alpha\beta}(kk')\,(\delta_{\gamma\delta}\delta_{\varepsilon\zeta}+\delta_{\gamma\zeta}\delta_{\delta\varepsilon})\\&\quad-(1/4\pi^2)\nabla_\delta\nabla_\zeta S'_{\alpha\beta\gamma\varepsilon}(kk';\mathbf{y})|_{\mathbf{y}\to 0}\,,\end{aligned} \tag{19}$$

where the limits $\mathbf{u}\to 0$ followed by $\mathbf{y}\to 0$ have been taken. The derivation uses the result

$$(1/v)\partial^2v/\partial u_{\alpha\beta}\partial u_{\gamma\delta}=\delta_{\alpha\beta}\delta_{\gamma\delta}-\delta_{\alpha\delta}\delta_{\beta\gamma} \tag{20}$$

(see Appendix). As before, individual terms have non-regular parts as $\mathbf{y}\to 0$ which must cancel. They are proportional to

$$\begin{aligned}(\nabla_\delta\nabla_\zeta y_\varepsilon y_\gamma-y_\gamma\nabla_\delta\nabla_\zeta y_\varepsilon-y_\varepsilon\nabla_\delta\nabla_\zeta y_\delta+y_\gamma y_\varepsilon\nabla_\delta\nabla_\zeta\\-\delta_{\gamma\zeta}\delta_{\delta\varepsilon}-\delta_{\gamma\delta}\delta_{\varepsilon\zeta})f_{\alpha\beta}(\mathbf{y})\,,\end{aligned}$$

which can be shown to be zero by repeated use of equation (10). In a form suitable for computation

$$\begin{aligned}S'_{\alpha\beta\gamma\varepsilon}(kk';\mathbf{y})&=H^0_{\alpha\beta\gamma\varepsilon}(kk')\cos 2\mathbf{Q}\,.\,\mathbf{R}_{kk'}(0)\\&\quad+\sum_l{}'\,\{H_{\alpha\beta\gamma\varepsilon}[\mathbf{R}_{kk'}(l)]\cos 2\mathbf{Q}\,.\,\mathbf{R}_{kk'}(l)\\&\quad+G_{\alpha\beta\gamma\varepsilon}[\mathbf{Q}(l)+\mathbf{Q}]\cos 2\mathbf{Q}(l)\,.\,\mathbf{R}_{kk'}(0)\}\,.\end{aligned} \tag{21}$$

It is again preferable to use the derivative $\bar{V}_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$ which is symmetrized with respect to interchange of γ with δ or ε with ζ. This quantity is also symmetric with respect to interchange of $\gamma\delta$ with $\varepsilon\zeta$, but not in general with respect to interchange of $\alpha\beta$ with $\gamma\delta$ or $\varepsilon\zeta$. From the invariance of $L_{\alpha\alpha}$ under strain comes the condition

$$\bar{V}_{\alpha\alpha,\gamma\delta,\varepsilon\zeta}=0\,, \tag{22}$$

and from the invariance of $L_{\alpha\beta}$ under a uniform strain comes the condition

$$\bar{V}_{\alpha\beta,\gamma\gamma,\varepsilon\varepsilon}=0\,. \tag{23}$$

These conditions provide two distinct sets of checks on calculations.

Numerical results

We have calculated the first and second strain derivatives for tetragonal hydrogen cyanide and anthracene. The results for hydrogen cyanide have been used to calculate the static-lattice contributions to the piezoelectric coefficients and the elastic constants (Munn & Newham, 1976*b*). The results for anthracene have been used to calculate the strain dependence of the effective molecular polarizability (Dunmur & Munn, unpublished results), and can be compared with exciton calculations in strained anthracene crystals (Schipper, 1974).

Our results for the first derivatives are shown in Table 1, which omits components which are zero by symmetry for both crystals. The differentiation with respect to $\mathbf{y}$ converges quite rapidly; for $y=0{\cdot}0001$, corresponding to about 0·1% of the reciprocal unit cell edge, all $\bar{U}_{\alpha\beta,\gamma\delta}$ for hydrogen cyanide have converged to the fifth decimal place. The results have been checked against derivatives obtained from calculations of $L_{\alpha\beta}$ for different structures near equilibrium. Convergence commensurate with that described above is obtained for 0·05% changes in the unit cell edges on either side of the equilibrium value. For anthracene the comparison entails expressing changes in the unit cell parameters in terms of the Cartesian components of strain (Newham, 1975; Schipper, 1974). Agreement within 0·01% is readily obtainable. The results in Table 1 also satisfy the condition (16) to 1 part in 10^5.

Table 1. *First strain derivatives $\bar{U}_{\alpha\beta,\gamma\delta}(kk')$ referred to crystal axes (taken as abc′ for anthracene)*

$\alpha\beta,\gamma\delta$	Hydrogen cyanide	Anthracene 11	Anthracene 12
xx,xx	−0·0164	−0·9976	0·0877
xx,yy	−0·0338	0·8507	−1·3343
xx,zz	0·0502	0·1469	1·2467
xx,xz	0	0·0922	−0·0910
yy,yy	−0·0164	−1·6843	0·9936
yy,zz	0·0502	0·8336	0·3407
yy,xz	0	0·0018	0·0018
zz,zz	−0·1004	−0·9805	−1·5874
zz,xz	0	−0·0940	0·0892
xz,xz	−0·2842	0·0634	0·9180
yz,yz	−0·2842	0·4101	0·4616
yz,xy	0	−0·0063	0·0096
xy,xy	−0·3650	0·3638	−2·1321

The strain derivatives of the $L_{\alpha\beta}$ for hydrogen cyanide are mostly rather small. As noted elsewhere (Munn & Newham, 1976*a*), this feature arises from a cancellation between contributions from points at the corners of the conventional unit cell and those from points at the body centres. For example, in $\bar{U}_{xx,xx}$ these contributions are respectively $-0{\cdot}4978$ and $+0{\cdot}4814$.

The results for anthracene may be compared with calculations of the strain dependence of dipole sums in anthracene, used in exciton theory (Schipper, 1974). For this comparison it is necessary to change the Lorentz-factor tensor into the plane-wise dipole sum (Philpott, 1973) as described in Part I (Cummins *et al.*, 1976). The relation between the plane-wise dipole sum and the Lorentz-factor tensor is:

$$I_{\alpha\beta}(kk')=(K/v)[L_{\alpha\beta}(kk')-n_\alpha n_\beta]\,, \qquad (24)$$

where K is a unit conversion factor and $\mathbf{n}$ is the unit normal to the planes used in the sum. For strains which do not change the direction of this normal, we obtain

$$\partial I_{\alpha\beta}(kk')/\partial u_{\gamma\delta}=(K/v)U_{\alpha\beta,\gamma\delta}(kk')-I_{\alpha\beta}(kk')\delta_{\gamma\delta}\,, \qquad (25)$$

where the last term comes from the strain dependence of $1/v$ in equation (24). After converting our values for equation (25) to give energies of interaction of dipoles along the principal axes of molecules on sublattices k and k', we obtain results which agree with Schipper's (1974) when allowance is made for his use of derivatives with respect to lattice parameter and for minor differences in the structural data he uses (Schipper, communication, 1975). Schipper remarks that the derivative sums are relatively lengthy to compute, but by the present method we find that the computation time scarcely exceeds that for the dipole sums themselves.

The independent non-zero second strain derivatives for tetragonal hydrogen cyanide are shown in Table 2;

Table 2. *Second strain derivatives* $\bar{V}_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$ *for tetragonal hydrogen cyanide*

	$\alpha\beta$			
$\gamma\delta,\varepsilon\zeta$	xx	zz	xy	xz
xx,xx	0·6667	−0·2969	0	0
xx,yy	−0·4038	0·8075	0	0
xx,zz	−0·2466	−0·5609	0	0
xx,xy	0	0	−0·1962	0
xx,xz	0	0	0	−0·1198
yy,yy	−0·3699	−0·2969	0	0
yy,zz	0·8075	−0·5609	0	0
yy,xy	0	0	−0·1962	0
yy,xz	0	0	0	0·7994
zz,zz	−0·6112	1·2223	0	0
zz,xy	0	0	0·7573	0
zz,xz	0	0	0	−0·3954
xy,xy	−0·3661	0·7322	0	0
xy,yz	0	0	0	1·0115
xz,xz	−0·2687	−0·5266	0	0
xz,yz	0	0	1·0327	0
yz,yz	0·7953	−0·5266	0	0

Table 3. *Second strain derivatives* $\bar{V}_{\alpha\beta,\gamma\delta,\varepsilon\zeta}(kk')$ *referred to crystal abc′ axes for anthracene*

		$\alpha\beta$			
$\gamma\delta,\varepsilon\zeta$	kk'	xx	yy	zz	xz
xx,xx	11	1·3906	−0·2121	−1·1785	0·3254
	12	−3·4968	4·6337	−1·1369	−0·3269
xx,yy	11	0·6386	−1·4884	0·8499	0·0056
	12	3·2994	−1·9647	−1·3346	0·0056
xx,zz	11	−1·0316	0·8499	0·1818	−0·4233
	12	0·1098	−1·3346	1·2249	0·4122
xx,xz	11	0·3796	0·0048	−0·3844	−0·6605
	12	−0·3802	0·0048	0·3755	−1·4840
yy,yy	11	−2·3392	4·7601	−2·4210	0·0097
	12	−0·6304	0·0760	0·5543	0·0096
yy,zz	11	0·8499	−1·5874	0·7375	−0·0170
	12	−1·3346	0·8951	0·4396	−0·0071
yy,xz	11	0·0057	0·0114	−0·0171	0·0139
	12	0·0057	0·0114	−0·0171	−0·8434
zz,zz	11	0·0349	−0·0961	0·0612	0·5343
	12	−0·0218	0·0989	−0·0770	−0·4844
zz,xz	11	−0·4775	−0·0179	0·4954	0·6078
	12	0·4652	−0·0179	−0·4477	1·3872
xz,xz	11	−0·4570	−0·4134	0·8703	−0·4219
	12	−1·8096	−0·5894	2·3990	0·4135

second strain derivatives for anthracene are shown in Table 3, where for brevity only symmetry-preserving strains have been included. Adequate convergence was again obtained with $y=0{\cdot}0001$, yielding results which satisfy the conditions (22) and (23) to about 2 parts in 10^5. Some components were also checked by calculating the $L_{\alpha\beta}$ for different structures, when agreement to better than 0·01% was obtained. This method is much more tedious for second derivatives because several structures must be treated for each derivative, and for anthracene the transformation of strains is also more complicated.

Examination of Tables 2 and 3 shows that although $\bar{V}_{\alpha\beta,\gamma\delta,\varepsilon\zeta}$ is not in general symmetric under interchange of $\alpha\beta$ with $\gamma\delta$ or $\varepsilon\zeta$, it may be so for certain values of the subscripts. For example, $\bar{V}_{xx,yy,zz}=\bar{V}_{zz,xx,yy}$ and $\bar{V}_{xx,yy,xz}=\bar{V}_{xz,xx,yy}$. These symmetries can be verified by writing a typical term in the sum as

$$\begin{aligned}&T_{\alpha\beta}[\delta_{\gamma\delta}\delta_{\varepsilon\zeta}-\tfrac{1}{2}(\delta_{\gamma\zeta}\delta_{\varepsilon\delta}+\delta_{\delta\zeta}\delta_{\varepsilon\gamma})]\\&\quad+\tfrac{1}{2}[\delta_{\gamma\delta}(T_{\alpha\beta\varepsilon}r_\zeta+T_{\alpha\beta\zeta}r_\varepsilon)\\&\quad+\delta_{\varepsilon\zeta}(T_{\alpha\beta\gamma}r_\delta+T_{\alpha\beta\delta}r_\gamma)]\\&\quad+\tfrac{1}{4}[T_{\alpha\beta\gamma\varepsilon}r_\delta r_\zeta+T_{\alpha\beta\delta\varepsilon}r_\gamma r_\zeta\\&\quad+T_{\alpha\beta\gamma\zeta}r_\delta r_\varepsilon+T_{\alpha\beta\delta\zeta}r_\gamma r_\varepsilon]\end{aligned}$$

and using the expressions for $T_{\alpha\beta}$, $T_{\alpha\beta\gamma}$ and $T_{\alpha\beta\gamma\delta}$ in terms of the components r_α *etc.* However, no compact general statement can be made about such symmetries.

Conclusions

The expressions derived here permit the first and second strain derivatives of Lorentz-factor tensors to be calculated using the Ewald method, with its attendant advantage of speed of convergence. Only the

equilibrium lattice geometry has to be treated, and Cartesian components of strain are used directly. Useful checks on the results have also been derived.

The numerical calculations confirm that the method is more convenient and more rapidly convergent than the obvious direct methods.

The work described here should facilitate routine calculation of strain derivatives of dipole sums. This in turn will facilitate work on piezoelectric and elastic constants, lattice dynamics, and the strain dependence of effective polarizabilities and exciton energies in molecular crystals.

APPENDIX

Strain derivatives of the volume

The volume v' in a strained configuration can be related to the volume v in the unstrained reference configuration by

$$v' = v \det(\mathsf{I}+\mathsf{u}) , \qquad (A1)$$

which can be written in terms of the components $x_{\alpha\beta}$ of $\mathsf{I}+\mathsf{u}$ as

$$v' = \tfrac{1}{6} v \varepsilon_{\alpha\beta\gamma} \varepsilon_{\delta\sigma\tau} x_{\alpha\delta} x_{\beta\sigma} x_{\gamma\tau} , \qquad (A2)$$

where $\varepsilon_{\alpha\beta\gamma}$ is the alternating tensor (Jeffreys, 1963). Since $\partial/\partial u_{\lambda\mu}$ equals $\partial/\partial x_{\lambda\mu}$, we obtain

$$\partial v'/\partial u_{\lambda\mu} = \tfrac{1}{2} v \varepsilon_{\lambda\beta\gamma} \varepsilon_{\mu\sigma\tau} x_{\beta\sigma} x_{\gamma\tau} , \qquad (A3)$$

where dummy indices have been relabelled after differentiation. In the reference configuration where $x_{\alpha\beta} = \delta_{\alpha\beta}$ we obtain

$$\partial \ln v/\partial u_{\lambda\mu} = \tfrac{1}{2} \varepsilon_{\lambda\beta\gamma} \varepsilon_{\mu\beta\gamma} = \delta_{\lambda\mu} \qquad (A4)$$

where the last equality is given by Jeffreys (1963).

Differentiating equation ($A3$) a second time, we obtain

$$\partial^2 v'/\partial u_{\lambda\mu} \partial u_{\nu\pi} = v \varepsilon_{\lambda\nu\gamma} \varepsilon_{\mu\pi\tau} x_{\gamma\tau} . \qquad (A5)$$

In the reference configuration this yields

$$(1/v)\partial^2 v/\partial u_{\lambda\mu} \partial u_{\nu\pi} = \varepsilon_{\lambda\nu\gamma} \varepsilon_{\mu\pi\gamma} \qquad (A6)$$

$$= \delta_{\lambda\mu}\delta_{\nu\pi} - \delta_{\lambda\pi}\delta_{\nu\mu} , \qquad (A7)$$

where again the last equality is given by Jeffreys (1963).

For completeness, we note that the third derivative is

$$(1/v)\partial^3 v/\partial u_{\lambda\mu} \partial u_{\nu\pi} \partial u_{\delta\sigma} = \varepsilon_{\lambda\nu\delta} \varepsilon_{\mu\pi\sigma} \qquad (A8)$$

$$= (\delta_{\lambda\mu}\delta_{\nu\pi} - \delta_{\lambda\pi}\delta_{\nu\mu})\delta_{\delta\sigma} + (\delta_{\lambda\pi}\delta_{\nu\sigma} - \delta_{\lambda\sigma}\delta_{\nu\pi})\delta_{\delta\mu} + (\delta_{\lambda\sigma}\delta_{\nu\mu} - \delta_{\lambda\mu}\delta_{\nu\sigma})\delta_{\delta\pi} . \qquad (A9)$$

These results are readily verified by expansion of $\det(\mathsf{I}+\mathsf{u})$ in terms of u_{11}, u_{12}, *etc.*

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