Lattice Summation of Multipole Interaction Energies in Crystals. Calculation of the Outer-sphere Contribution to the Crystal-field Splitting in Nickel(II) Oxide

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The Bertaut method for calculating the lattice energy of an ionic crystal is extended to include multipole–multipole interactions. Equations are obtained for the electrostatic-interaction energy of compact multipolar ions or molecules of any symmetry in a crystal of arbitrary structure, and their application is illustrated using α-N_2, $K[HF_2]$, and $Pb[NO_3]_2$ as examples. The method is used to estimate the contribution to the ligand-field splitting Δ in NiO from outside the first co-ordination sphere; the interaction between cation multipoles is too small to account for observed differences between spectroscopic and thermochemical estimates of Δ.

RAPIDLY convergent series for lattice sums of coulombic interaction energies in ionic crystals of arbitrary structure have been available since the work of Ewald in 1921.[1] The lattice summation of multipole–multipole interactions was considered shortly afterwards by Kornfeld,[2] who used Ewald's theta-function transformation to obtain corresponding formulae for a lattice of point dipoles and one of point quadrupoles. More recently, Neckel *et al.*[3] used similar methods to derive formulae for a crystal composed of cylindrically symmetrical particles having multipole moments of any order. Other workers [4] have discussed methods of calculating related sums for a crystal composed of dipoles.

The formulae obtained by these workers consist, like the Ewald formula, of two infinite sums, one over the reciprocal and one over the direct lattice. An important advance in the calculation of lattice sums was made in 1952 by Bertaut,[5] who showed that the Ewald method for ionic crystals is equivalent to replacing the point ions by spherical charge clouds of gaussian profile; Fourier-transform methods then yield a rapidly convergent reciprocal-lattice sum for the total energy, but it is necessary to subtract a direct-lattice sum to correct for the overlap between charge clouds. Bertaut pointed out that the necessity for this correction can be eliminated by using a discontinuous charge-density function, the density being zero outside a sphere small enough to avoid overlap. This device is now widely used in lattice-energy calculations, usually with a linearly or parabolically decreasing radial density function.[6] It has not previously been used in the summation of multipolar interactions, although its advantages here are especially marked; even with cylindrical charge clouds, the calculation of the overlap correction is a very difficult problem.[3a]

In this paper I apply Bertaut's approach to the summation of general multipole–multipole interactions in crystals. The formulae obtained are relatively simple, and apply to multipoles of any order and any symmetry. The method is illustrated by computation of the electrostatic-interaction energies of solid α-N_2, $K[HF_2]$, and $Pb[NO_3]_2$ in terms of the multipole moments of the particles, and is then used to investigate the ' outer-sphere ' contribution to the crystal-field splitting in NiO. (By ' outer-sphere ' is meant the whole crystal outside of a particular cation and its adjacent anions. It is assumed that in a fairly ionic crystal it is possible to calculate this contribution by classical electrostatics, provided reasonable assumptions can be made about the charge distribution on the cation.)

THEORY

Bertaut's Method for Ionic Crystals.—In this method an array of point charges q_j at locations $\boldsymbol{x}_j$, represented by the discontinuous periodic function (1), is convoluted with a

$$\tau(\boldsymbol{r}) = \sum_j q_j \delta(\boldsymbol{r} - \boldsymbol{x}_j) \qquad (1)$$

radial density function $\sigma(\boldsymbol{r})$, centred at the origin, to give a periodic charge density $\rho(\boldsymbol{r})$ with maxima at $\boldsymbol{x}_j$ [equation (2)]. Provided $\sigma(\boldsymbol{r})$ is spherically symmetric and the charge

$$\rho(\boldsymbol{r}) = \int \sigma(\boldsymbol{r})\tau(\boldsymbol{r} - \boldsymbol{u})\mathrm{d}\boldsymbol{u} \qquad (2)$$

clouds of adjacent ions do not overlap, the interaction energy of the distribution $\rho(\boldsymbol{r})$ is the same as that of the original point charges. The total electrostatic energy T is then obtained by convoluting $\rho(\boldsymbol{r})$ with itself, dividing the resulting ' electrostatic Patterson function ' $P(\boldsymbol{u})$ by the length of the charge-separation vector $\boldsymbol{u}$, and integrating over vector space within the unit cell:

$$T = \tfrac{1}{2}\int P(\boldsymbol{u})u^{-1}\mathrm{d}\boldsymbol{u} \qquad (3)$$

$$\text{where} \quad P(\boldsymbol{u}) = \int \rho(\boldsymbol{r} + \boldsymbol{u})\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$$

From the convolution theorem, the Fourier transform of $\rho(\boldsymbol{r})$ is given by (4) where Φ is the Fourier transform of σ and $F(\boldsymbol{h})$, equation (5), is that of τ. Similarly, the Fourier trans-

$$G(\boldsymbol{h}) = \Phi(\boldsymbol{h})F(\boldsymbol{h}) \qquad (4)$$

$$F(\boldsymbol{h}) = \sum_j q_j \exp(2\pi i \boldsymbol{h}.\boldsymbol{x}_j) \qquad (5)$$

form of $P(\boldsymbol{u})$ is $|G(\boldsymbol{h})|^2$. Since $P(\boldsymbol{u})$ has the periodicity of the lattice, it can be expanded as a Fourier series on the reciprocal lattice with $|G(\boldsymbol{h})|^2$ as coefficients. Substituting this series into (3) and integrating over vector space, one

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[1] P. P. Ewald, *Ann. Physik*, 1921, **64**, 253.

[2] H. Kornfeld, *Z. Physik*, 1924, **22**, 27.

[3] A. Neckel, P. Kuzmany, and G. Vinek, *Z. Naturforsch.*, 1971, **A26**, (*a*) 561; (*b*) 569.

[4] B. R. A. Nijboer and F. W. de Wette, *Physica*, 1957, **23**, 309; 1958, **24**, 422; F. W. de Wette, *Phys. Rev.*, 1961, **123**, 103; F. W. de Wette and G. E. Schacher, *ibid.*, 1965, **A137**, 78, 92.

[5] F. Bertaut, *J. Physique*, 1952, **13**, 499.

[6] D. H. Templeton, *J. Chem. Phys.*, 1955, **23**, 1629; T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 157; H. D. B. Jenkins, *Chem. Phys. Letters*, 1971, **9**, 473.

obtains (6) where V is the unit-cell volume, $\boldsymbol{h}$ is the reciprocal-lattice vector $\boldsymbol{a}_1'h_1 + \boldsymbol{a}_2'h_2 + \boldsymbol{a}_3'h_3$ ($\boldsymbol{a}_1' = \boldsymbol{a}_2 \times \boldsymbol{a}_3/V$, *etc.*, $\boldsymbol{a}_i$ being the unit-cell vectors), and the sum is taken over all positive and negative integral values of h_1, h_2, and h_3. The $h = 0$ term is omitted, since it can be

$$T = \frac{1}{2\pi V}\sum_{\boldsymbol{h}} h^{-2}|G(\boldsymbol{h})|^2 \qquad (6)$$

shown (see below) to be zero if the crystal is electrically neutral and unpolarised.

In the case of point charges, (3) would include an infinite contribution from the self-energies of the ions, but when the charges are assumed to be extended in space the self-energy S becomes finite, and can therefore be calculated and subtracted to give the net interaction energy U per unit cell:

$$U = T - S \qquad (7)$$

where
$$S = \sum_j q_j^2 W \qquad (8)$$

$$W = \tfrac{1}{2}\int \sigma(\boldsymbol{r} + \boldsymbol{u})\sigma(\boldsymbol{u})u^{-1}\mathrm{d}\boldsymbol{r}\mathrm{d}\boldsymbol{u} \qquad (9)$$

A General Expression for the Electrostatic-interaction Energy of a Crystal containing Multipoles.—It is assumed that the values of the multipole moments of the particles are known (*e.g.* from physical measurements or molecular-orbital calculations). Following Bertaut, the ions or molecules are replaced by charge clouds wholly contained within non-overlapping spheres, and their density functions $\sigma(\boldsymbol{r})$ are convoluted with the lattice function $\tau(\boldsymbol{r})$, which now consists simply of a Dirac delta function at the location of each particle of appropriate type in the crystal. Provided that each $\sigma(\boldsymbol{r})$ has the same multipole moments as the real ion or molecule that it represents, the resulting periodic charge distribution will have essentially the same electrostatic-interaction energy as the actual crystal.*

We can now expand each $\sigma(\boldsymbol{r})$ in spherical harmonics about the centre of the sphere [equation (10), where $\hat{r}_{ij}$ represents the angular components of $\boldsymbol{r}$ in the co-ordinate system of the ith kind of particles in their jth orientation]. It is convenient to choose the radial functions such that $[R(r)]^2$ decreases linearly to zero at some limiting radius. Although the series (9) is infinite, only small values of l will be significant in practice, and the presence of symmetry will impose further restrictions on l and m provided the axes to which the Y_l^m are referred coincide as far as possible

$$\sigma_{ij}(\boldsymbol{r}) = \sum_{lm} a_{ilm}[R_i(r)]^2 Y_l^m(\hat{r}_{ij}) \qquad (10)$$

$$Q_{lm} = \int \sigma(\boldsymbol{r})r^l P_l^m(\cos\theta)\mathrm{e}^{im\phi}\mathrm{d}\boldsymbol{r} \qquad (11)$$

with any symmetry axes of the particle. (A detailed discussion of the application of symmetry to spherical harmonic expansions is given in ref. 7.) The multipole moments of a continuous charge distribution such as $\sigma(\boldsymbol{r})$ are defined by [8] (11) and hence we can rewrite $\sigma(\boldsymbol{r})$ in the form (12):

$$\sigma_{ij}(\boldsymbol{r}) = \sum_{lm} Q_{ilm}\xi_{ijlm}(\boldsymbol{r}) \qquad (12)$$

where
$$\xi_{ijlm}(\boldsymbol{r}) = N_{lm}\langle r^l\rangle_i^{-1}[R_i(r)]^2 Y_l^{-m}(\hat{r}_{ij})$$

The normalisation factor is given by (13) and $\langle f(r)\rangle$ represents the expectation value $\int_0^\infty [R(r)]^2 f(r)r^2\mathrm{d}r$.

To obtain the Fourier transform $X(\boldsymbol{h})$ of $\xi(\boldsymbol{r})$, we make use of the expansion [9] (14) where $j_l(z)$ is a spherical Bessel function; taking account of the orthonormality of the

$$N_{lm} = i^{m+|m|}\left[\frac{2l+1}{4\pi}\cdot\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}} \qquad (13)$$

$$\mathrm{e}^{2\pi i\boldsymbol{h}.\boldsymbol{r}} = 4\pi\sum_{lm} i^l j_l(2\pi hr)Y_l^{m*}(\hat{h})Y_l^m(\hat{r}) \qquad (14)$$

spherical harmonics, one finds expression (15) where $I_{il}(h) = \langle j_l(2\pi hr)\rangle$. The Fourier transform of $\rho(\boldsymbol{r})$ is thus given by (16) where $g_{ilm}(\boldsymbol{h}) = \sum_j F_{ij}(\boldsymbol{h})X_{ijlm}(\boldsymbol{h})$, the Fourier transform of $\tau(\boldsymbol{r})$ being simply (17) in which the sum

$$X_{ijlm}(\boldsymbol{h}) = 4\pi i^l N_{lm}\langle r^l\rangle_i^{-1}I_{il}(h)Y_l^{-m}(\hat{h}_{ij}) \qquad (15)$$

$$G(\boldsymbol{h}) = \sum_{ilm} Q_{ilm}g_{ilm}(\boldsymbol{h}) \qquad (16)$$

$$F_{ij}(\boldsymbol{h}) = \sum_k \exp(2\pi i\boldsymbol{h}.\boldsymbol{x}_{ijk}) \qquad (17)$$

is over identical particles in the same orientation.† Hence the total energy is as in (18):

$$T = \sum_{ilm}\sum_{i'l'm'} T(ilm;\ i'l'm')Q_{ilm}^*Q_{i'l'm'} \qquad (18)$$

where
$$T(ilm;\ i'l'm') = \frac{1}{2\pi V}\sum_{\boldsymbol{h}} h^{-2}g_{ilm}^*(\boldsymbol{h})g_{i'l'm'}(\boldsymbol{h}) \qquad (19)$$

I show in the Appendix that, provided the crystal is electrically neutral and has no dipole moment arising either from the distribution of charges or from the arrangement of molecular dipoles in the unit cell, the $h = 0$ term in (19) vanishes.

The self-energy is now as in (20) where n_i is the number of

$$S = \sum_i n_i W_i \qquad (20)$$

particles of the ith shape. From equations (9) and (12) we obtain (21), F_i^l being a radial Slater integral.[10] The forms

$$S = \sum_{ilm} S(ilm)|Q_{ilm}|^2 \qquad (21)$$

$$S(ilm) = \tfrac{1}{2}\frac{(l-|m|)!}{(l+|m|)!}\frac{n_i F_i^l}{\langle r^l\rangle_i^2} \qquad (22)$$

$$U = \sum\sum U(ilm;\ i'l'm')Q^*_{ilm}Q_{i'l'm'} \qquad (23)$$

of $I_l(h)$ and F^l appropriate to a linearly decreasing radial function are given in the Appendix.

The net interaction energy can be written as in (23) and (24)—(26) follow:

$$\frac{\partial U}{\partial Q_{ilm}} = 2\sum_{i'l'm'} U(ilm;\ i'l'm')Q_{i'l'm'} \qquad (24)$$

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* If the distance between the centres of two molecules is less than the largest radial extent of either, their interaction cannot be accurately represented by a multipole expansion. It is assumed, however, that the particles are sufficiently compact that such an expansion is valid to a good approximation. This restriction also applies, of course, to the earlier work.[2–4]

† $Y_l^{-m} = (-1)^m Y_l^{m*}$, $X_{l,-m} = (-1)^l X_{lm}^*$, and $Q_{l,-m} = Q_{l,m}^*$.

[7] J. L. Prather, 'Atomic Energy Levels in Crystals,' N.B.S. Monograph 19, U.S. National Bureau of Standards, Washington, 1961.

[8] H. Morgenau and N. R. Kestner, 'Theory of Intermolecular Forces,' Pergamon, Oxford, 1969, p. 281.

[9] M. E. Rose, 'Elementary Theory of Angular Momentum,' Wiley, New York, 1957.

[10] E. U. Condon and G. H. Shortley, 'The Theory of Atomic Spectra,' Cambridge, 1963.

$$\frac{\partial^2 U}{\partial Q_{ilm}\partial Q_{i'l'm'}{}^*} = \frac{\partial^2 U}{\partial Q_{i'l'm'}{}^*\partial Q_{ilm}} = 4U(ilm;\, i'l'm') \quad (25)$$

$$\frac{\partial^2 U}{\partial Q_{ilm}\partial Q_{i'l'm'}} = \frac{\partial^2 U}{\partial Q_{i'l'm'}\partial Q_{ilm}} = 0 \quad (26)$$

where $U(ilm;\ i'l'm') = T(ilm;\ i'l'm') - S(ilm)\delta_{ii'}\delta_{ll'}\delta_{mm'}$

The derivatives are in general complex.

It must be emphasised that in the above formulation the radial function $R(r)$ is chosen arbitrarily (subject to the no-overlap condition) and does not itself affect the results; the properties of the particles enter only *via* their multipole moments.

An Alternative Method for Non-spherical Atoms or Monatomic Ions.—In the method described above, the electrostatic effect of each molecule or ion is simulated by means of a one-centre charge cloud having the same multipole moments. For an atom or monatomic ion, however, an accurate radial wavefunction may be available, and this suggests a slightly different formulation.

Let us assume that $\sigma(\boldsymbol{r})$ can be represented by a normalised sum of n one-electron (or one-' hole ') contributions [equation (27)] in which each orbital function is of the form (28). In order to obtain the Fourier transform [*] of $|\psi(\boldsymbol{r})|^2$,

$$\sigma(\boldsymbol{r}) = \frac{1}{n}\sum_k |\psi_k(\boldsymbol{r})|^2 \quad (27)$$

$$\psi(\boldsymbol{r}) = R(\boldsymbol{r})\sum_m c_m Y_l^m(\hat{\boldsymbol{r}}) \quad (28)$$

$$\Phi(\boldsymbol{h}) = \sum_\lambda I_\lambda(h) Z_\lambda(\hat{h}) \quad (29)$$

where $Z_\lambda(\hat{h}) = i^\lambda[4\pi(2\lambda + 1)]^{\frac{1}{2}} \langle \lambda l 0 0 | \lambda l l 0\rangle \sum_\mu A_{\lambda\mu} Y_\lambda{}^{\mu *}(\hat{h})$

and $A_{\lambda\mu} = \sum_{mm'} c_{m'}{}^* c_m \langle \lambda l \mu m | \lambda l l m'\rangle$

(14) is used as before, and integrated over the angular coordinates by means of the integral theorem for a triple product of spherical harmonics.[9] The result is (29); $I_\lambda(h)$ is defined as above; $\langle l_1 l_2 m_1 m_2 | l_1 l_2 l m\rangle$ is a Wigner coefficient, and equation (29) includes only terms for which λ is even, $0 \leqslant \lambda \leqslant 2l$, $m' - m = \mu$, and $|\mu| \leqslant \lambda$. The total energy can then be calculated from equations (4) and (6), modified to allow for more than one kind of ion. Some examples of $\Phi(\boldsymbol{h})$ for various wavefunctions are given in Table 1.

The self-energy integral W is equivalent to a two-electron one-centre Coulomb integral, and for a single wavefunction ψ_{lm} we have (30), the coefficients c^λ being tabulated.[10] The general case is rather more complicated, but for real d orbitals the form of W can readily be found from Table A26 of ref. 13.

$$W = \tfrac{1}{2}\sum_\lambda [c^\lambda(lm, lm)]^2 F^\lambda \quad (30)$$

In order to obtain accurate results with this method one must exercise some care in the choice of radial function. The Hartree–Fock (HF) function is the ideal, but because of the overlap problem, and the difficulty of working with an accurate representation, its use is not practicable. Simpler functions can, however, be used to reproduce particular properties of the HF function, *e.g.* a truncated Slater-type orbital or a density function of triangular profile, both of which provide two adjustable parameters. In the case of Ni^{2+} only the fourth moment of the radial density function is relevant, and I use a linear $[R(r)]^2$ with r_0 chosen so as to give the correct value of $\langle r^4\rangle$. For spherical ions the radial function is arbitrary, and the linear form is used here too.

TABLE 1

(*a*) The Fourier transform $\Phi(\boldsymbol{h})$ of the electron density for some atomic wavefunctions

$\psi(\boldsymbol{r})$	$\Phi(\boldsymbol{h})/(4\pi)^{\frac{1}{2}}$
s	$Y_0{}^0 I_0$
d_{z^2}	$Y_0{}^0 I_0 - (2.5^{\frac{1}{2}}/7) Y_2{}^0 I_2 + \frac{6}{7} Y_4{}^0 I_4$
$d_{x^2-y^2}$ or d_{xy}	$Y_0{}^0 I_0 + (2.5^{\frac{1}{2}}/7) Y_2{}^0 I_2 + \frac{1}{7}[Y_4{}^0 \pm (70^{\frac{1}{2}}/2)(Y_4{}^4) + Y_4{}^{-4})] I_4$
$e_g{}^2$, ${}^3A_{2g}$	$2Y^0{}_0 I_0 + [Y_4{}^0 + (5/14)^{\frac{1}{2}} (Y_4{}^4 + Y_4{}^{-4})] I_4$
$t_{2g}{}^1 e_g{}^1$, ${}^3T_{2g}(\zeta)$	$2Y^0{}_0 I_0 + [Y_4{}^0 - (5/14)^{\frac{1}{2}} (Y_4{}^4 + Y_4{}^{-4})] I_4$

(*b*) The self-energy integrals W for superimposition of two atomic electron-density functions $|\psi_\mathrm{A}|^2$ and $|\psi_\mathrm{B}|^2$

ψ_A	ψ_B	$2W$
s	Arbitrary	F^0
d	ψ_A	$F^0 + \frac{4}{49}F^2 + \frac{4}{49}F^4$
d_{z^2}	$d_{x^2-y^2}$ or d_{xy}	$F^0 - \frac{4}{49}F^2 + \frac{2}{147}F^4$
$d_{x^2-y^2}$	d_{xy}	$F^0 - \frac{4}{49}F^2 - \frac{34}{441}F^4$
$e_g{}^2$, ${}^3A_{2g}$	$e_g{}^2$, ${}^3A_{2g}$	$F^0 + \frac{1}{21}F^4$
$e_g{}^2$, ${}^3A_{2g}$	$t_{2g}{}^1 e_g{}^1$, ${}^3T_{2g}$	$F^0 + \frac{1}{126}F^4$

The Lattice Energy of a Localised Process.—Besides considering the convolution of a given charge-density distribution with itself [equation (3)] we can also consider the convolution of one structure, P, with another, Q. The energy of interaction of P with Q when the two are superimposed is given by (31) where S_PQ is given by an obvious modification of (8). Such mixed convolutions arise in the expression for the electrostatic energy of a unit cell of one type (P) substituted into a crystal of another type (Q) having the same unit-cell dimensions. In particular, if a single molecule or ion M in one unit cell undergoes a change (of shape, orientation, or location) to M′, all the other particles in the crystal remaining as they were, the lattice energy absorbed during this transition is given by (32) where X represents all particles other than M.[†]

$$U_\mathrm{PQ} = \frac{1}{2\pi V}\sum_h h^{-2} G_\mathrm{P}{}^*(\boldsymbol{h}) G_\mathrm{Q}(\boldsymbol{h}) - S_\mathrm{PQ} \quad (31)$$

$$\begin{aligned} U_{\mathrm{M}\rightarrow\mathrm{M'}} &= 2[U_{(\mathrm{M+X})(\mathrm{M+X})} - U_{(\mathrm{M'+X})(\mathrm{M+X})}] \\ &= 2(U_\mathrm{MM} + U_\mathrm{MX} - U_\mathrm{M'M} - U_\mathrm{M'X}) \quad (32) \end{aligned}$$

Computation.—The method expressed by equations (12)—(26) is embodied in a computer program, MULTMAD-A, which is applicable to any crystal structure and to all multipoles up to fourth order. The output includes U and its first and second derivatives. The method of equations (27)—(31) is incorporated in a second program, MULTMAD-B, written specifically for the NiO problem. It is restricted to orthogonal crystal systems, centric structures, and multipoles of even order, but it is much faster than MULT-

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[*] The Fourier transform of the total electron-density distribution in an atom is the well known scattering factor for X-rays, which for certain non-spherical electron configurations has been considered by McWeeny [11] and Freeman.[12]

[†] If M is an ion or a dipole, a term such as U_MM is meaningless in isolation because the $h = 0$ term is infinite. Provided M + X is neutral and non-polar, however, the infinities cancel when the terms are combined as above.

[11] R. McWeeny, *Acta Cryst.*, 1951, **4**, 513.

[12] A. J. Freeman, *Acta Cryst.*, 1959, **12**, 261, 274, 929.

[13] J. S. Griffith, ' The Theory of Transition Metal Ions,' Cambridge, 1961.

MAD-A and can handle mixed convolutions. Both programs were developed from a Madelung-energy program,[14] and are written in Fortran. They are available from the author.

RESULTS

The Electrostatic-interaction Energies of Crystals containing Molecules or Complex Ions.—α-N_2. For a linear centrosymmetric molecule the only non-zero multipole moments Q_{lm} are those with l even and m zero. The experimental value of the quadrupole moment Q_2 of N_2 is $(1.4 \pm 0.1) \times 10^{-26}$ 1 e.s.u. cm^2 (1 e.s.u. $= 3.3356 \times 10^{-10}$ C), or 0.29 eÅ^2.[15] For the cubic structure[16] of crystalline α-N_2 I calculate $\partial^2 U/\partial Q_2{}^2 = 58.212$ kJ mol^{-1} e^{-2} Å^{-4}, giving a net stabilisation of 1.237 kJ mol^{-1} from the quadrupole–quadrupole interaction.

K[HF_2]. Again, only even l and zero m are possible. The $Q_l (l \leqslant 8)$ have been calculated by a molecular-orbital method by Neckel *et al.*,[3b] who also performed the lattice summation. I have calculated the contributions to the lattice energy of the tetragonal K[HF_2] structure[16] due to interactions with $l + l' \leqslant 4$, and their values are listed in Table 2.

Pb[NO_3]$_2$. For the nitrate ion (symmetry D_{3h}) the non-zero moments Q_{lm} are those with $l + m$ even and $m = 0, \pm 3, \pm 6$, *etc.* The second derivatives of the lattice energy with respect to all the multipole moments with $l \leqslant 3$ in the cubic Pb[NO_3]$_2$ structure[16] are listed in Table 3. The multipole moments of [NO_3]$^-$ do not appear to have been calculated, but we can estimate them roughly from a fractional-charge model. If r is the bond length and q the charge on each O atom, we have $Q_{20} = -1.5qr^2$ and $Q_{3,\pm 3} = 45\, qr^3$,[8] and taking $r = 1.243$ and $q = 0.569$ (from a SCF MO calculation[17]) we obtain the values 1.32 eÅ^2 and -49.2 eÅ^3, respectively. The resulting contributions to the lattice energy are given in Table 3.

TABLE 2

Contributions to the electrostatic lattice energy (kJ mol^{-1}) of K[HF_2]

$l + l'$	This work	Ref. 3*b*
0	727.354 5	727.336 9
2	43.566 5	43.562 1
4	−12.690 3	−12.691 5

The Outer-sphere Contribution to the Crystal-field Splitting in NiO.—This compound has the NaCl structure with $a = 4.1684$ Å.[16] The ground state of Ni^{2+}, $^3A_{2g}(t_{2g}{}^6e_g{}^2)$, and the first excited state, $^3T_{2g}(t_{2g}{}^5e_g{}^3)$, are separated by an energy Δ, the major part of which is due to the six nearest oxide ions. I call this part Δ^{inner}, and the contribution from the rest of the crystal Δ^{outer}. In crystal-field theory terms, the splitting Δ is the result of the different energies of interaction of the multipole moments of the $^3A_{2g}$ and $^3T_{2g}$ states of Ni^{2+} with the non-spherical charge distribution surrounding it. I note that Δ^{outer} includes multipole–multipole interactions between cations, and its value will therefore depend on whether the other Ni^{2+} ions (*i*) remain in their ground states or (*ii*) make a simultaneous transition to the excited state. Spectroscopic measurement of Δ is made under conditions approximating to case (*i*). The value of Δ estimated from thermochemical data, however, is defined as five sixths of the difference in lattice energy between the actual crystal, in which all ions are in the $^3A_{2g}$ state, and a hypothetical crystal in which all Ni^{2+} ions have the spherical electron distribution $t_{2g}{}^{4.8}e_g{}^{3.2}$, the interionic distance being unchanged.[18] This corresponds to case (*ii*) above, and we may thus expect the outer-sphere contribution here, $\Delta_t{}^{\text{outer}}$, to differ from that in the spectroscopic process, $\Delta_s{}^{\text{outer}}$, because of the different orientations of the cation multipoles. Clearly the difference $\Delta_t - \Delta_s$ will be equal to $\Delta_t{}^{\text{mm}} - \Delta_s{}^{\text{mm}}$, where Δ^{mm} represents the contribution to Δ from multipole–multipole interactions alone (*i.e.* not involving the charges of the cations or anions).

The crystal-field splittings can be calculated as follows.

TABLE 3

Second derivatives[a] of the lattice energy (kJ mol^{-1}) with respect to the multipole moments,[b] and corresponding energy contributions for Pb[NO_3]$_2$

Type i	l	m	Type i'	l'	m'	$\partial^2 U/\partial Q_{ilm}\partial Q_{i'l'm'}$	Energy/ kJ mol^{-1}
Pb^{2+}	0	0	Pb^{2+}	0	0[c]	$1.523\,8 \times 10^3$	1 523.82
			[NO_3]$^-$	0	0[c]	$3.648\,7 \times 10^2$	−364.87
				2	0	$1.742\,5 \times 10^2$	230.01
				3	±3	0.0	0.00
[NO_3]$^-$	0	0	[NO_3]$^-$	0	0[c]	$3.675\,2 \times 10^3$	918.81
				2	0	$-3.725\,4 \times 10^2$	24.59
				3	±3	$-3.173\,3 \times 10^{-1}$	−7.81
	2	0		2	0	$-1.523\,3 \times 10^1$	−6.64
				3	±3	$2.788\,2 \times 10^{-3}$	−0.09
	3	±3		3	±3	$-4.740\,4 \times 10^{-3}$	−2.87
				3	∓3	$-3.233\,2 \times 10^{-3}$	−3.91
						Total	2 300.28

[a] The second derivatives are real. [b] The units of Q_{lm} are assumed to be eÅ. [c] Since the charges of the ions are not independently variable (the crystal must be electrically neutral), the partial derivatives in these cases have no meaning in isolation.

If the ground-state crystal structure is represented as A + X, the structure in which all the cations are in the $^3T_{2g}$ state as T + X, and the hypothetical crystal with spherical Ni^{2+} ions as S + X, then for my electrostatic model one obtains (33) and (34) where U is the electrostatic

$$\Delta_s = 2(U_{AA} + U_{AX} - U_{AT} - U_{TX}) \qquad (33)$$

$$\Delta_t = \tfrac{5}{6}(U_{AA} + 2U_{AX} - U_{SS} - 2U_{SX}) \qquad (34)$$

part of the lattice energy. These values include an inner-sphere contribution, Δ^{inner} (not, of course, the *true* value of this quantity, which cannot be obtained from a purely ionic model), which we must subtract so as to obtain the outer-sphere contributions; since the anions are spherical and therefore behave electrostatically like point charges, Δ^{inner} can be obtained by a simple point-charge CF calculation, *i.e.* $\Delta^{\text{inner}} = 10\,Dq$.

It can be seen from Table 1 that the only spherical harmonics $Y_l{}^m$ and Slater integrals F^l that contribute to Δ_s and Δ_t are those with $l = 0$ or 4. The corresponding multipole moments are proportional to $\langle r^0 \rangle$ and $\langle r^4 \rangle$, and since $\langle r^0 \rangle = 1$ the only variable parameter is $\langle r^4 \rangle$. Using an approximate representation[19] of the Hartree–

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Fock radial function for Ni^{2+}, I calculate $\langle r^4 \rangle = 0.2637$ Å^4. This value can be reproduced by a linear radial density function $[R(r)]^2$ decreasing to zero at $r_0 = 1.0532$ Å, and I therefore use the latter as the radial function in MULTMAD-B. The results are $\Delta_s = 31.49$ and $\Delta_t = 31.62$ kJ mol^{-1}. For an octahedron of point charges $-2e$ at a distance R from Ni^{2+}, $10Dq = 10e^2 \langle r^4 \rangle / 3R^5$, which gives $\Delta^{inner} = 31.05$ kJ mol^{-1}. Hence $\Delta_s^{outer} = 0.44$, $\Delta_t^{outer} = 0.57$, and $\Delta_t - \Delta_s = +0.13$ kJ mol^{-1}.

The difference $\Delta_t - \Delta_s$ can also be calculated more directly, by considering only the multipolar ($l = 4$) components of the cation charge clouds. With all the monopole terms removed we have $\Delta_s^{mm} = 2(U_{AA}^{mm} - U_{AT}^{mm})$ and $\Delta_t^{mm} = \frac{5}{6} U_{AA}^{mm}$; computation gives $U_{AA}^{mm} = -0.156$ and $U_{AT}^{mm} = -0.026$, whence $\Delta_s^{mm} = -0.26$ and $\Delta_t^{mm} = -0.13$ kJ mol^{-1}.

It is noteworthy that $U_{AA}^{mm} = 6U_{AT}^{mm}$, and hence $\Delta_s^{mm} = 2\Delta_t^{mm}$. This is a general result, which can be shown to follow from the angular dependence of the particular wavefunctions involved. Thus it is not actually necessary to calculate U_{AT}^{mm} in order to find $\Delta_t - \Delta_s$. I remark here that U_{AA}^{mm} can also be calculated by means of MULTMAD-A, using the relations $Q_{40} = \frac{1}{3} \langle r^4 \rangle$ and $Q_{4,\pm 4} = 40 \langle r^4 \rangle$, which are valid for the ${}^3A_{2g}$ function.

DISCUSSION

In recent years there has been a growth of interest in the lattice energies of crystals containing multipolar molecules or complex ions.[20] Most calculations have involved assigning fractional charges to the atoms; often the values assigned have been based on electronegativities or similar considerations, but even when they are derived from a detailed quantum-mechanical treatment (*via* a population analysis) such numbers bear a rather artificial relation to the actual molecular charge-density distribution. For small symmetrical atomic clusters a more accurate representation is given by the multipole moments of the charge density, and methods are now available for calculating these in a routine manner.[3b,21] This paper describes a method for computing the electrostatic-interaction energy of a crystal composed of multipolar particles of any symmetry in terms of their multipole moments, and also (in principle) for calculating the electrostatic energy of a localised process involving a change in the position or multipolar properties of one such particle.

The calculations for α-N_2, $K[HF_2]$, and lead nitrate illustrate the application to straightforward lattice-energy problems. The result for α-N_2, $U = 1.237$ kJ mol^{-1}, agrees well with the value obtained by Kohin,[22] $U = -21.47Q^2/2R^5 = 1.238$ kJ mol^{-1}, by direct summation over 27 unit cells. (For this relatively simple structure, direct summation is probably the most efficient method of calculation.) The results for $K[HF_2]$ (Table 2) are in good agreement with those obtained by Neckel *et al.*,[3b] using an extension of the Ewald method to cylindrical multipoles. For $Pb[NO_3]_2$, the dependence of the lattice energy on the quadrupole and octapole moments of the nitrate ion is readily computed (Table 3), but the values of the moments are not yet known. However, by assigning fractional charges to the atoms I have made plausible estimates, from which it appears that the multipoles contribute altogether *ca.* 10% of the total electrostatic binding energy.

An example of a more sophisticated application is the calculation on nickel oxide, in which mixed convolutions are used to obtain the outer-sphere contributions to the energy of the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition. It is found: (*a*) that the charges of all the ions beyond the first co-ordination sphere contribute 0.92 kJ mol^{-1} to Δ; and (*b*) that, in addition, the cation multipoles contribute -0.26 kJ mol^{-1} to Δ_s and -0.13 to Δ_t.

A difference between Δ_t and Δ_s is observed experimentally, and one of the aims of the present study was to investigate the possibility that the inequality arises from differences in the outer-sphere contribution to Δ. In NiO, the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition has been observed at *ca.* 9 000 cm^{-1}, so that Δ_s is 107 ± 2 kJ mol^{-1}.[23] Δ_t can be defined as five sixths of the energy of transition to the hypothetical state in which all the Ni^{2+} ions adopt the spherical configuration, the lattice enthalpy in the latter state being estimated by interpolation from data for oxides containing spherical ions (CaO, MnO, and ZnO). The value obtained in this way is 113 ± 2 kJ mol^{-1}, although this value should probably be increased slightly to take account of the fact that ZnO has the wurtzite rather than the NaCl structure.[18] Similar data for other transition-metal compounds were collected by George and McClure,[18] who first drew attention to the fact that one generally finds $\Delta_t > \Delta_s$. However, the results above clearly rule out the possibility that a significant part of the difference is due to outer-sphere electrostatic interactions.

In conclusion, it should be pointed out that my estimate of the multipole–multipole contribution to $\Delta_t - \Delta_s$ is only approximate because, being proportional to $\langle r^4 \rangle^2$, it is very sensitive to the radial function. If, for example, the Hartree–Fock function appropriate to the nickel atom rather than the Ni^{2+} ion had been used, we should have obtained a value of 0.75 kJ mol^{-1}, nearly six times that actually found; had the value of $\langle r^4 \rangle$ used been that which makes $10Dq$ equal to the observed value of Δ, the value calculated for $\Delta_t - \Delta_s$ would have been 1.5 kJ mol^{-1}.

Other Applications.—The method described here could usefully be applied to problems like one recently discussed by Owens,[24] who calculated the CF splitting of the π orbitals of an $[N_2]^-$ ion in crystalline barium azide, using a point-charge representation of the $[N_3]^-$ quadrupole. It seems likely that it would also be useful

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in the study of other solid-state phenomena, such as the energies of formation of Schottky and Frenkel defects, the lattice energies of electron-transfer processes, factor-group splittings of vibrational spectra, and the magnetic-dipole and electric-multipole contributions to spin–spin interactions.

APPENDIX

The $h = 0$ *Term in Equation* (19).—From the power series expansion of the Bessel function,[25] it follows that as $h \longrightarrow 0$, $\langle j_l(2\pi hr)\rangle/\langle r^l\rangle \longrightarrow [(4\pi)^l l!/(2l+1)!]h^l$, and hence:

$$T_{\boldsymbol{h}}(ilm;\ i'l'm') \longrightarrow \text{constant} \times h^{l+l'-2} \times \sum_{jk}\sum_{j'k'} \exp[2\pi i\boldsymbol{h}.(\boldsymbol{x}_{i'j'k'} - \boldsymbol{x}_{ijk})]\, Y_l^{-m*}(\hat{h}_{ij}\, Y_{l'}^{-m'}(\hat{h}_{i'j'}) \quad \text{(A1)}$$

Terms with $l + l' > 2$ vanish. By expanding the exponential we find that, in order for the remaining terms to vanish as $h \longrightarrow 0$, the following conditions must be satisfied: $\sum_i Q_{i00} = 0$ (otherwise T is infinite); $\sum_{ijk} Q_{i00}\boldsymbol{x}_{ijk} = 0$, and $\sum_{ij} Q_{i10}\cos\theta_{hij} = 0$ for any $\boldsymbol{h}$ (otherwise T is indeterminate).

The Integrals I_l *and* F^l *for a linearly decreasing Radial Density Function.*—Here $\alpha = 2\pi hr_0$.

$$[R(r)]^2 = \begin{cases} 12(r_0 - r)/r_0^4 & (0 < r < r_0) \\ 0 & (r > r_0) \end{cases} \quad \text{(A2)}$$

$$\langle r^l\rangle = [12/(3+l)(4+l)]r_0^l \quad \text{(A3)}$$

$$F^l = [48(13+2l)/35(3+l)(4+l)]r_0^{-l} \quad \text{(A4)}$$

$$I_0 = 12(2 - 2\cos\alpha - \alpha\sin\alpha)/\alpha^4 \quad \text{(A5)}$$

$$I_1 = 12(2\alpha - 3\sin\alpha + \alpha\cos\alpha)/\alpha^4 \quad \text{(A6)}$$

$$I_2 = 12[-8 + 8\cos\alpha + \alpha\sin\alpha + 3\alpha \mathrm{S_i}(\alpha)]/\alpha^4 \quad \text{(A7)}$$

$$I_3 = 12[8\alpha + 8\sin\alpha - \alpha\cos\alpha - 15\mathrm{S_i}(\alpha)]/\alpha^4 \quad \text{(A8)}$$

$$I_4 = 12[-48 - 4.5\cos\alpha - \alpha\sin\alpha + 52.5(\sin\alpha/\alpha) + 7.5\mathrm{S_i}(\alpha)]/\alpha^4 \quad \text{(A9)}$$

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