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# Electrostatic Lattice Energy in Ionic Crystals: Optimization of the Convergence of Ewald Series

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Ewald's method is reconsidered to express the dependence of Madelung energy on the ionic charges explicitly, also taking into account the space-group symmetry of the structure. Upper bounds for the residues of the two partial series have been calculated by integral approximation; that relative to the direct-lattice series is shown to depend on the cube root of the unit-cell volume. The optimum value of the parameter $A$, which equalizes the rates of convergence of the two sums and minimizes the total number of terms, has been determined numerically for a given termination error and for a range of unit-cell dimensions. Theoretical results are tested by calculations on some specific crystal structures.

## Introduction

In recent years, a new interest has arisen in calculations of cohesion energy in ionic or partially ionic* crystals according to the simple Born model (Tosi, 1964): the energy is divided into a dominant (Coulombic) term, which can be computed exactly, and two secondary (repulsive and dispersive) terms which require a semi-empirical parametrization. However, the modern approach seems to aim at a quantitative interpretation of the crystal chemistry of complicated structures, which are important in mineralogy or in solid-state technology, rather than at an accurate *ab initio* calculation of physical properties of crystals with very simple structures, as in earlier times. In this respect, maximum computing efficiency of the time-consuming electrostatic term of the energy should be even more important than an accurate parametrization of the other two terms; this holds particularly if the energy is to be minimized by letting the atomic positions change, since the amount of computation then required may rise strikingly (Baur, 1965; Ladd, 1968; Giese & Datta, 1973).

The Coulombic formula for the electrostatic (or Madelung) lattice energy of a unit cell is:

$$\mathscr{E} = \frac{1}{2} e^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{-\infty\,\mathbf{l}}^{+\infty} \frac{z_i z_j}{|\mathbf{x}_{ij} + \mathbf{l}|} \quad (\text{if } i=j,\ \mathbf{l} \neq 0), \quad (1)$$

where $e$ is the electron charge, $N$ is the number of ions in the cell, $z_i$ is an ionic charge referred to the electron charge, $\mathbf{x}_{ij} = \mathbf{x}_i - \mathbf{x}_j$ is an interatomic vector between ions contained in the cell, and $\mathbf{l}$ is a vector of the direct lattice. This straightforward calculation is not very convenient, as the Coulombic potential decreases slowly for large distances. However, the convergence of (1) may be improved by suitably ordering the terms in the sum (Evjen, 1932): a computer program has been based on this method (Boeyens & Gafner, 1969), but it can handle only centrosymmetric structures. In his classic paper, Bertaut (1952) showed that expression

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* A 'partially ionic' crystal is meant here to contain both prevalently ionic and prevalently covalent bonds, and not bonds all having an intermediate character between ionic and covalent.

(1) can be replaced by a much faster converging series if the ions are considered to be charge distributions with spherical symmetry, instead of point charges. In the case of charge densities falling to zero at some distance from the ions, without overlapping, a reciprocal-lattice sum only is obtained; this will be called Bertaut series henceforth. If, on the other hand, charge distributions never go to zero so that overlap arises, a reciprocal-lattice sum plus a direct-lattice sum are necessary: in the particular case that the charge-density distribution is Gaussian, the Ewald double series is obtained, which had already been derived from (1) in a purely mathematical way (Ewald, 1921).

Some computing programs are based on the Bertaut series (Ladd, 1968; Jenkins & Waddington, 1972; Ohashi, 1976), some on the Ewald series (Baur, 1965; Bonnin & Legrand, 1975; Fischer & Ludwiczek, 1975; Weenk & Harwig, 1977), and some on both series (Born & Zemann, 1964). The first method has the clear advantage that a reciprocal-lattice sum only is used; in addition, the computing accuracy can be improved by estimating the termination error of the series (Templeton, 1955). However, the rate of convergence of the Bertaut series is not high, because the charge densities are approximated very roughly by discontinuous functions. On the other hand, Ewald's method, which is consistent with a more realistic physical model for the charge distribution, allows in principle a very fast convergence of both partial series, provided that a suitable width is chosen for the Gaussian (Tosi, 1964; Jones & Templeton, 1956). Besides, in the case that interatomic distances must be calculated for the repulsive and dispersive terms of the cohesion energy, the advantage of excluding the direct-lattice sum in Bertaut's method is somehow lost.

In the present work the conditions for optimal convergence of the Ewald double series are investigated, so as to exploit its potentially greater efficiency for Madelung-energy calculations thoroughly.

## Ewald's method and symmetry

The physical meaning of Madelung energy depends strictly on how reliable the charges assigned to the single ions are. It is then very useful to express the functional dependence between energy and charges explicitly, so that the effect of changing charges upon the energy value can be evaluated directly, keeping the structural parameters constant (Jenkins & Waddington, 1972). This approach will be applied to Ewald's formula, which can then be written as:

$$\mathscr{E}=\frac{1}{2}e^2\sum_{i=1}^{N}\sum_{j=1}^{N}z_iz_jF(\mathbf{x}_{ij}); \tag{2}$$

$$F(\mathbf{x}_{ij})=\frac{2}{\pi V}\sum_{-\infty\,\mathbf{h}}^{+\infty}{}'\,\frac{1}{h^2}\exp\left(-\frac{\pi^2h^2}{A^2}\right)\cos(2\pi\mathbf{h}.\mathbf{x}_{ij})$$
$$+\sum_{-\infty\,\mathbf{l}}^{+\infty}\frac{\operatorname{erfc}(A|\mathbf{x}_{ij}+\mathbf{l}|)}{|\mathbf{x}_{ij}+\mathbf{l}|}-\frac{2A}{\sqrt{\pi}}\delta_{ij}\quad(\text{if } i=j,\mathbf{l}\neq0), \tag{3}$$

where $\operatorname{erfc}(y)=2/\sqrt{\pi}\int_y^{+\infty}\exp(-t^2)\,\mathrm{d}t$ is the complementary error function, $V$ is the volume of the unit cell, $\mathbf{h}$ is a vector of the reciprocal lattice, $\delta_{ij}$ is the Kronecker symbol, and $\sum'$ is a sum over noncentrosymmetric lattice vectors only, excluding the zero vector. The parameter $A$ is inversely proportional to the width of the Gaussian representing the ionic-charge distribution and conditions the relative rate of convergence of the two series: for small values of $A$, the first series converges rapidly and the second slowly, and *vice versa* for large values.

However, a direct use of formula (2) is not the most efficient calculation, since the space-group symmetry is not taken into account. The symmetry properties of the function $F(\mathbf{x})$, defined by (3), can easily be proved to be:

$$F(-\mathbf{x})=F(\mathbf{x}), \tag{4}$$

$$F(\mathbf{x}+\mathbf{l})=F(\mathbf{x}), \tag{5}$$

$$F(\mathscr{R}\mathbf{x})=F(\mathbf{x}), \tag{6}$$

where $\mathscr{R}$ is any symmetry operator of the space group of the crystal structure. On the basis of (4) and (6) the sum (2) can be contracted to just the $n$ ions contained in the asymmetric unit:

$$\mathscr{E}=\frac{1}{2}e^2\sum_{r=1}^{n}\sum_{s=1}^{n}z_rz_s\left[p_r\sum_{m=1}^{p_s}F(\mathbf{x}_{s,m}-\mathbf{x}_{r,1})\right], \tag{7}$$

where $p_r$ and $p_s$ are the multiplicities of the crystallographic sites occupied by the $r$th and the $s$th ions, respectively, $\mathbf{x}_{r,1}$ and $\mathbf{x}_{s,m}$ are the position vectors of the $r$th ion in the asymmetric unit and of the $s$th ion in the $m$th equivalent position. The expression in square brackets is symmetrical with respect to an exchange of $r$ with $s$. Eventually, the electrostatic lattice energy of a mole of crystalline substance can be written as:

$$E=\sum_{r=1}^{n}\sum_{s=r}^{n}z_rz_sC_{rs}, \tag{8}$$

$$C_{rr}=\frac{\mathscr{N}e^2}{2Z}p_r\sum_{m=1}^{p_r}F(\mathbf{x}_{r,m}-\mathbf{x}_{r,1}), \tag{9}$$

$$C_{rs}=\frac{\mathscr{N}e^2}{Z}p_r\sum_{m=1}^{p_s}F(\mathbf{x}_{s,m}-\mathbf{x}_{r,1})\quad(r\neq s), \tag{10}$$

where $\mathscr{N}$ is Avogadro's number and $Z$ is the number of formula units in the unit cell.

The expression (8) can be further contracted, so as to obtain a bilinear form in the charges of the independent ionic species only, by simply summing the coefficients (9) and (10) which correspond to equally charged ions. This form is the most suitable for separating the effects of the structural features and the ionic charges on the Madelung energy. A computer program performing these calculations is described in Appendix I.

## Analysis of the convergence

In order to estimate the termination errors of the two series in (3), two spheres of radii $h_0$ and $l_0$ are considered, with a centre at the origin of the reciprocal and direct lattices. Each sum is assumed to be limited to lattice points lying inside the corresponding sphere only; its residue can then be approximated by a triple integral extended to all space outside the sphere itself; spherical coordinates are suitable for the calculations. An upper bound for the residue of the first series is obtained by putting $\mathbf{x}_{ij} = 0$; taking into account that the density of terms in reciprocal space is $V$:

$$R_1 \le \frac{1}{\pi}\iiint \frac{1}{h^2}\exp\left(-\frac{\pi^2 h^2}{A^2}\right)\mathrm{d}\tau$$
$$= \frac{1}{\pi}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_{h_0}^{+\infty}\exp\left(-\frac{\pi^2 h^2}{A^2}\right)\mathrm{d}h$$
$$= \frac{2A}{\sqrt{\pi}}\,\mathrm{erfc}\left(\frac{\pi h_0}{A}\right). \tag{11}$$

As for the residue of the second series, it is not possible to derive an upper bound independent of $\mathbf{x}_{ij}$ directly, but the integral must be calculated as an explicit function of $\mathbf{x}_{ij}$. The subscripts have been omitted for simplicity:

$$R_2(x) = \frac{1}{V}\iiint \frac{\mathrm{erfc}\,(A\,|\mathbf{x}+\mathbf{l}|)}{|\mathbf{x}+\mathbf{l}|}\,\mathrm{d}\tau$$
$$= \frac{1}{V}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi}\sin\theta\,\mathrm{d}\theta\int_{l_0}^{+\infty}\frac{\mathrm{erfc}[A\sqrt{(l^2+2xl\cos\theta+x^2)}]}{\sqrt{(l^2+2\,xl\cos\theta+x^2)}}\,l^2\,\mathrm{d}l$$
$$= \frac{2\pi}{V}\left\{\left[-\frac{(l_0-x)^3}{3x}+\frac{(l_0+x)^2}{2}+\frac{1}{4A^2}\right]\mathrm{erfc}[A(l_0+x)]\right.$$
$$+\left[\frac{(l_0-x)^3}{3x}+\frac{(l_0-x)^2}{2}+\frac{1}{4A^2}\right]\mathrm{erfc}\,[A(l_0-x)]$$
$$+\frac{1}{\sqrt{(\pi)}A}\left[\frac{(l_0+x)^2}{3x}-\frac{l_0+x}{2}-\frac{1}{6A^2x}\right]$$
$$\times\exp[-A^2(l_0+x)^2]+\frac{1}{\sqrt{(\pi)}A}$$
$$\times\left[-\frac{(l_0-x)^2}{3x}-\frac{l_0-x}{2}+\frac{1}{6A^2x}\right]$$
$$\left.\times\exp[-A^2(l_0-x)^2]\right\};\tag{12}$$

for mathematical details of the calculation see Appendix II.

Taking into account (5), in (12) $x$ represents the modulus of a 'reduced' interatomic vector, *i.e.* the shortest one in the class of all those obtained by adding lattice vectors $\mathbf{l}$ to it. $R_1$ and $R_2(x)$ are decreasing functions of $h_0$ and $l_0$ respectively. As $A$ gets larger $R_1$ increases and $R_2(x)$ decreases, since the rates of convergence of the two series are affected oppositely by changes of $A$. Besides, $R_2(x)$ rises greatly as $x$ increases, showing that the convergence becomes slower for longer interatomic vectors. It is necessary, however, to get rid of the dependence of $R_2(x)$ on the length of the single interatomic vector, in order to obtain an estimate of the termination error valid for the whole calculation. It is then convenient to assume the value of (12) calculated for the longest reduced interatomic vector in the unit cell as an upper bound of the residue of the direct-lattice series. By examining a sample of crystal structures, the length of that vector has been shown to be always very close to 80–90% of the cube root of the unit-cell volume (which is called $x_0$); a reasonable bound for the residue is then $R_2 \le R_2(x_0)$, and this depends only on $A$, $l_0$ and the unit-cell volume.

We now need to investigate at which values of $h_0$ and $l_0$ the two series must be terminated to obtain an equal residue $R = R_1 = R_2$. These values depend on $A$, and by solving equations (11) and (12) numerically with respect to $h_0$ and $l_0$ the functions $h_0(A)$ and $l_0(A)$, which comply with the required condition, have been derived;

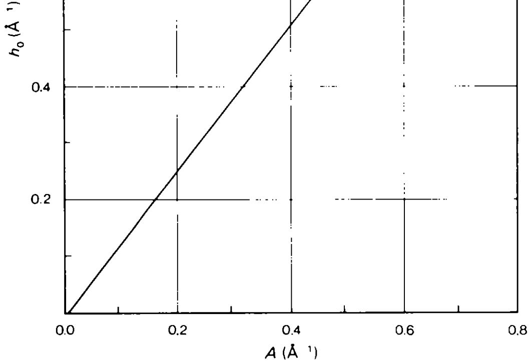

Fig. 1. Graph of the convergence function $h_0(A)$ of the reciprocal-lattice series, obtained by solving equation (11), for a residue $R = 10^{-8}$ Å$^{-1}$.

their graphs are shown in Figs. 1 and 2 for particular values of $R$ and $x_0$. The numbers of terms in the two sums of (3) terminated at $h = h_0$ and $l = l_0$ are, respectively:

$$n_R = \frac{2\pi}{3} h_0^3(A) x_0^3, \tag{13}$$

$$n_D = \frac{4\pi}{3} \frac{l_0^3(A)}{x_0^3}. \tag{14}$$

As $A$ rises, the number of terms $n_R$ necessary for the convergence (within the error $R$) of the reciprocal series increases, whereas $n_D$ decreases. The fastest convergence of the Ewald series as a whole can then be defined by either the equality $n_R = n_D$, or the condition that the sum $n_R + n_D$ is a minimum: the value (or values) of $A$ which satisfies these conditions has to be found. With $R$ and $x_0$ fixed, the functions $n_R(A)/n_D(A)$ and $n_R(A) + n_D(A)$ have been calculated for variable $A$; it has turned out that the value of $A$ which equals $n_R$ and $n_D$ also minimizes $n_R + n_D$, so that the two conditions are equivalent. In Table 1 the results of these calculations are reported for two values of the residue $R$, and for several values of $x_0$ covering a wide range of unit-cell dimensions. It is interesting to remark that the minimum number of terms $n_R = n_D$ is independent of $x_0$ to a good approximation, and amounts to about 60 and 50, respectively, for the two values of $R$ considered. Besides, for changes of $R$ of an order of magnitude, very small changes are observed in the values of $A$ which equalize the rates of convergence of the two partial series.

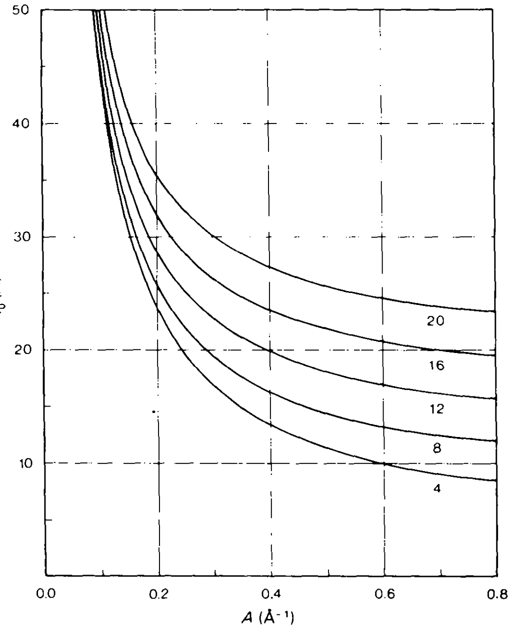

Fig. 2. Graph of the convergence function $l_0(A)$ of the direct-lattice series, obtained by solving equation (12), for a residue $R = 10^{-8}$ Å$^{-1}$ and for different values of $x_0 = V^{1/3}$ (Å).

Table 1. *Optimum $A$ (Å$^{-1}$) values for the convergence of Ewald series* (3) *terminated with $l \le l_0$* (Å) *and $h \le h_0$* (Å$^{-1}$), *according to residues $R$ of* $10^{-8}$ *and* $10^{-7}$ Å$^{-1}$ *respectively*; $x_0$ (Å) *is the cube root of the unit-cell volume*

| | $R = 10^{-8}$ Å$^{-1}$ | | | $R = 10^{-7}$ Å$^{-1}$ | | |
|---|---|---|---|---|---|---|
| $x_0$ | $A$ | $l_0$ | $h_0$ | $A$ | $l_0$ | $h_0$ |
| 4 | 0·615 | 10·0 | 0·785 | 0·615 | 9·5 | 0·725 |
| 5 | 0·485 | 12·5 | 0·615 | 0·490 | 11·5 | 0·580 |
| 6 | 0·405 | 15·0 | 0·510 | 0·405 | 14·0 | 0·475 |
| 7 | 0·345 | 17·0 | 0·435 | 0·350 | 16·0 | 0·410 |
| 8 | 0·300 | 19·5 | 0·380 | 0·305 | 18·5 | 0·355 |
| 9 | 0·270 | 21·5 | 0·340 | 0·275 | 20·5 | 0·315 |
| 10 | 0·240 | 24·0 | 0·300 | 0·245 | 22·5 | 0·285 |
| 11 | 0·220 | 26·5 | 0·270 | 0·225 | 24·5 | 0·255 |
| 12 | 0·200 | 29·0 | 0·250 | 0·205 | 27·0 | 0·235 |
| 13 | 0·185 | 31·5 | 0·230 | 0·190 | 29·0 | 0·220 |
| 14 | 0·175 | 33·0 | 0·215 | 0·175 | 31·0 | 0·200 |
| 15 | 0·160 | 36·0 | 0·200 | 0·165 | 33·0 | 0·185 |
| 16 | 0·150 | 38·0 | 0·180 | 0·155 | 35·5 | 0·175 |
| 17 | 0·145 | 40·0 | 0·175 | 0·145 | 37·5 | 0·165 |
| 18 | 0·135 | 42·5 | 0·165 | 0·135 | 40·0 | 0·155 |
| 19 | 0·125 | 45·5 | 0·155 | 0·125 | 43·0 | 0·145 |
| 20 | 0·120 | 47·5 | 0·150 | 0·120 | 44·5 | 0·140 |

## Discussion

In order to test the theoretical results of the preceding section, the crystal structures reported in Table 2 have been considered, and the convergence functions $h_0(A)$

Table 2. *Madelung energies $E$* (kJ mol$^{-1}$) *and crystal data for some structures*

$\Delta E$ (kJ mol$^{-1}$) is the termination error corresponding to a residue $R = 10^{-8}$ Å$^{-1}$. Previous calculations are reported in the references shown.

| | Space group | $Z$ | $x_0$ | $z$(O) | $E$ | $\Delta E$ | $\Delta E/E$ | |
|---|---|---|---|---|---|---|---|---|
| $CaTiO_3$ | *Pm3m* | 1 | 3·84 | −2·00 | −17912·674 | $2.0 \times 10^{-3}$ | $1.1 \times 10^{-7}$ | Johnson & Templeton (1961) |
| $CaCO_3$ | $R\bar{3}c$ | 2 | 4·96 | −0·60 | −2009·942 | $4.5 \times 10^{-4}$ | $2.2 \times 10^{-7}$ | Jenkins & Waddington (1972) |
| $K_2SO_4$ | *Pnma* | 4 | 7·57 | −0·85 | −3896·835 | $2.6 \times 10^{-3}$ | $6.6 \times 10^{-7}$ | Jenkins (1972) |
| $MgAl_2O_4$ | *Fd3m* | 8 | 8·08 | −2·00 | −22807·845 | $2.9 \times 10^{-2}$ | $1.2 \times 10^{-6}$ | Johnson & Templeton (1961) |
| $Ca_3Al_2(SiO_4)_3$ | *Ia3d* | 8 | 11·85 | −2·00 | −75822·091 | $2.6 \times 10^{-1}$ | $3.4 \times 10^{-6}$ | Born & Zemann (1964) |

and $l_0(A)$ have been checked in these specific cases. Starting from (8), (9) and (10), the maximum termination error of the Ewald series $\Delta F_{\max} = R_1 + R_2 = 2R$ can be shown to propagate onto the energy error as follows:

$$\Delta E < \frac{\mathcal{N}e^2}{Z}\left(\frac{1}{2}\sum_{r=1}^{n} p_r^2 z_r^2 + \sum_{r=1}^{n}\sum_{s=r+1}^{n} p_r p_s |z_r z_s|\right)\Delta F_{\max} = \frac{\mathcal{N}e^2}{Z}\left(\sum_{r=1}^{n} p_r |z_r|\right)^2 R = \mathcal{N}e^2 Z\left(\sum_{r=1}^{n'} |z_r|\right)^2 R, \qquad (15)$$

where $n'$ represents the number of ions in the formula unit of the compound. For each structure, the $\Delta E$ error corresponding to $R = 10^{-8}$ Å$^{-1}$ has been calculated; then, with $A$ fixed, the energy was repeatedly computed for increasing $h_0$ and $l_0$ until the change was less than or equal to $\Delta E$: from the corresponding $h_0$ and $l_0$ values, determined in this way for different values of $A$, 'empirical' convergence curves $h_0(A)$ and $l_0(A)$ were built up for all the structures. The results show a satisfactory agreement with the theoretical curves of Figs. 1 and 2; as an example, the curves for $K_2SO_4$ are reported in Figs. 3 and 4. Also, in Table 3 the detailed behaviour of the energy convergence for $K_2SO_4$ is shown with $A = 0{\cdot}30$ Å$^{-1}$: $E_1$ and $E_2$ are the components of the electrostatic energy due to the first term and to the sum of the other two, respectively, in (3). By computing the energy for different values of $A$ in all the structures considered, the minimum computation time was always obtained for the optimal $A$ value given by Table 1.

The problem of determining the optimum value of the parameter $A$ yielding the fastest convergence of the Ewald series has been dealt with by an analytical approach, and has led to a dependence of $A$ on the cube root of the unit-cell volume. A similar attempt (Bonnin & Legrand, 1975) produced a relation analogous to (11) for the residue of the reciprocal-space series, but questionable results for the residue of the other series: indeed, the integral in (12) was calculated only in the special case $x = 0$, and the result was assumed as a bound for the residue, whereas it has been shown that the integral increases strongly as $x$ grows. On purely empirical bases, Weenk & Harwig (1977) have proposed the relation $A = \sqrt{(\pi)}/x_0$ for the optimum parameter; this $A$ value is too small, but it reproduces the qualitative dependence on $x_0$ correctly.

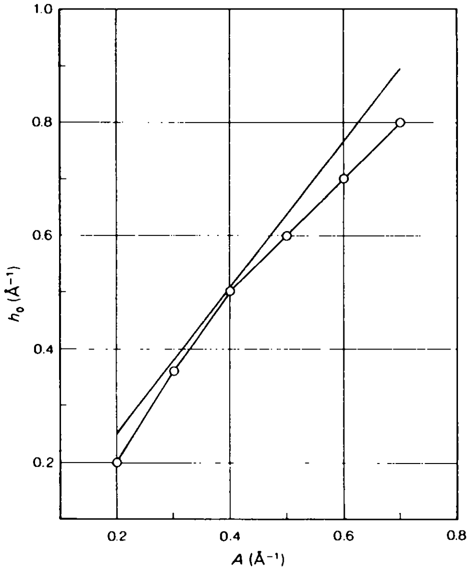

Fig. 3. Empirical convergence curve $h_0(A)$ for $K_2SO_4$ (circles), compared with the theoretical curve ($R = 10^{-8}$ Å$^{-1}$).

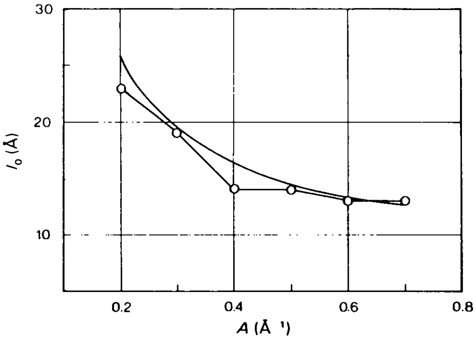

Fig. 4. Empirical convergence curve $l_0(A)$ for $K_2SO_4$ (circles), compared with the theoretical curve ($R = 10^{-8}$ Å$^{-1}$).

Table 3. *Values of the two components* $E_1$ *and* $E_2$ (kJ mol$^{-1}$) *of the Madelung energy of* $K_2SO_4$ *for different termination parameters* $h_0$ (Å$^{-1}$) *and* $l_0$ (Å), *with* $A = 0{\cdot}30$ Å$^{-1}$

| $h_0$ | $E_1$ | $l_0$ | $E_2$ |
|---|---|---|---|
| 0·30 | 0·969 | 17 | −3897·772 |
| 0·33 | 0·972 | 18 | −3897·820 |
| 0·36 | 0·980 | 19 | −3897·815 |
| 0·39 | 0·979 | 20 | −3897·815 |

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## APPENDIX I

The program *MADEWA*, written in Fortran IV, computes the Madelung energy of a crystal structure by Ewald's method on the basis of formulas (3), (8), (9), and (10). Any cell parameters and any space group are accepted; 20 atoms in the asymmetric unit are the maximum allowable in the present version (150 K of core); this, however, can easily be enlarged. By means of a subroutine, indexes and moduli are computed and stored in the core for all reciprocal- and direct-lattice vectors which are contained within the spheres of radii $h_0$ and $l_0$, respectively, and are not related by a centre of symmetry. Ewald series (3) is calculated by another subroutine for all interatomic vectors $\mathbf{x}_{ij}$ which are not symmetry-related, using the relation $|\mathbf{x} \pm \mathbf{l}| = x^2 + l^2 \pm \sum_{1}^{3}{}_{p}\, l_p \left(\sum_{1}^{3}{}_{q}\, G_{pq} x_q\right)$, where the $G_{pq}$'s are metric tensor elements. The output of the program shows: the total electrostatic lattice energy of a mole, $E$, and its two components $E_1$ and $E_2$, the coefficients (9) and (10) and the coefficients referring to the independent ionic species. As an example, running the program on $K_2SO_4$ in the optimal convergence conditions required 5·5 s of execution time on an IBM 370/158 computer.

## APPENDIX II

The triple integral in (12) was calculated in spherical coordinates assuming $\theta = 0$ for the direction of vector $\mathbf{x}$. In the first step, the substitution $t = A\sqrt{(l^2 + 2xl\cos\theta + x^2)}$ was used:

$$\int_0^{\pi} \frac{\operatorname{erfc}\lbrack A\sqrt{(l^2 + 2xl\cos\theta + x^2)}\rbrack}{\sqrt{(l^2 + 2xl\cos\theta + x^2)}} \sin\theta\, d\theta = \frac{(l+x)\operatorname{erfc}\lbrack A(l+x)\rbrack - (l-x)\operatorname{erfc}\lbrack A(l-x)\rbrack}{xl} - \frac{\exp\lbrack -A^2(l+x)^2\rbrack - \exp\lbrack -A^2(l-x)^2\rbrack}{\sqrt{(\pi)}Axl};$$

multiplying this function by $l^2 dl$ and integrating by parts repeatedly between the limits $l_0$ and $+\infty$ gave the result of (12).

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# Comparisons of Atomic Thermal Motions for Graphite at 300 K Based on X-ray, Neutron, and Phonon-Spectrum Data

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The mean-square amplitudes of vibration in graphite based on an X-ray charge-density analysis are 0·0032 (2) and 0·0140 (3) Å$^2$ parallel to and perpendicular to the basal plane, respectively. Values for the parallel vibrations of 0·0031 (6) and 0·0032 Å$^2$ were derived from temperature-dependent neutron measurements and a calculated phonon spectrum. The neutron measurements and the phonon spectrum both predict lower values [0·0090 (20) and 0·0098 Å$^2$] for the out-of-plane vibrations. This small discrepancy may be caused by small changes in the core atomic scattering factors from the free-atom values or by a deficiency in the phonon-spectrum model.

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