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The electrostatic energy of a lattice of point charges

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Résumé. — L'énergie électrostatique limite par maille E d'un réseau ionique de charges ponctuelles est définie comme la valeur limite de l'énergie d'un cristal fini divisée par son nombre de mailles (lorsque ce nombre tend vers $+\infty$). La valeur explicite de E est calculée, et reliée à l'énergie d'Ewald. Cette énergie E dépend de la suite des cristaux finis croissants (plus précisément, de la suite des ensembles finis croissants d'ions). En d'autres termes, et brièvement : E est une énergie volumique qui dépend de la surface.

Abstract. — The limit electrostatic energy per cell E of a ionic lattice of point charges is defined as the limit value of the energy of a finite crystal divided by its number of cells (when this number tends towards $+\infty$). The explicit value of E is calculated and related to the Ewald energy. This energy E depends on the sequence of the increasing finite crystals (more precisely, on the sequence of the increasing finite sets of ions). In other words, and briefly : E is a volumic energy which depends on the surface.

1. Introduction.

The electrostatic energy of an ionic lattice, in which the ions are considered as point charges (with electrical neutrality of the cell), may be written as

$$\begin{aligned}
 E &= \sum_{\substack{\{\mathbf{n}+\mathbf{s}, \mathbf{p}+\mathbf{t}\} \\ \mathbf{n}+\mathbf{s} \neq \mathbf{p}+\mathbf{t}}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{n} + \mathbf{s} - \mathbf{p} - \mathbf{t}\|} \\
 &= \frac{1}{2} \sum_{\mathbf{n}} \sum_{\substack{\mathbf{p} \\ \mathbf{n}+\mathbf{s} \neq \mathbf{p}+\mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{n} + \mathbf{s} - \mathbf{p} - \mathbf{t}\|}
 \end{aligned} \tag{1}$$

where $\mathbf{n} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$ and $\mathbf{p} = p_1 \mathbf{a}_1 + p_2 \mathbf{a}_2 + p_3 \mathbf{a}_3$ ($\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are cell vectors; $n_1, n_2, n_3, p_1, p_2, p_3$ are integers); $\mathbf{s}, \mathbf{t}$ are the positions of the ions of the origin cell ($\mathbf{n} = \mathbf{0}$); q_s is the charge of the ion $\mathbf{s}$. Ewald [1] and Bertaut [2] considered that this energy may be written as

$$E = \frac{1}{2} \sum_{\mathbf{p}} \sum_{\substack{\mathbf{m} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_s q_t}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|}$$

where $\mathbf{m} = \mathbf{n} - \mathbf{p}$ is supposed to run over all the lattice vectors; thus

$$E = \frac{1}{2} N \sum_{\mathbf{m}} \sum_{\substack{\mathbf{s} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{t}} \frac{q_s q_t}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|}$$

where N is the number of cells, which leads to the electrostatic energy per cell :

$$E_0 = \frac{1}{2} \sum_{\mathbf{m}} \sum_{\substack{\mathbf{s} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{t}} \frac{q_s q_t}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|}. \quad (2)$$

Ewald [1] and Bertaut [2] obtained, for this energy, the value

$$E_0 = E_E \quad (3)$$

with

$$E_E = E_1 - E_2 + E_3$$

$$E_1 = \frac{1}{2\pi V} \sum_{\mathbf{h} \neq \mathbf{0}} \frac{|F(\mathbf{h}) \varphi(\mathbf{h})|^2}{h^2}$$

$$E_2 = 2\pi \sum_{\mathbf{s}} q_s^2 \int_0^{+\infty} u p(u) du$$

$$= 2 \sum_{\mathbf{s}} q_s^2 \int_0^{+\infty} (\varphi(h))^2 dh$$

$$E_3 = \frac{1}{2} \sum_{\substack{\mathbf{m} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_s q_t}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \int_{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|}^{+\infty} 4\pi u (u - \|\mathbf{m} + \mathbf{s} - \mathbf{t}\|) p(u) du$$

$$= \frac{1}{2} \sum_{\substack{\mathbf{m} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_s q_t}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \left(1 - \frac{2}{\pi} \int_0^{+\infty} (\varphi(h))^2 \frac{\sin(2\pi h \|\mathbf{m} + \mathbf{s} - \mathbf{t}\|)}{h} dh \right) \quad (4)$$

where V is the volume of the cell; $\mathbf{h}$ is a vector of the reciprocal lattice; $F(\mathbf{h}) = \sum_{\mathbf{s}} q_s e^{2\pi i \mathbf{h} \cdot \mathbf{s}}$; p and φ are defined by

$$p(\mathbf{u}) = \int \sigma(\mathbf{x}) \sigma(\mathbf{x} + \mathbf{u}) d\mathbf{x}$$

$$\varphi(\mathbf{h}) = \int \sigma(\mathbf{x}) e^{2\pi i \mathbf{h} \cdot \mathbf{x}} d\mathbf{x}$$

($p(\mathbf{u})$ depends only on $u = \|\mathbf{u}\|$ and $\varphi(\mathbf{h})$ on $h = \|\mathbf{h}\|$), the function σ being non-negative,

of spherical symmetry and such that

$$\int \sigma(\mathbf{x}) \, d\mathbf{x} = 1.$$

De Leeuw *et al.* [3] calculated the value of E_0 , for a cubic lattice, and with the spherical mode of summation :

$$E_0 = \frac{1}{2} \lim_{N \rightarrow +\infty} \sum_{\substack{\|\mathbf{m}\| \leq N \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|}; \quad (5)$$

they found

$$\begin{aligned} E_0 &= E_1 - E_2 + E_3 + E_4 \\ &= E_E + E_4 \end{aligned} \quad (6)$$

with the values of E_1 , E_2 and E_3 obtained by Ewald and

$$E_4 = \frac{2 \pi \mathbf{M}^2}{3 a^3} \quad (7)$$

where a is the side length of the cubic cell and $\mathbf{M} = \sum_{\mathbf{s}} q_{\mathbf{s}} \mathbf{s}$ (dipole moment of the cell). Smith [4] extended the preceding result to other modes of summation.

In this paper, we present two results : in section 2, the calculation of E_0 , and its relation to the Ewald energy E_E ; in section 3, the calculation of the limit electrostatic energy per cell E (defined in section 3), and its relation to E_0 (and then to E_E). These results hold for an arbitrary lattice of point charges — in which the cell is electrically neutral, but its dipole moment may be different from $\mathbf{0}$ — and for arbitrary modes of summation.

2. Calculation of E_0 .

The mathematical proof corresponding to this section has been given in another paper [5]. We have observed that the result (3)-(4) of Ewald and Bertaut may be considered as an incorrect application of Poisson's formula to the function f

$$\begin{aligned} f(\mathbf{h}) &= \frac{|F(\mathbf{h}) \varphi(\mathbf{h})|^2}{\mathbf{h}^2}, \quad \mathbf{h} \neq \mathbf{0} \\ f(\mathbf{0}) &= 0, \end{aligned}$$

since f is not continuous at $\mathbf{h} = \mathbf{0}$ (if the dipole moment of the cell $\mathbf{M} = \sum_{\mathbf{s}} q_{\mathbf{s}} \mathbf{s}$ is different from $\mathbf{0}$).

We have then replaced the function f by a sequence of continuous functions f_N — to which Poisson's formula may be applied — and we have taken the limit of Poisson's formula as $N \rightarrow +\infty$.

We obtain the following result, if $\mathbf{M} \neq \mathbf{0}$:

Let (B_k) be any sequence of finite subsets of $\mathbb{Z}^3$ such that

(i) $B_k \subset B_{k+1}$, for all k ;

(ii) $\bigcup_k B_k = \mathbb{Z}^3$;

(iii) $\sum_{\mathbf{m} \in B_k \setminus \{\mathbf{0}\}} \frac{1 - 3 \cos^2 \theta_{\mathbf{m}}}{\|\mathbf{m}\|^3}$ has a finite limit as $k \rightarrow +\infty$; notations : $\mathbf{m} = (m_1, m_2, m_3) \in \mathbb{Z}^3$;

and $\theta_{\mathbf{m}}$ is the angle between $\mathbf{M}$ and $\mathbf{m}$.

Then

$$E_0 = \frac{1}{2} \lim_{k \rightarrow +\infty} \sum_{\substack{\mathbf{m} \in \mathbf{B}_k \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (8)$$

exists and is equal to

$$\begin{aligned} E_0 &= E_1 - E_2 + E_3 + E_4 + E_5 - E_5^0 \\ &= E_E + E_4 + E_5 - E_5^0 \end{aligned} \quad (9)$$

where E_1 , E_2 and E_3 are given by (4) and

$$\begin{aligned} E_4 &= \frac{2 \pi \mathbf{M}^2}{3 V} \\ E_5 &= \frac{\mathbf{M}^2}{2} \lim_{k \rightarrow +\infty} \sum_{\mathbf{m} \in \mathbf{B}_k \setminus \{0\}} \frac{1 - 3 \cos^2 \theta_{\mathbf{m}}}{\|\mathbf{m}\|^3} \\ E_5^0 &= \frac{\mathbf{M}^2}{2} \lim_{N \rightarrow +\infty} \sum_{0 < \|\mathbf{m}\| \leq N} \frac{1 - 3 \cos^2 \theta_{\mathbf{m}}}{\|\mathbf{m}\|^3}. \end{aligned} \quad (10)$$

If $\mathbf{M} = \mathbf{0}$, the sum

$$E_0 = \frac{1}{2} \sum_{\substack{\mathbf{m} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (11)$$

is absolutely convergent and

$$\begin{aligned} E_0 &= E_1 - E_2 + E_3 \\ &= E_E. \end{aligned} \quad (12)$$

The term E_4 generalizes the expression (7) found by de Leeuw *et al.* [3] for cubic crystals (Felderhof [6] obtained this term from a virtual uniform polarization $\mathbf{M}/V$). The terms E_5 and E_5^0 represent two sums of the same family of numbers $\left(\frac{\mathbf{M}^2(1 - 3 \cos^2 \theta_{\mathbf{m}})}{2 \|\mathbf{m}\|^3} \right)_{\mathbf{m} \neq \mathbf{0}}$, with the mode of summation ($\mathbf{B}_k$) for E_5 (as for E_0), and the spherical mode of summation for E_5^0 . The contribution $E_5 - E_5^0$ is generally different from 0, if $\mathbf{M} \neq \mathbf{0}$ and ($\mathbf{B}_k$) is not the spherical mode of summation.

3. The limit electrostatic energy per cell E .

We may note that the considerations of the introduction leading to (2) are contradictory : the crystal is supposed to be at the same time infinite ($\mathbf{m}$ runs over the whole lattice) and finite (N cells). The limit electrostatic energy per cell E may be correctly defined as the limit of the energy of a finite crystal (formed by a finite number of cells) divided by its number of cells (when this number tends towards $+\infty$) :

$$E = \lim_{k \rightarrow +\infty} \frac{1}{\text{card } \mathbf{A}_k} \frac{1}{2} \sum_{\mathbf{n} \in \mathbf{A}_k} \sum_{\substack{\mathbf{p} \in \mathbf{A}_k \\ \mathbf{n} + \mathbf{s} \neq \mathbf{p} + \mathbf{t}}} \sum_{\mathbf{s}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{n} + \mathbf{s} - \mathbf{p} - \mathbf{t}\|} \quad (13)$$

where $(\mathbf{A}_k)$ is an increasing sequence of finite subsets of $\mathbb{Z}^3$ such that $\bigcup_k \mathbf{A}_k = \mathbb{Z}^3$ (each $\mathbf{A}_k$ represents the shape of a finite crystal.).

3.1 RESULT. — Let (A_k) be any sequence of finite subsets of $\mathbb{Z}^3$ such that

1) $A_k \subset A_{k+1}$, for all k ;

2) $\bigcup_k A_k = \mathbb{Z}^3$;

3) if $\mathbf{M} \neq \mathbf{0}$, we suppose that $\sum_{\mathbf{m} \in B_k \setminus \{0\}} \frac{1 - 3 \cos^2 \theta_{\mathbf{m}}}{\|\mathbf{m}\|^3}$ has a finite limit as $k \rightarrow +\infty$; notations : $B_k = \{n - p \mid n \text{ and } p \in A_k\}$; $\theta_{\mathbf{m}}$ = angle between $\mathbf{M}$ and $\mathbf{m}$;

4) there exists $(f(k))$, $a > 0$, $b \geq 0$, $\alpha > 0$, such that

4a) $a \cdot d(k) \leq f(k)$, for all k ; notation : $d(k) = \sup_{\mathbf{n} \in A_k} \|\mathbf{n}\|$;

4b) $1 - c(A_k, m) \leq b \left(\frac{\|\mathbf{m}\|}{f(k)} \right)^\alpha$, for all k and $m \in B_k$; notation : $c(A_k, m) = \frac{\text{card}(A_k \cap m + A_k)}{\text{card } A_k}$;

4c) if $\mathbf{M} \neq \mathbf{0}$, we suppose that, for almost every $x \in \mathbb{R}^3$, $c(A_k, m_k)$ has a finite limit as $k \rightarrow +\infty$, which is denoted by $c(x)$. m_k is defined by $x \in \frac{1}{f(k)}(m_k + C)$; $C = [0, 1]^3$;

4d) if $\mathbf{M} \neq \mathbf{0}$, we suppose that, for almost every $x \in \mathbb{R}^3$, $\varphi_{\frac{1}{f(k)}(B_k + C)}(x)$ has a limit as $k \rightarrow +\infty$, which is denoted by $\varphi_B(x)$. φ_A is a characteristic function of a subset A of $\mathbb{R}^3$.

Then the limit electrostatic energy per cell E defined by (13) exists and is equal to

$$E = E_0 - E_6$$

where

$$\begin{aligned} E_0 &= \lim_{k \rightarrow +\infty} \frac{1}{2} \sum_{\mathbf{m} \in B_k} \sum_{\mathbf{s}} \sum_{\substack{\mathbf{t} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \\ E_6 &= \frac{\mathbf{M}^2}{2V} \int_{x \in B} (1 - c(x)) \frac{1 - 3 \cos^2 \theta_x}{\|\mathbf{x}\|^3} d\mathbf{x} \end{aligned} \quad (14)$$

if $\mathbf{M} \neq \mathbf{0}$ (θ_x = angle between $\mathbf{M}$ and $\mathbf{x}$); and, if $\mathbf{M} = \mathbf{0}$

$$E = E_0$$

where

$$E_0 = \frac{1}{2} \sum_{\mathbf{m}} \sum_{\mathbf{s}} \sum_{\substack{\mathbf{t} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (15)$$

(the sum on $\mathbf{m}$ is here absolutely convergent). In all cases, the value of E_0 is given in section 2.

3.2 EXAMPLES. — If

$$A_k = \{n \mid \|\mathbf{n}\| \leq k\} \quad (16)$$

we have

$$\begin{aligned} c(A_k, m) &\approx 1 - \frac{3 \|\mathbf{m}\|}{4k} + \frac{\|\mathbf{m}\|^3}{16k^3} \quad (\text{for } k \text{ and } 2k - \|\mathbf{m}\| \gg 1) \quad \text{if } \|\mathbf{m}\| \leq 2k, \\ c(A_k, m) &= 0 \quad \text{if } \|\mathbf{m}\| > 2k. \end{aligned}$$

All the above conditions 1) to 4) are satisfied : condition 3) has been proved in [5], and condition 4) is satisfied with $f(k) = d(k) = k$ and $\alpha = 1$. Since $c(x)$ depends only on $\|\mathbf{x}\|$, the integral E_6 is

equal to 0 (with $\mathbf{M}$ as polar axis, the integral on θ is equal to 0), so that

$$E = E_0 \quad (17)$$

with

$$E_0 = \lim_{k \rightarrow +\infty} \frac{1}{2} \sum_{\|\mathbf{m}\| \leq k} \sum_{\substack{\mathbf{s} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (18)$$

if $\mathbf{M} \neq \mathbf{0}$, and

$$E_0 = \frac{1}{2} \sum_{\mathbf{m}} \sum_{\substack{\mathbf{s} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (19)$$

if $\mathbf{M} = \mathbf{0}$.

If

$$A_k = \{n \mid |n| \leq k\} \quad (20)$$

(we note $|n| = \sup\{|n_1|, |n_2|, |n_3|\}$), we have

$$\begin{aligned} c(A_k, m) &= \left(1 - \frac{|m_1|}{2k+1}\right) \left(1 - \frac{|m_2|}{2k+1}\right) \left(1 - \frac{|m_3|}{2k+1}\right) & \text{if } |m| \leq 2k \\ c(A_k, m) &= 0 & \text{if } |m| > 2k, \end{aligned}$$

and the above condition 4) is satisfied ($f(k) = k$ and $\alpha = 1$). If condition 3) is also satisfied, we may then write

$$E = E_0 - E_6 \quad (21)$$

where

$$E_0 = \lim_{k \rightarrow +\infty} \frac{1}{2} \sum_{\|\mathbf{m}\| \leq k} \sum_{\substack{\mathbf{s} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (22)$$

$$E_6 = \frac{\mathbf{M}^2}{2V} \int_{|x| \leq 1} [1 - (1 - |x_1|)(1 - |x_2|)(1 - |x_3|)] \frac{1 - 3 \cos^2 \theta_x}{\|\mathbf{x}\|^3} d\mathbf{x}$$

if $\mathbf{M} \neq \mathbf{0}$, or

$$E = E_0 \quad (23)$$

where

$$E_0 = \frac{1}{2} \sum_{\mathbf{m}} \sum_{\substack{\mathbf{s} \\ \mathbf{m} + \mathbf{s} \neq \mathbf{t}}} \sum_{\mathbf{t}} \frac{q_{\mathbf{s}} q_{\mathbf{t}}}{\|\mathbf{m} + \mathbf{s} - \mathbf{t}\|} \quad (24)$$

if $\mathbf{M} = \mathbf{0}$.

4. Numerical example.

As a numerical example, we have computed the different terms in a simple case : orthogonal cell vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ with $\|\mathbf{a}_1\| = \|\mathbf{a}_2\| = 1$, $\|\mathbf{a}_3\| = 2$, $q_{\mathbf{s}} = +1$ at $\mathbf{s} = \mathbf{0}$, $q_{\mathbf{s}} = -1$ at $\mathbf{s} = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$.

Calculation of E_0 : we have found : $E_1 - E_2 + E_3 = E_E = -0.74$ (calculation time ~ 5 s), $E_4 = 1.57$, $E_5 = 1.33$ with the « $|n|$ mode of summation » ($B_k = \{n \mid |n| = \sup(|n_1|, |n_2|, |n_3|) \leq k\}$), $E_5^0 = 1.82$ (calculation time ~ 20 s); thus : $E_1 - E_2 + E_3 + E_4 = 0.83$ (calculation time ~ 5 s), $E_1 - E_2 + E_3 + E_4 + E_5 - E_5^0 = 0.34$ (calculation time ~ 25 s). These

last two values have been also obtained by the direct calculation (8) of E_0 , with, respectively, the spherical mode of summation and the $|n|$ mode of summation (with calculation times of ~ 15 s). All the calculations were made on a 16 bit minicomputer (PDP 11/45 of DEC).

Calculation of E : With the spherical shape (16) and according to (17) and (18), we obtain $E = 0.83$ (from the above value of E_0). With the $|n|$ shape (20) and according to (21) and (22), we obtain : $E_0 = 0.34$ (see above), $E_6 = -0.17$ (calculation time 40 min), so that $E = 0.51$. These two values $E = 0.83$ (spherical shape) and $E = 0.51$ ($|n|$ shape) may be directly calculated with the help of (13), but the convergence is extremely slow. For the spherical shape, we have obtained, $E = 0.66$ at $k = 8$ (calculation time 5 h) and $E = 0.69$ at $k = 10$ (calculation time 15 h); and, for the $|n|$ shape, $E = 0.43$ at $k = 8$ (calculation time 20 h) and $E = 0.44$ at $k = 10$ (calculation time 62 h). These results show that the expression (14)-(15) of E is much more interesting for calculation than the definition (13).

5. Conclusion.

The results presented in sections 2 and 3 show that — under the conditions 1) to 4) of section 3.1 — the limit electrostatic energy per cell E (defined by (13)) exists and is related to the Ewald energy E_E by

$$\begin{aligned} E &= E_E \quad \text{if } \mathbf{M} \text{ (dipôle moment of the cell)} = \mathbf{0} \\ E &= E_E + E_4 + E_5 - E_5^0 - E_6 \quad \text{if } \mathbf{M} \neq \mathbf{0}, \end{aligned}$$

where the terms E_4 , E_5 and E_5^0 are given by (10) and E_6 by (14).

The finite crystals — used to define E — are formed by the sets of ions

$$S_k = \{ \mathbf{n} + \mathbf{s}/n \in A_k, \mathbf{s} \in \text{cell} \}$$

($\mathbf{n}$ are the lattice vectors which give the positions of the cells; $\mathbf{s}$ are the vectors which give the positions of the ions of the cell $\mathbf{n} = \mathbf{0}$).

For a given crystal, each S_k depends on A_k and on the cell which has been chosen. The dependence of all the terms E_4 , E_5 , E_5^0 and E_6 on $\mathbf{M}$ (which depends on the cell), clearly shows the dependence of E on the choice of the cell (for a given crystal). The dependence of E on the sequence (A_k) appears in the terms E_5 and E_6 ((B_k) , B and $c(x)$ depend on (A_k)).

References

- [1] EWALD, P. P., *Ann. Physik* **64** (1921) 253.
- [2] BERTAUT, F., *J. Phys. Rad.* **13** (1952) 499.
- [3] DE LEEUW, S. W., PERRAM, J. W. and SMITH, E. R., *Proc. R. Soc. London A* **373** (1980) 27.
- [4] SMITH, E. R., *Proc. R. Soc. London A* **375** (1981) 475.
- [5] OLIVES, J., 1985, submitted to *J. Phys. A*.
- [6] FELDERHOF, B. U., *Physica A* **101** (1980) 275.