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ELECTROSTATIC ENERGY IN IONIC CRYSTALS BY THE PLANEWISE SUMMATION METHOD

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An expression for the potential field of an ideal crystal made of point charges is derived by the planewise summation method. The dependence of the potential on the shape of the specimen is discussed, as well as the connection of the present work with that of previous investigators. Using the above results a general expression for the electrostatic energy of a slab-shaped specimen of an ionic crystal is obtained. The formula is applied to slabs of NaCl, CsCl and $BaTiO_3$ crystals (for the latter both the cubic and the tetragonal phases are considered).

1. Introduction

The knowledge of the potential field created by a lattice of point charges is of the greatest importance in the calculation of the electrostatic energy (as well as the energy of several kinds of defects) of ionic crystals. In fact, according to the Born–Mayer model, an ionic crystal can be considered in a first approximation as composed of spherical, non-overlapping charge distributions interacting through the coulombic potential, plus a short-range repulsion which prevents the structure from collapsing [1]. The coulombic part of the interaction, which gives the main contribution to the cohesive energy of an ionic crystal, is the same as the electrostatic energy of a crystal made of point charges located at the centres of the above-mentioned charge distributions: in fact, the potential of a fmite, spherically symmetric charge distribution at points outside it is the same as if the total charge were concentrated at its centre.

The electrostatic energy of a given crystal structure is usually characterized by a parameter α called the Madelung constant, which is defined in terms of the electrostatic energy per molecule U_{mol} by

$$U_{\mathrm{mol}} = -\frac{q^2}{4\pi\epsilon_0 d}\alpha \tag{1}$$

(here, q is some characteristic charge of the crystal and d some characteristic length, such as the lattice constant or the nearest-neighbour distance).

In order to calculate U_{mol} one needs to know the potential created by each sublattice at all the sublattice sites. However, it is important to notice that eq. (1) contains an ambiguity that is not usually recognized in the literature. In fact, the electrostatic energy of an ideal ionic crystal depends on the shape of the specimen, unless the net dipole moment $\boldsymbol{p}$ of the cell that is used as a building block for the crystal is equal to zero [2–4]. The reason why this fact is usually not attached importance to is that in a real case free charges will be attracted by the crystal surface so as to compensate for the polarization $\boldsymbol{P} = \boldsymbol{p}/v$ (v = volume of the unit cell). However, from a conceptual viewpoint it is desirable to have a way of calculating U_{mol} for an ideal case. Furthermore, there might be situations in which the effect of the surface charge could in principle be eliminated (for instance, a para- to ferro-electric transition in the vacuum).

In the next section we discuss some problems arising in the calculation of the potential and the electrostatic energy in point-charge lattices.

In section 3 we present a calculation of the electrostatic potential for an ionic crystal shaped as a circular slab using the "planewsie summation method"; our derivation avoids some of the problems of previous calculations.

In section 4 we discuss the connection between the above results and those of previous authors.

In section 5 the results are extended to points belonging to an xy crystal plane.

In section 6 the electrostatic energy of a slab-shaped ionic crystal is derived in terms of the formulae given by the planewise summation method and is evaluated for different specimens of NaCl, CsCl and $BaTiO_3$.

2. General discussion

The calculation of the lattice sum giving the electrostatic potential (EP) at an arbitrary point of a point-charge lattice presents two different problems:

(a) the convergence of the sum is extremely slow;

(b) the convergence of the sum is conditional, i.e. the result depends on the order of summation.

While the difficulty arising from (a) has led many authors in the last 60 years to propose several practical methods of calculation, point (b) has not received great attention until quite recently. The most well-known example of a difficulty arising from (b) is the ambiguity found by Evjen [5] in the determination of the Madelung constant of crystals with the CsCl structure. Point (b), of course, is the reason why the electrostatic energy (EE) of an ideal ionic crystal depends in general (i.e., when the dipole moment of the unit cell is different from zero) on the shape of the specimen. The convergence properties of the lattice sums giving the EP at a given point and the EE can be discussed in the following terms.

Let us write the position vector of the centre of an arbitrary cell with respect to the field point P_j as*

$$r_{\lambda j} = (\lambda_1 + j_1)\boldsymbol{a}_1 + (\lambda_2 + j_2)\boldsymbol{a}_2 + (\lambda_3 + j_3)\boldsymbol{a}_3. \tag{2}$$

Here, λ_1, λ_2 and λ_3 are integers labelling the cell; the j_i are $\geqslant 0$ and < 1, and give the position of the field point in its cell; $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$ are the primitive lattice vectors. The contribution of the above cell to the EP at P_j can be expanded as

$$4\pi\epsilon_0 V_\lambda(P_j) = -\sum_\nu \frac{p_\nu r_{\lambda,j,\nu}}{r^3_{\lambda,j}} + \tfrac{1}{2}\sum_{\nu,\kappa} Q_{\nu\kappa}\,\frac{3r_{\lambda,j,\nu}r_{\lambda,j,\kappa} - r^2_{\lambda,j}\delta_{\kappa\nu}}{r^5_{\lambda,j}} + \ldots \tag{3}$$

Here, p_ν, $Q_{\nu\kappa}$, etc. are the components of the electric dipole, quadrupole, etc. moments of the unit cell with respect to its centre (the net charge is zero for a neutral crystal). The convergence properties of a lattice sum are determined by the contributions of the lattice points at great distances from the field point. It has been proved by Sholl [6] that the series

$$\sum_{\lambda_1,\lambda_2,\lambda_3} r^{-n}_{\lambda,j}, \tag{4}$$

summed over the lattice points contained in a given solid angle is divergent for $n \leqslant 3$ and convergent for $n > 3$. Using this result it can be shown that the EP as given by (3) is shape-dependent if $\boldsymbol{p}$ and/or $\mathbf{Q}$ are different from zero.

* The subindices λ and j stand, respectively, for $(\lambda_1, \lambda_2, \lambda_3)$ and (j_1, j_2, j_3); it must be noticed, however, that they do not represent vectors.

In this paper we are going to deal with a summation method that is suited for a slab-shaped specimen. In order to know the convergence properties of the lattice sum giving the EP in a slab let us notice that adding the contributions of the cells at great distances is equivalent to evaluating

$$-\int \frac{\boldsymbol{p}\cdot\boldsymbol{r}}{r^3}\, r\, \mathrm{d}r\, \mathrm{d}\varphi + \int \mathcal{O}(r^{-3})\, r\, \mathrm{d}r\, \mathrm{d}\varphi, \tag{5}$$

with r lying in the xy plane. As the integral

$$\int_{\varphi_0}^{\varphi_0+\Delta\varphi} \mathrm{d}\varphi \int_{r_0}^{\infty} \frac{\boldsymbol{p}\cdot\boldsymbol{r}}{r^2}\, \mathrm{d}r$$

diverges unless $p_x = p_y = 0$, we conclude that if this condition is not fulfilled the EP in a slab depends (a) on the shape of the slab and (b) on the position of the cell containing the field point.

Let us repeat the above reasonings for the EE per unit cell. The contribution of a cell at a distance $r_{\lambda,j}$ from the field point is now

$$\sum_{\nu,\kappa} p_\nu p_\kappa \frac{3r_{\lambda,j,\nu}r_{\lambda,j,\kappa} - r_{\lambda,j}^2\delta_{\nu\kappa}}{r_{\lambda,j}^5} + \sum_{\nu,\kappa,\rho} p_\nu Q_{\kappa\rho}\mathcal{O}(r_{\lambda,j}^{-4}) + \ldots .$$

It can be seen that for a "three-dimensional" specimen* the EE depends on the shape if $\boldsymbol{p} \neq 0$. In the case of a slab, however, all the integrals analogous to those in (5) converge, so that the EE, contrarily to the EP, does not depend on the slab shape. Using this result, it can also be shown that the EE of the unit cell in a slab does not depend on the location of the cell inside the slab (the reasoning is similar to that on p. 313 of [7]).

In this paper we are going to calculate the EP and the EE of an ionic crystal using the planewise summation method (PSM) of Nijboer and de Wette [8], which is a general method for calculating lattice sums. As the PSM consists in adding up separately the contributions of the different xy lattice planes, its results refer to slab-shaped crystals. With our derivation we will obtain the EP in an infinite circular slab (or, equivalently, near the centre of a finite circular slab) and the EE per unit cell of an arbitrarily shaped slab.

The PSM, as well as other methods for calculating lattice sums, deals with each sublattice in a separate way. Due to this and to the fact that the EP of each sublattice diverges when the volume of the specimen is made to tend to infinity, the PSM cannot be applied in a straightforward manner to calculating the EP in a crystal made of point charges. In order to avoid the divergent contributions (which should cancel out each other when all the sublattices are taken into account, due to the charge neutrality of the unit cell) many of the earlier methods (e.g.: Redlack and Grindlay's method [3, 4]; the well-known Ewald method: see ref. 9 or app. A of [1]) introduce for each sublattice a uniform cloud with a density equal to minus the charge of the sublattice divided by the volume of the unit cell. The assumption implicit in such methods is that when all the sublattices are superposed the neutralizing clouds cancel out each other everywhere. However, since the sublattices are displaced with respect to each other there will be in general thin regions at the crystal surface where the clouds do not overlap. In the general case these non-compensated charge distributions give a non-vanishing contribution to the EP and its derivatives even when the volume tends to infinity. An example of the errors that may appear when the effect of non-compensated clouds is neglected will be seen in section 6.

The shape dependence of the EP for a lattice of point charges plus a neutralizing background has been investigated by us in a previous paper [7]. There we showed that the EP of this charge distribution depends on the

* I.e., a specimen for which none of the indices λ_1, λ_2 and λ_3 is made to tend to infinity after some of the others (for a slab parallel to the xy plane one takes $\lambda_1, \lambda_2 \to \infty$ first and then $\lambda_3 \to \infty$).

crystal shape, and that the result given by the Ewald method, which is shape-independent, actually refers to a specimen with a suitable dipole distribution on its surface. The calculation of the EP of a point-charge lattice immersed in a neutralizing background using the PSM has been carried out by Sholl [10].

In the present paper we calculate the EP in an arbitrary crystal made of point charges. As we do not introduce non-compensated charge distributions, our results are free from the ambiguities that are so often associated with calculations of this kind (the price we have to pay is that we must restrict ourselves to circular (for the EP) or arbitrary (for the EE) slabs). The connection between our results and those of Sholl will be discussed in section 4.

3. Derivation of the formula for the potential

Throughout this paper we will consider the ideal case of a perfect crystal made of A sublattices of point charges q_α ($\alpha = 1,2,\ldots,A$). The condition of electrical neutrality implies

$$\sum_{\alpha=1}^{A} q_\alpha = 0. \tag{6}$$

The sublattices are identical and slightly displaced with respect to each other. Their primitive vectors are a_1, a_2 and a_3. We consider lattices with monoclinic or higher symmetry, unless otherwise stated. The x and z axes are taken parallel to a_1 and a_3 respectively, while $\cos\gamma \equiv a_1 \cdot a_2/a_1a_2 \neq 0$ for monoclinic, rhomboedric or hexagonal symmetry. The crystal we are dealing with is shaped as an infinite circular slab parallel to the a_1a_2 plane and is schematically depicted in fig. 1. We assume that the slab is cut in such a way that it contains an integer number of unit cells. Each cell contains one ion belonging to each sublattice, and the index α is chosen in such a way that the z-coordinate of the ions of the unit cell increases with increasing α.

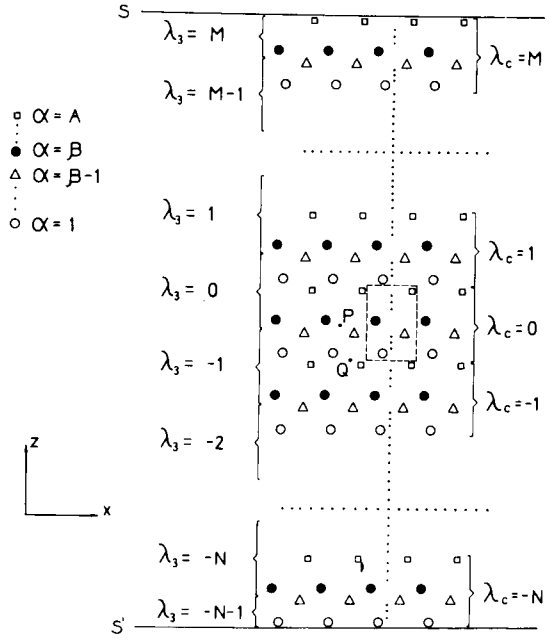

Fig. 1. Cross section of the crystal in the xz plane (projection onto the $y = 0$ plane). The drawing extends to infinity in the $\pm x$ directions. Enclosed by a broken line is shown the unit cell that is the building block of the crystal.

We consider a general field point $P(x_P, y_P, z_P)$ (fig. 1). Let us denote by β the sublattice satisfying

$$z_1 \leqslant z_2 \leqslant \ldots \leqslant z_{\beta-1} < z_P \leqslant z_\beta \leqslant \ldots \leqslant z_A .$$

For a point such as Q (fig. 1) we have

$$z_Q \leqslant z_1 \leqslant z_2 \leqslant \ldots \leqslant z_A ,$$

so that $\beta = 1$. If $z_1 = z_2 = \ldots = z_A$ our definition implies $\beta = 1$. The coordinate of a source point belonging to the α sublattice relative to the field point is written as

$$r_{\lambda, j_\alpha} = (\lambda_1 + j_{\alpha,1})\, a_1 + (\lambda_2 + j_{\alpha,2})\, a_2 + (\lambda_3 + j_{\alpha,3})\, a_3, \tag{7}$$

following the notation of [6, 7, 10] [see also eq. (2)].
For point P we have

$$0 \leqslant j_{\beta,3} \leqslant j_{\beta+1,3} \leqslant \ldots \leqslant j_{A,3} < j_{1,3} \leqslant \ldots \leqslant j_{\beta-1,3} < 1.$$

If $\beta = 1$ this reduces to

$$0 \leqslant j_{1,3} \leqslant \ldots \leqslant j_{A,3} < 1.$$

It can be seen (fig. 1) that λ_3 goes from $-N-1$ to $M-1$ for $\alpha < \beta$ and from $-N$ to M for $\alpha \geqslant \beta$ ($M, N \geqslant 0$). Due to this it is convenient to write r_{λ, j_α} with the following notation:

$$r_{\lambda, j_\alpha} \equiv r_{\lambda', j'_\alpha} = (\lambda_1 + j_{\alpha,1})\, a_1 + (\lambda_2 + j_{\alpha,2})\, a_2 + (\lambda_c + j'_{\alpha,3})\, a_3 . \tag{7'}$$

Again, λ_c is an integer labelling the cell with the source point, but now it takes the same value for all the sublattice points belonging to the same cell; therefore, it goes from $-N$ to M for all the sublattices. Subindices λ' and j'_α stand for $(\lambda_1, \lambda_2, \lambda_c)$ and $(j_{\alpha,1}, j_{\alpha,2}, j'_{\alpha,3})$ respectively. The $j'_{\alpha,3}$ variables are given by

$$\begin{aligned} j'_{\alpha,3} &= j_{\alpha,3}, \qquad \text{for } \alpha \geqslant \beta, \\ j'_{\alpha,3} &= j_{\alpha,3} - 1, \quad \text{for } \alpha < \beta, \end{aligned} \tag{8}$$

so that

$$-1 < j'_{1,3} \leqslant \ldots \leqslant j'_{\beta-1,3} < 0 \leqslant j'_{\beta,3} \leqslant \ldots \leqslant j'_{A,3} < 1, \quad j'_{A,3} - j'_{1,3} < 1.$$

The potential at an arbitrary point P of the crystal in the MKS system is given by

$$4\pi\epsilon_0 V(P) = \sum_{\lambda} \sum_{\alpha} q_\alpha / r_{\lambda, j_\alpha} = \sum_{\lambda'} \sum_{\alpha} \frac{q_\alpha}{|(\lambda_1 + j_{\alpha,1})\, a_1 + (\lambda_2 + j_{\alpha,2})\, a_2 + (\lambda_c + j'_{\alpha,3})\, a_3|} . \tag{9}$$

Here, λ_1 and λ_2 go from $-\infty$ to $+\infty$, while $-N \leqslant \lambda_c \leqslant M$. As the EP depends on the slab shape (see section 2), the order of summation must be the one corresponding to the given shape. In the present case we must first sum over λ_1 and λ_2 such that the source points lie within a circumference of radius R, and then take the limit $R \to \infty$. If $(j_{\alpha,1}, j_{\alpha,2}, j_{\alpha,3}) = (0,0,0)$ for a given α (EP at a lattice point) the term with $\lambda_1 = \lambda_2 = \lambda_c = 0$ has to be omitted

from the sum for that value of α. If $j_{\alpha,3} = 0$ for some α the treatment by the PSM is somewhat different (see, for instance, ref. 11, where the field at an arbitrary point of a dipole lattice is evaluated). This case will be dealt with in section 5; throughout this section we assume $j_{\alpha,3} \neq 0$ for all the α's.

We are going to apply the PSM to the sum (9). We will first consider the cells with the same value of λ_c; they form a planar layer perpendicular to the z axis, with thickness a_3:

$$4\pi\epsilon_0 V_{\lambda_c}(P) = \sum_{\lambda_1,\lambda_2} \sum_{\alpha} q_\alpha / r_{\lambda',j'_\alpha}.$$

Let us define, following [11],

$$\sigma_\lambda \equiv \lambda_1 \frac{a_1}{a_1} + \lambda_2 \frac{a_2}{a_2} \quad \text{and} \quad \sigma_{j_\alpha} \equiv j_{\alpha,1} \frac{a_1}{a_1} + j_{\alpha,2} \frac{a_2}{a_2}.$$

Therefore, $(\sigma_\lambda)_x = \lambda_1 + \lambda_2(a_2/a_1)\cos\gamma$ and $(\sigma_\lambda)_y = \lambda_2(a_2/a_1)\sin\gamma$, while analogous relations hold for $(\sigma_{j_\alpha})_x$ and $(\sigma_{j_\alpha})_y$. We also set

$$\zeta_\alpha \equiv (\lambda_c + j'_{\alpha,3})\, a_3/a_1.$$

$V_{\lambda_c}(P)$ is evaluated by means of Parseval's identity for Fourier integrals:

$$\int F^*(\boldsymbol{h})\, G(\boldsymbol{h})\, \mathrm{d}\boldsymbol{h} = \int f^*(\boldsymbol{\sigma})\, g(\boldsymbol{\sigma})\, \mathrm{d}\boldsymbol{\sigma}.$$

Here $\boldsymbol{\sigma} = \sigma_x \boldsymbol{i} + \sigma_y \boldsymbol{j}$, $\boldsymbol{h} = h_x \boldsymbol{i} + h_y \boldsymbol{j}$,

$$F(\boldsymbol{h}) = FT_2\ \{f(\boldsymbol{\sigma})\} \equiv \int f(\boldsymbol{\sigma})\, \mathrm{e}^{2\pi i \boldsymbol{h}\cdot\boldsymbol{\sigma}}\, \mathrm{d}\boldsymbol{\sigma}$$

and an analogous formula relates $G(\boldsymbol{h})$ to $g(\boldsymbol{\sigma})$. We choose $f(\boldsymbol{\sigma})$ and $g(\boldsymbol{\sigma})$ in a slightly different way as in [6] and [11]. So, taking

$$f(\boldsymbol{\sigma}) = \sum_{\lambda_1,\lambda_2} \delta(\boldsymbol{\sigma} - \boldsymbol{\sigma}_\lambda) \quad \text{and} \quad g(\boldsymbol{\sigma}) = \sum_{\alpha} \frac{q_\alpha}{[|\boldsymbol{\sigma} + \boldsymbol{\sigma}_{j_\alpha}|^2 + \zeta_\alpha^2]^{\frac{1}{2}}},$$

we can write

$$4\pi\epsilon_0 a_1 V_{\lambda_c}(P) = \int F^*(\boldsymbol{h})\, G(\boldsymbol{h})\ \mathrm{d}\boldsymbol{h}. \tag{10}$$

By eq. (A.8) of [12] we have

$$F^*(\boldsymbol{h}) = \frac{a_1}{a_2 \sin\gamma} \sum_{\mu_1,\mu_2} \delta(\boldsymbol{h} - \boldsymbol{h}_{\mu_1\mu_2}),$$

with

$$\boldsymbol{h}_{\mu_1\mu_2} = \mu_1 \boldsymbol{i} + (-\mu_1 \cot\gamma + \mu_2 a_1/a_2 \sin\gamma)\boldsymbol{j} \quad (\mu_1, \mu_2 = \text{integers}).$$

On the other hand,

$$G(\boldsymbol{h}) = FT_2\left\{\sum_\alpha \frac{q_\alpha}{[|\sigma+\sigma_{j_\alpha}|^2+\zeta_\alpha^2]^{\frac{1}{2}}}\right\} = FT_2\left\{\sum_\alpha \exp\left[-2\pi i\,(j_{\alpha,1}\mu_1' + j_{\alpha,2}\mu_2')\right]\frac{q_\alpha}{(\sigma^2+\zeta_\alpha^2)^{\frac{1}{2}}}\right\},$$

where μ_1' and μ_2' are continuous variables defined by $\mu_1' = h_x$, $-\mu_1'\cot\gamma + \mu_2' a_1/a_2 \sin\gamma = h_y$; the last step follows from the change of variables $(\sigma_x, \sigma_y) \to (\sigma_x - (\sigma_{j_\alpha})_x, \sigma_y - (\sigma_{j_\alpha})_y)$ for each sublattice. The way of evaluating this expression depends on whether $h_x = h_y = 0$ or not. If $(h_x, h_y) \neq (0,0)$ we can use eqs. (4.9) to (4.11) of [6] for the case $n = m = 0$. In this case the contribution of each sublattice is finite and can be calculated separately*. We obtain

$$G(\boldsymbol{h} \neq \boldsymbol{0}) = \sum_\alpha \exp\left[-2\pi i\,(j_{\alpha,1}\mu_1 + j_{\alpha,2}\mu_2)\right]\frac{q_\alpha}{h}\,e^{-2\pi|\zeta_\alpha|h} \quad (h \equiv |\boldsymbol{h}|).$$

If $\boldsymbol{h} = \boldsymbol{0}$ we have

$$G(\boldsymbol{0}) = FT_2\left\{\sum_\alpha \frac{q_\alpha}{(\sigma^2+\zeta_\alpha^2)^{\frac{1}{2}}}\right\}. \tag{11}$$

This is the term in which the dependence of the EP on the shape of the slab manifests itself (see section 2). The rhs of (11) is proportional to the EP of a set of A infinite planar surfaces, each with a uniform charge q_α/ω per unit surface ($\omega = a_1 a_2 \sin\gamma$ = area of the xy side of the unit cell), all of them parallel to each other. The EP of each surface is of course infinite, but after summing over α the divergent contributions cancel out, as we shall see, due to the charge neutrality. The integration limits in the Fourier transform (11) must be taken accordingly to the shape of the surface one is dealing with. For a circular slab we have

$$G(\boldsymbol{0}) = \frac{1}{a_1}\lim_{R\to\infty}\sum_\alpha q_\alpha \int_0^{2\pi} d\varphi \int_0^R \frac{r'\,dr'}{|r'+r_\alpha|}.$$

Here r_α gives the position of the centre of the αth disc with respect to the field point and is easily obtained in terms of σ_λ, σ_{j_α} and ζ_α. Let us write it as

$$r_\alpha = d_\alpha \cos\theta_\alpha \boldsymbol{i} + d_\alpha \sin\theta_\alpha \boldsymbol{j} + z_\alpha \boldsymbol{k}.$$

The integration over r' is carried out analytically and the result is written for $R \gg d_\alpha, z_\alpha$. After integrating over φ some of the terms vanish or are easily evaluated. We arrive at

$$\int_0^{2\pi} d\varphi \int_0^R \frac{r'\,dr'}{|r'+r_\alpha|} \simeq 2\pi[R - (d_\alpha^2+z_\alpha^2)^{\frac{1}{2}}] - d_\alpha \int_0^{2\pi} \cos\varphi \log\left[(d_\alpha^2+z_\alpha^2)^{\frac{1}{2}} - d_\alpha\cos\varphi\right] d\varphi.$$

For the latter term we use the expression

$$\int_0^{2\pi} \cos\varphi \log(c - \cos\varphi)\,d\varphi = -2\pi[c - (c^2-1)^{\frac{1}{2}}],$$

* In ref. 6 eqs. (4.11) are said to hold for $n > 0$. However, it can be seen from [13] that they actually hold for $n > -\frac{1}{2}$. The divergence that prevents one from extending Sholl's formulae of [6] to the evaluation of the series (4) with $n = 1$ manifests itself in $G(\boldsymbol{0})$ (see below), not in $G(\boldsymbol{h} \neq \boldsymbol{0})$.

which is arrived at by integrating by parts and setting $\cos\varphi = t$. Finally we get

$$G(\mathbf{0}) = \frac{2\pi}{a_1} \lim_{R\to\infty} \sum_{\alpha} q_\alpha (R - |z_\alpha|) = -2\pi \sum_{\alpha} q_\alpha |\zeta_\alpha|. \tag{12}$$

Substituting $F(\boldsymbol{h})$ and $G(\boldsymbol{h})$ into (10) we obtain

$$V_{\lambda_c}(P) = \frac{1}{4\pi\epsilon_0 a_2 \sin\gamma} \left\{ \sum_{\alpha} q_\alpha \sum_{\mu_1,\mu_2}{}' \frac{1}{h_{\mu_1\mu_2}} \exp[-2\pi i(j_{\alpha,1}\mu_1 + j_{\alpha,2}\mu_2)]\, e^{-2\pi|\zeta_\alpha| h_{\mu_1\mu_2}} - 2\pi \sum_{\alpha} q_\alpha |\zeta_\alpha| \right\}$$

$$\equiv V'_{\lambda_c}(P) + V''_{\lambda_c}(P),$$

where

$$h_{\mu_1,\mu_2} = \left[\mu_1^2 + \left(-\mu_1 \cot\gamma + \mu_2 \csc\gamma \frac{a_1}{a_2}\right)^2\right]^{\frac{1}{2}}.$$

From what we said above about the meaning of $G(\mathbf{0})$ it can be seen that if a uniform surface charge density $\Gamma_\alpha = q_\alpha/\omega$ is subtracted and added to each plane $z = (\lambda_c + j'_{\alpha,3})a_3$, then $V''_{\lambda_c}(P)$ is the potential of all the Γ's while $V'_{\lambda_c}(P)$ is that of the actual point charges plus neutralizing planar distributions $-\Gamma_\alpha$. Notice also that if $\lambda_c \neq 0$, so that all the ζ_α have the same sign s_c, we have

$$V''_{\lambda_c}(P) = -\frac{s_c p_z}{2\epsilon_0 \omega},$$

where

$$p_z = \sum_{\alpha} q_\alpha j'_{\alpha,3} a_3.$$

This is the EP of a plane with a uniform dipole distribution (dipole moment per unit surface $= p_z/\omega$) [14].

Now we sum over λ_c in order to obtain the EP. For $V'_{\lambda_c}(P)$ we have two geometrical series. The result, written in terms of the $j_{\alpha,3}$ variables, is

$$V'(P;M,N) = \frac{a_1}{4\pi\epsilon_0 \omega} \left\{ \sum_{\alpha=1}^{\beta-1} q_\alpha \sum_{\mu_1,\mu_2}{}' \frac{f(\alpha,\mu)}{1 - e^{-H_\mu}} [(1 - e^{-(N+1)H_\mu})\, e^{-(1-j_{\alpha,3})H_\mu} \right.$$

$$+ (1 - e^{-MH_\mu})\, e^{-j_{\alpha,3}H_\mu}] + \sum_{\alpha=\beta}^{A} q_\alpha \sum_{\mu_1,\mu_2}{}' \frac{f(\alpha,\mu)}{1 - e^{-H_\mu}} [(1 - e^{-NH_\mu})\, e^{-(1-j_{\alpha,3})H_\mu}$$

$$\left. + (1 - e^{-(M+1)H_\mu})\, e^{-j_{\alpha,3}H_\mu}] \right\}, \tag{13}$$

where

$$f(\alpha,\mu) \equiv \frac{1}{h_{\mu_1\mu_2}} \exp\left[-2\pi i\,(j_{\alpha,1}\mu_1 + j_{\alpha,2}\mu_2)\right]$$

and $H_\mu \equiv 2\pi h_{\mu_1\mu_2} a_3/a_1$. All the sums with α running from 1 to $\beta - 1$ disappear when $\beta = 1$.

Eq. (13) is an exact expression, holding everywhere inside the crystal (a similar expression could be obtained for points outside the crystal). If the distance from the field point inside the crystal to the slab surface is much larger than a_3 (as will be assumed in the following) the terms containing M and N can be neglected and we get

$$V'(P) \equiv \sum_{\alpha=1}^{A} V'_\alpha(P_{j_\alpha}) = \lim_{M,N\to\infty} V'(P;M,N) = \frac{a_1}{4\pi\epsilon_0\omega} \sum_{\alpha=1}^{A} q_\alpha \sum_{\mu_1,\mu_2}{}' f(\alpha,\mu)\, \frac{e^{-j_{\alpha,3}H_\mu} + e^{-(1-j_{\alpha,3})H_\mu}}{1 - e^{-H_\mu}} \,. \tag{14}$$

A comment is in order about the notation. In this paper, as in [7], we denote by P_j an arbitrary point in the unit cell of a single sublattice. The quantities j_1, j_2 and j_3 determine the position of the origin of the sublattice with respect to that point [$\lambda_1 = \lambda_2 = \lambda_3 = 0$ in (2) or (7)]. Therefore, by writing $V'(P_{j_\alpha})$ we are explicitly displaying that the potential V' is taken at a point characterized by $j_{\alpha,1}, j_{\alpha,2}, j_{\alpha,3}$. In a crystal made of A sublattices there are A sets of j's so that a consistent notation would be quite cumbersome: in that case the field point is simply denoted by P. In section 6 we will denote by $V'(j_{\alpha\alpha'})$ the V' potential created by the α' sublattice at the sites of the α sublattice.

Now we calculate $\sum_{\lambda_c} V''_{\lambda_c}(P)$:

$$4\pi\epsilon_0 V''(P) = 4\pi\epsilon_0 \sum_{\lambda_c=-N}^{M} V''_{\lambda_c}(P) = 2\pi\frac{a_1}{\omega} \sum_{\lambda_c=-N}^{M} \sum_{\alpha=1}^{A} q_\alpha |\zeta_\alpha|$$

$$= \frac{2\pi a_1}{\omega}\left\{ \sum_{\lambda_c=1}^{M} \sum_{\alpha=1}^{A} q_\alpha \zeta_\alpha - \sum_{\lambda_c=-N}^{1} \sum_{\alpha=1}^{A} q_\alpha \zeta_\alpha + \frac{a_3}{a_1} \sum_{\alpha=1}^{\beta-1} q_\alpha (1 - j_{\alpha,3}) + \frac{a_3}{a_1} \sum_{\alpha=\beta}^{A} q_\alpha j_{\alpha,3} \right\}$$

$$= \frac{2\pi}{\omega}\left\{ (M - N + 1)\, p_z + 2a_3 \sum_{\alpha=1}^{\beta-1} q_\alpha (1 - j_{\alpha,3}) \right\}. \tag{15}$$

The final expression for the EP in a circular slab (neglecting the exponentials containing M and N) is

$$V(P) = V'(P) - \frac{1}{2\epsilon_0\omega}\left[(M - N + 1) p_z + 2a_3 \sum_{\alpha=1}^{\beta-1} q_\alpha (1 - j_{\alpha,3}) \right], \tag{16}$$

where $V'(P)$ is given by (14). We recall that if p_x and/or p_y are different from zero this expression holds for a circular slab, at points whose distances to the centre of the slab are negligibly small as compared with its radius. If $p_x = p_y = 0$, however, eq. (16) holds for an arbitrarily shaped slab and arbitrary position of P in the plane of the slab (not too near to the boundary).

If $p_z = 0$ the EP depends on the position of the field point in the cell, but not on the position of the cell inside the crystal, provided P is near the centre of the slab. If $p_z \neq 0$ the EP tends to be very large near the slab faces, where $|M - N| \gg 1$. This is due to the fact that the EP of a planar dipole layer is finite and space-independent, its sign depending on whether the dipole moment points towards the half space where the field point is located. For an arbitrary point there are $(M - N)$ uncompensated layers, each giving a contribution $p_z/2\epsilon_0\omega$. This, of course, is an ideal situation, because in a real case free charges will accumulate on the crystal faces, until cancelling the macroscopic internal field. However, eq. (16) can be applied, for instance, to a ferroelectric crystal immediately after the transition from the paraelectric phase has taken place.

4. Connection with previous results

It is interesting to compare our result, eq. (16), with those obtained by Sholl [10] or Ewald (app. A of [1], [9]). The results of ref. 10 for the EP relative to infinity [eqs. (3.11) and (3.12)] and to the average potential (3.15) differ from each other by a constant. The value given by (3.15), on the other hand, is equal to that obtained by Ewald's method (see ref. 7).

Sholl applies the PSM to the calculation of the EP in a crystal made of point charges q immersed in a uniform neutralizing background. His result* is

$$V_S(P_j) = V'(P_j) + \frac{qa_3}{2\epsilon_0\omega}(j_3 - \tfrac{1}{2})^2. \tag{17}$$

The first term of the rhs is the same as that obtained by us for a single sublattice in eq. (14).

In order to apply Sholl's formula to the crystal depicted in fig. 1 we need to consider a neutralizing background for each sublattice and then to correct for the contribution of the thin layers near the slab faces where the backgrounds do not compensate each other. The calculation of this contribution in the general case is straightforward but lengthy. However, one can first consider the simple case $A = 2$. In that case it is easy to see that the contribution of the uncompensated layers coincides with our $V''(P)$ of (15). The general case can then be treated in terms of the $A = 2$ case by adding and subtracting suitable uniform distributions. Therefore, eq. (3.11) with (3.12) of [10] applied to an arbitrary ionic crystal gives the same result as our (16), provided the contributions of the non-overlapping parts of the backgrounds are taken into account.

Let us also mention another interesting result, whose proof is elementary and will not be given here. We have already said that in crystals with a permanent polarization free charges tend to attach to the surface until an external charge sees no net dipole moment, i.e. no electric field. In our ideal case of fig. 1 this means that a surface density $\Gamma = p_z/a_3\omega$ will be deposited on the face looking in the negative z direction, and an opposite density on the opposite face, the distance between them being $(M + N + 1)a_3$ (planes S and S' in fig. 1). Using eq. (16), it can be seen that the EP inside the slab of point charges with the above-described surface distribution is the same (except for an additive constant depending on the exact location of the external charges) as that calculated by the Ewald method or, equivalently, by the Sholl formula.

5. Case $j_{\alpha,3} = 0$ for a given sublattice

In this section we consider the case of the field point lying on the xy plane of a crystal sublattice, a situation always arising when the electrostatic energy is calculated for an ionic crystal. This case has to be treated separately in the PSM because the Fourier transform of $g(\sigma)$ (see section 3) does not exist if one of the $j_{\alpha,3}$ is zero [11]. If

* Throughout this paper by Sholl's result we always refer, unless otherwise stated, to Sholl's potential relative to infinity and not to that relative to the average potential (i.e. eq. (3.11), not (3.15), of [10]).

$j_{\alpha,3} = 0$ for a given α the two following cases have to be treated differently: (i) $j_{\alpha,1}$ and/or $j_{\alpha,2} \neq 0$ and (ii) $j_{\alpha,1} = j_{\alpha,2} = 0$.

For the field of a point-charge lattice and its derivatives different formulae have been derived for both cases [6, 11]. For the EP of a point-charge lattice plus a uniform neutralizing background an expression is derived for case (ii) in ref. 10; for case (i) no formula is available in the literature, but in ref. 7 it is shown how Sholl's result for $j_3 \neq 0$ [10] can be used.

We are going to find an expression for the EP of a crystal made of point charges in cases (i) and (ii) by using the results of refs. 7 and 10. The result applies to a slab, with the same limitations as in the discussion on eq. (16). In our derivation we will add and subtract suitable planar and volume charge distributions. Since in each case we will subtract the same distribution as that previously added, there will be no uncompensated distributions to worry about. According to the notation of section 3, the sublattice for which $j_{\alpha,3}$ is zero is labelled by $\alpha = \beta$ (if there are n such sublattices, they are labelled by $\alpha = \beta, \beta + 1, \ldots, \beta + n - 1$).

Our first step for both cases (i) and (ii) is to consider the contributions of all the cells with $\lambda_c \neq 0$. The treatment is the same as in section 3. A straightforward calculation leads to

$$\sum_{\lambda_c \neq 0} V'_{\lambda_c}(P) = \frac{a_1}{4\pi\epsilon_0\omega} \sum_{\mu_1,\mu_2}{}' \left\{ \sum_{\alpha=1}^{\beta-1} q_\alpha f(\alpha,\mu) \frac{e^{-j_{\alpha,3}H_\mu} + e^{-(2-j_{\alpha,3})H_\mu}}{1 - e^{-H_\mu}} + \sum_{\alpha=\beta}^{A} q_\alpha f(\alpha,\mu) \frac{e^{-(1+j_{\alpha,3})H_\mu} + e^{-(1-j_{\alpha,3})H_\mu}}{1 - e^{-H_\mu}} \right\}, \tag{18}$$

$$\sum_{\lambda_c \neq 0} V''_{\lambda_c}(P) = -\frac{(M-N)p_z}{2\epsilon_0\omega}. \tag{18'}$$

Eq. (18) gives the EP of the point charges of all the planes with $\lambda_c \neq 0$ plus their neutralizing planar distributions, as in section 3. Eq. (18') gives the EP of planar distributions with the same sign as the point charges.

For the layer with $\lambda_c = 0$ we add and subtract planar charge distributions $\Gamma_\alpha = q_\alpha/\omega$ at $z = j'_{\alpha,3}\, a_3$. For $\alpha \neq \beta$ the contribution of the point charges q_α together with the neutralizing distributions $-\Gamma_\alpha$ is obtained as for $\lambda_c \neq 0$:

$$V'_{\lambda_c=0}(P) - V'_{\lambda_c=0,\beta}(P_{j_\beta}) = \frac{a_1}{4\pi\epsilon_0\omega} \sum_{\mu_1,\mu_2}{}' \left\{ \sum_{\alpha=1}^{\beta-1} q_\alpha f(\alpha,\mu)\, e^{-(1-j_{\alpha,3})H_\mu} + \sum_{\alpha=\beta+1}^{A} q_\alpha f(\alpha,\mu)\, e^{-j_{\alpha,3}H_\mu} \right\}.$$

When this is added to (18) the same expression as in (14) is obtained for the sublattices with $\alpha \neq \beta$:

$$V'(P) = \frac{a_1}{4\pi\epsilon_0\omega} \sum_{\alpha\neq\beta} q_\alpha \sum_{\mu_1,\mu_2}{}' f(\alpha,\mu) \frac{e^{-(1-j_{\alpha,3})H_\mu} + e^{-j_{\alpha,3}H_\mu}}{1 - e^{-H_\mu}} + \frac{a_1 q_\beta}{2\pi\epsilon_0\omega} \sum_{\mu_1,\mu_2}{}' f(\beta,\mu) \frac{e^{-H_\mu}}{1 - e^{-H_\mu}} + V'_{\lambda_c=0,\beta}(P_{j_\beta}). \tag{19}$$

We have still to calculate the contribution of the planar charge distributions $+\Gamma_\alpha$, in addition to the last term of the above equation. The former is $a_1/4\pi\epsilon_0\omega$ times the $G(\mathbf{0})$ which has been evaluated in section 3 (eq. 12):

$$V''_{\lambda_c=0}(P) = -\frac{a_3}{2\epsilon_0\omega} \sum_{\alpha=1}^{A} q_\alpha\, |j'_{\alpha,3}| = -\frac{1}{2\epsilon_0\omega} \left[p_z + 2a_3 \sum_{\alpha=1}^{\beta-1} q_\alpha (1 - j_{\alpha,3}) \right]. \tag{20}$$

When this is added to (18′) the same result as in section 3 (eq. 15) is obtained for the EP of the planar distributions:

$$V''(P) = -\frac{1}{2\epsilon_0\omega}\left[(M-N+1)\,p_z + 2a_3 \sum_{\alpha=1}^{\beta-1} q_\alpha(1-j_{\alpha,3})\right]. \tag{21}$$

Finally, we have to calculate the EP of the two-dimensional sublattice of the point charges q_β at $z = 0$, together with its planar neutralizing distribution $-\Gamma_\beta$ (the last term in (19)). Let us introduce a uniform volume distribution ρ extending from $z = (\lambda_c - \frac{1}{2})\,a_3$ to $z = (\lambda_c + \frac{1}{2})\,a_3$. Using Gauss' theorem it is easy to find that the potential V_a created by this distribution plus a planar charge density $-\Gamma = -\rho a_3$ at $z = \lambda_c a_3$ is

$$\begin{aligned} &V_a = -(\Gamma/2\epsilon_0 a_3)\,(|z-\lambda_c a_3| - \tfrac{1}{2}a_3)^2, && \text{if } |z-\lambda_c a_3| \leqslant \tfrac{1}{2}a_3,\\ &V_a = 0, && \text{if } |z-\lambda_c a_3| > \tfrac{1}{2}a_3. \end{aligned} \tag{22}$$

Let us associate to each xy plane of the β sublattice a planar charge distribution $\Gamma_\beta = q_\beta/\omega$, and the volume density $\rho_\beta = q_\beta/a_3\omega$ between the planes $z = (\lambda_c - \frac{1}{2})\,a_3$ and $z = (\lambda_c + \frac{1}{2})\,a_3$. Adding and subtracting these distributions, we can think of the contribution to the EP of the β sublattice as follows (the notation is easily understood):

$$V_\beta = V'_\beta + V_{\Gamma,\beta},$$

with

$$V'_\beta = (V_q - V_\rho)_{\text{all }\lambda_c\text{'s}} + (V_\rho - V_\Gamma)_{\lambda_c \neq 0} + (V_\rho - V_\Gamma)_{\lambda_c = 0}.$$

The first term in the latter equation is Sholl's potential (17), while the second and the third are equal to zero and to $-q_\beta a_3/8\epsilon_0\omega$, respectively (eqs. 22). Therefore, the contribution of the β sublattice to V' (eq. 19) is

$$V'_\beta(j_{\beta,1}, j_{\beta,2}, 0) = V_S(j_{\beta,1}, j_{\beta,2}, 0) - q_\beta a_3/8\epsilon_0\omega. \tag{23}$$

Notice that this equation is formally identical to (17). However, in the latter $V'(P_j)$ stands for a functional expression (eq. 14) that is not defined for $j_3 = 0$.

On the other hand, $V_{\Gamma,\beta}$ has already been taken into account: it has been included into (21), through (18′) and (20), where its divergent contributions are cancelled.

Sholl's potential has not been calculated for the case $j_3 = 0, j_1$ and/or $j_2 \neq 0$. Let us assume $j_{\beta,1} \neq 0$. In ref. 7 we showed that in such a case for orthorhombic crystals the EP can be evaluated in terms of the EP in a slab perpendicular to the a_1 crystallographic axis:

$$V_S(j_{\beta,1}, j_{\beta,2}, 0; a_1 a_2 a_3) = V_S(j_{\beta,2}, 0, j_{\beta,1}; a_2 a_3 a_1) + q_\beta\,(a_3^2 - a_1^2)/24\epsilon_0 a_3\omega.$$

Substituting into (23) and using (17) we finally get

$$V'_\beta(j_{\beta,1}, j_{\beta,2}, 0; a_1 a_2 a_3) = V'_\beta(j_{\beta,2}, 0, j_{\beta,1}; a_2 a_3 a_1) + \frac{q_\beta a_1}{2\epsilon_0 a_2 a_3}\left[(j_{\beta,1} - \tfrac{1}{2})^2 - \tfrac{1}{12}\right] - \frac{q_\beta a_3}{12\epsilon_0 a_1 a_2}. \tag{24}$$

The first term in the rhs is, from (14),

$$V'_\beta(j_{\beta,2}, 0, j_{\beta,1}; a_2 a_3 a_1) = \frac{q_\beta}{4\pi\epsilon_0 a_3} \sum_{\mu_1,\mu_2}{}' \frac{e^{-2\pi i j_{\beta,2}\mu_1}}{\tilde{h}_{\mu_1\mu_2}} \frac{e^{-j_{\beta,1}\tilde{H}_\mu} + e^{-(1-j_{\beta,1})\tilde{H}_\mu}}{1 - e^{-\tilde{H}_\mu}}, \tag{25}$$

with $\tilde{h}_{\mu_1\mu_2} \equiv [\mu_1^2 + (a_2\mu_2/a_3)^2]^{\frac{1}{2}}$ and $\tilde{H}_\mu \equiv 2\pi\tilde{h}_{\mu_1\mu_2}a_1/a_2$.

An analogous procedure can be followed if $j_{\beta,2} \neq 0$ while $j_{\beta,1} = 0$.

In the case (ii), i.e. $j_{\beta,1} = j_{\beta,2} = j_{\beta,3} = 0$ (the field point will now be denoted by O), Sholl's result is obtained from eq. (3.22) of [10], giving the EP relative to the average potential, by subtracting $(-q_\beta a_3/24\epsilon_0\omega)$. Substituting into (23) we get

$$V'_\beta(\mathrm{O}) = V_\mathrm{S}(\mathrm{O}) - q_\beta a_3/8\epsilon_0\omega = \frac{q_\beta}{4\pi\epsilon_0}\left\{\frac{2a_1}{\omega}\sum_{\mu_1,\mu_2}{}' \frac{\mathrm{e}^{-H_\mu}}{\tilde{h}_{\mu_1\mu_2}(1-\mathrm{e}^{-H_\mu})}\right.$$
$$\left. + \frac{8}{a_1}\sum_{\lambda=1}^{\infty}\sum_{\mu=1}^{\infty}\cos(2\pi\mu\lambda\delta_1)K_0(2\pi\mu\lambda\delta_2) + \frac{1}{a_1}[2C - \log(16\pi^2 a_1^4/\omega^2)]\right\}. \tag{26}$$

Here, $\delta_1 = a_2\cos\gamma/a_1$, $\delta_2 = a_2\sin\gamma/a_1$, C = Euler's constant = 0.5772156649. $K_0(x)$ is the modified Bessel function of zero order (see eq. (9.6.21) of [15]; eqs. (9.8.5) and (9.8.6) of [15] furnish convenient series expansions).

Let us summarize the results of this section. We write

$$V(P) = \sum_{\alpha\neq\beta} V'_\alpha(P_{j_\alpha}) + V'_\beta(P_{j_\beta}) + V''(P). \tag{27}$$

(i) $j_{\beta,1}$ and/or $j_{\beta,2} \neq 0, j_{\beta,3} = 0$.

The first term in (27) is equal to the first term in (19); the second one is given by (24) with (25) (this is true if $j_{\beta,1} \neq 0$; if $j_{\beta,1} = 0$, so that $j_{\beta,2} \neq 0$, a similar expression can be found) and the last one by (21). This result only holds for a crystal with orthorhombic, or higher, symmetry.

(ii) $j_{\beta,1} = j_{\beta,2} = j_{\beta,3} = 0$.

The first and the third terms in (27) are obtained as in case (i); the second one is given by (26).

6. Electrostatic energy per unit cell of a slab-shaped ionic crystal

In this section we are going to write down an expression for the EE of a slab-shaped ionic crystal using the formulae for the EP that we derived in sections 3 and 5. Such formulae apply to circular slabs, but as we saw in section 2 the result obtained for the EE is independent of the shape of the slab.

The EE associated with the unit cell of a slab-shaped ionic crystal is given by

$$E_\mathrm{c} = \tfrac{1}{2}\sum_{\alpha=1}^{A} q_\alpha V_\alpha, \tag{28}$$

V_α being the EP at the α site. The $\frac{1}{2}$ factor appears because the interaction energy of each pair of ions has to be considered as shared by them in equal amounts. Let

$$r_\alpha \equiv \xi_{\alpha,1}a_1 + \xi_{\alpha,2}a_2 + \xi_{\alpha,3}a_3,$$

be the position vector of the α site with respect to an arbitrary origin. Using (16) we have

$$V_\alpha = \sum_{\alpha'=1}^{A} V'(j_{\alpha\alpha'}) - (M-N+1)p_z/2\epsilon_0\omega - (a_3/\epsilon_0\omega)\sum_{\alpha'=1}^{\bar{\alpha}} q_{\alpha'}(1-j_{\alpha\alpha',3}),$$

where

$$j_{\alpha\alpha',i} = \xi_{\alpha',i} - \xi_{\alpha,i}, \qquad \text{for } \xi_{\alpha',i} \geqslant \xi_{\alpha,i},$$

$$j_{\alpha\alpha',i} = \xi_{\alpha',i} - \xi_{\alpha,i} + 1 \qquad \text{for } \xi_{\alpha',i} < \xi_{\alpha,i}.$$

Here $\bar{\alpha}$ is defined so that the last sum runs over the α' values such that $\xi_{\alpha',3} < \xi_{\alpha,3}$ (if the $\xi_{\alpha,3}$ were all different from each other, then $\bar{\alpha} = \alpha - 1$). $V'(j_{\alpha\alpha'})$ is the potential created by the α' sublattice plus its neutralizing planar distribution at the α site, and can be obtained from (14). Let us write $V'(j_{\alpha\alpha'}) \equiv q_{\alpha'} v'(j_{\alpha\alpha'})$. Substituting the above expression into (28) we get

$$E_c = \tfrac{1}{2} \sum_{\alpha=1}^{A} q_\alpha \left[q_\alpha v'(0) + \sum_{\alpha' \neq \alpha} q_\alpha v'(j_{\alpha\alpha'}) \right] - \frac{a_3}{2\epsilon_0 \omega} \sum_{\alpha=1}^{A} q_\alpha \sum_{\alpha'=1}^{\bar{\alpha}} q_{\alpha'} (\xi_{\alpha,3} - \xi_{\alpha',3}),$$

which can be rewritten more conveniently as

$$E_c = \tfrac{1}{2} v'(0) \sum_{\alpha=1}^{A} q_\alpha^2 + \sum_{\alpha=1}^{A} \sum_{\alpha'>\alpha} q_\alpha q_{\alpha'} v'(j_{\alpha\alpha'}) + (a_3/2\epsilon_0\omega) \sum_{\alpha=1}^{A} \sum_{\alpha'>\alpha} q_\alpha q_{\alpha'} (\xi_{\alpha',3} - \xi_{\alpha,3}). \tag{29}$$

This is the expression giving the EE of a slab-shaped ionic crystal, using the planewise summation method.

Eq. (29) can be applied to the calculation of the Madelung constant of a slab-shaped crystal. Let us consider, for example, the cases of NaCl, CsCl and $BaTiO_3$. In all cases we will consider a slab with its large faces perpendicular to (a) the [001] and (b) [110] crystallographic directions. We will also calculate the contribution to the EE of $BaTiO_3$ in the ferroelectric phase coming from the ionic polarizability. The values of the dimensionless quantity $\tilde{v}'(j) \equiv 4\pi\epsilon_0 a_2 v'(j)$ needed in these calculations are given in table I.

Table I
Values of $\tilde{v}'(j) \equiv 4\pi\epsilon_0\, av'(j)$ used in the calculation of the Madelung constants of NaCl, CsCl and $BaTiO_3$.

a_2/a_1	a_3/a_1	j_1	j_2	j_3	$\tilde{v}'(j)$
1	1	0	0	0	−3.88449503
1	1	½	0	½	−0.05892276
1	1	½	½	½	−0.27833719
1	1	0	0	½	0.42766647
1	1	½	½	0	−1.62971909
1	1	½	0	0	−1.14312986
$1/\sqrt{2}$	1	0	0	0	−3.20604119
$1/\sqrt{2}$	1	½	0	½	−0.15485506
$1/\sqrt{2}$	1	0	½	½	0.12263079
$1/\sqrt{2}$	1	½	½	½	−0.18420268
$1/\sqrt{2}$	1	0	0	½	0.23233801
$1/\sqrt{2}$	1	½	½	0	−1.44816554
$1/\sqrt{2}$	1	½	0	0	−1.33845832
$1/\sqrt{2}$	1	0	½	0	−0.43532841
$1/\sqrt{2}$	1	¼	0	¼	0.08293354
$1/\sqrt{2}$	1	¼	½	¼	−0.16036108

NaCl In case (a) we have 8 cubic sublattices ($a_1 = a_2 = a_3 = a$) and (b) 16 tetragonal sublattices ($a_1 = a_3 = \sqrt{2}\,a$, $a_2 = a$). We found that in both cases the energy per mol, which defines the Madelung constant [eq. (1)], is given by

$$U_{\mathrm{mol}} = -\frac{q}{4\pi\epsilon_0 a}\,3.4951292,$$

(q = charge of the Na, a = lattice constant), in excellent agreement with the result of Sakamoto [16] (α_{NaCl} = 3.49512 91892 663643).

CsCl By an analogous procedure we obtained

$$\alpha_{\mathrm{CsCl},\,001} = 0.46456519 \quad \text{(case (a))},$$
$$\alpha_{\mathrm{CsCl},\,110} = 2.035361505 \quad \text{(case (b))}.$$

The difference between the two values is $\frac{1}{2}\pi$, and it is due to the following. We saw in section 2 that the EE of any crystal (not necessarily ionic) depends on the shape of the specimen if the dipole moment of the unit cell is different from zero. Let us consider a fictitious crystal whose cell is that of the CsCl plus two neutralizing distributions (one for each ionic species). In other words, the primitive cell of such a crystal consists of a Cs ion with charge q at (x,y,z), a cube with uniform density $-q/a^3$ centred at (x,y,z), a Cl ion with charge $-q$ at $(x+\frac{1}{2}a, y+\frac{1}{2}a, z+\frac{1}{2}a)$ and a cube with uniform density q/a^3 centred at $(x+\frac{1}{2}a, y+\frac{1}{2}a, z+\frac{1}{2}a)$. For this cell $p = 0$, so that the EE of a slab-shaped specimen of the fictitious crystal under consideration must be the same irrespective of the orientation of the crystallographic axes with respect to the slab faces. Now, for case (b) the effects of the uncompensated neutralizing clouds at the slab faces cancel out each other, so that the EE coincides with that of the CsCl. In case (a), however, the fictitious crystal differs from the CsCl by two layers with thickness $\frac{1}{2}a$ and densities $\pm q/a^3$ at the $\pm z$ faces. These layers give a contribution $\frac{1}{2}\pi$ to the Madelung constant, as can be easily seen. Therefore,

$$\alpha_{\mathrm{CsCl\,+\,neutr.\,clouds}} = \alpha_{\mathrm{CsCl},\,110} = \alpha_{\mathrm{CsCl},\,001} + \tfrac{1}{2}\pi,$$

in agreement with our result. In ref. 3 Redlack and Grindlay obtained

$$\alpha_{\mathrm{CsCl},\,110} = \alpha_{\mathrm{CsCl},\,001} + \tfrac{1}{3}\pi.$$

We believe that Redlack and Grindlay's assumption about the uncompensated surface distribution, namely the fact that their term $L(x, V - V_{\mathrm{N}})$ is constant, is not valid and that this causes an error manifesting itself whenever there are uncompensated distributions at the crystal surface. For NaCl (a) and (b) and CsCl (b), where the effects of the uncompensated surface distributions cancel each other, Redlack and Grindlay's results coincide with ours.

$BaTiO_3$ (cubic, paraelectric structure) Our results are

$$\alpha_{\mathrm{BaTiO_3},\,001} = 0.80505226\,q_{\mathrm{Ba}}^2 + 1.81524026\,q_{\mathrm{Ti}}^2 + 2.15572734\,q_{\mathrm{Ba}}\,q_{\mathrm{Ti}}, \tag{30a}$$

$$\alpha_{\mathrm{BaTiO_3},\,110} = 1.15411810\,q_{\mathrm{Ba}}^2 + 1.64070734\,q_{\mathrm{Ti}}^2 + 0.75946394\,q_{\mathrm{Ba}}\,q_{\mathrm{Ti}}. \tag{30b}$$

It can be seen that in both cases if $q_{\mathrm{Ba}} = -q_{\mathrm{Ti}}$ (so that $q_{\mathrm{O}} = 0$) the above results reduce to those obtained for the CsCl structure. As for CsCl, the difference between the two values of $\alpha_{\mathrm{BaTiO_3}}$ is explained by considering a fictitious crystal with a neutralizing cloud for each ionic sublattice. We obtain the relation

$$\alpha_{BaTiO_3 + \text{neutr. clouds}} = \alpha_{BaTiO_3,\,001} + \frac{\pi}{18}(4\,q_{Ba}^2 + q_{Ti}^2 - 4\,q_{Ba}\,q_{Ti})$$

$$= \alpha_{BaTiO_3,\,110} + \frac{\pi}{9}(q_{Ba}^2 + q_{Ti}^2 + 2\,q_{Ba}\,q_{Ti}),$$

in complete agreement with eqs. (30). In this case too Redlack and Grindlay's results differ from ours.

$BaTiO_3$ (tetragonal, ferroelectric structure)

Let us consider a $BaTiO_3$ slab-shaped specimen, with the large faces perpendicular to the ferroelectric axis (the z axis). In the ferroelectric tetragonal phase the ions are displaced in the z direction with respect to each other. Referring all the displacements to the oxygen at $(\frac{1}{2}, \frac{1}{2}, 0)$ we have a unit cell with a Ba ion at $(0, 0, \delta_{Ba})$, a Ti ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + \delta_{Ti})$ and three O at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2} - \delta_O)$ and $(0, \frac{1}{2}, \frac{1}{2} - \delta_O)$, respectively. Eq. (29) takes the form

$$E_{BaTiO_3,\,FE,\,001} = \tfrac{1}{3}(2\,q_{Ba}^2 + 2\,q_{Ti}^2 + q_{Ba}\,q_{Ti})\,v'(0,0,0) - \tfrac{1}{3}(q_{Ba}^2 + q_{Ba}\,q_{Ti})\,v'(\tfrac{1}{2}, \tfrac{1}{2}, \delta_{Ba})$$

$$+ \tfrac{2}{9}(q_{Ba}^2 + q_{Ti}^2 + 2\,q_{Ba}\,q_{Ti})\,v'(0, \tfrac{1}{2}, \tfrac{1}{2} - \delta_O) - \tfrac{1}{3}(q_{Ti}^2 + q_{Ba}\,q_{Ti})\,v'(0, 0, \tfrac{1}{2} + \delta_{Ti})$$

$$- \tfrac{2}{3}(q_{Ba}^2 + q_{Ba}\,q_{Ti})\,v'(0, \tfrac{1}{2}, \tfrac{1}{2} - \delta_O - \delta_{Ba}) + q_{Ba}\,q_{Ti}\,v'(\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} + \delta_{Ti} - \delta_{Ba})$$

$$+ \tfrac{1}{9}(q_{Ba}^2 + q_{Ti}^2 + 2\,q_{Ba}\,q_{Ti})\,v'(\tfrac{1}{2}, \tfrac{1}{2}, 0) - \tfrac{2}{3}(q_{Ti}^2 + q_{Ba}q_{Ti})\,v'(0, \tfrac{1}{2}, \delta_{Ti} + \delta_O)$$

$$- 2\pi\{-\tfrac{1}{18}(2\,q_{Ba} - q_{Ti})^2 + \tfrac{1}{3}(q_{Ba}^2 - 2\,q_{Ba}\,q_{Ti})\,\delta_{Ba} + \tfrac{4}{9}(q_{Ba}^2 - 2\,q_{Ti}^2 - q_{Ba}q_{Ti})\delta_O - q_{Ti}^2\delta_{Ti}\}. \qquad (31)$$

We recall that $v'(j_1, j_2, j_3)$ is equal to the $V'_\alpha(j_\alpha)$ of eq. (14) divided by q_α.

Using this result we can calculate the electrostatic contribution to the specific heat of the ferro- to para-electric transition of $BaTiO_3$ coming from the ionic displacements. In doing this we must take into account that in a standard experimental arrangement a slab with electrodes attached to its faces is employed, so that when the reading of the voltmeter is zero the plates bear an electric charge such that the macroscopic dipole field is cancelled (see section 1 of [11]). It is easy to show that in each case the contribution to the energy from the charges on the electrodes is

$$E_\sigma = -p_z^2/\epsilon_0 a_3 \omega.$$

In our case $p_z = \frac{1}{6}a\,(q_{Ti} - 2\,q_{Ba})$ and $p_z = a[\,\frac{1}{6}(q_{Ti} - 2\,q_{Ba}) + (\delta_{Ba} + \frac{2}{3}\delta_O)\,q_{Ba} + (\delta_{Ti} + \frac{2}{3}\delta_O)q_{Ti}\,]$ for para- and ferro-electric $BaTiO_3$ respectively.

The ionic electrostatic contribution to the transition heat of $BaTiO_3$ is therefore

$$\Delta E = E_{BaTiO_3,\,PE} + E_{\sigma,\,PE} - E_{BaTiO_3,\,FE} - E_{\sigma,\,FE}, \qquad (32)$$

where the first and the third terms are given by (30a) and (31), respectively. In view of the lack of accuracy in the experimental determination of the ionic displacements it is not actually necessary to use eq. (31), because a more practical expression can be obtained by expanding $E_{BaTiO_3,\,PE} - E_{BaTiO_3,\,FE}$ in terms of the δ's. The result is

Table II
Values of $(1/2\pi)\partial\,\tilde{v}'(j)/\partial j_3$ and $(1/2\pi)\partial^2\,\tilde{v}'(j)/\partial j_3^2$, which are used in the calculation of eq. (32).

a_2/a_1	a_3/a_1	j_1	j_2	j_3	$(1/2\pi)\partial\,\tilde{v}'(j)/\partial j_3$	$(1/2\pi)\partial^2\,\tilde{v}'(j)/\partial j_3^2$
1	1	$\frac{1}{2}$	0	$\frac{1}{2}$	0	−0.64357719
1	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	−1.33333333
1	1	0	0	$\frac{1}{2}$	0	3.45437216
1	1	$\frac{1}{2}$	$\frac{1}{2}$	0	1	−2.71284562
1	1	$\frac{1}{2}$	0	0	1	−3.72718608

$$E_{BaTiO_3,\,PE} - E_{BaTiO_3,\,FE} = -\frac{1}{2\epsilon_0 a}\{\tfrac{1}{9}[-(6\delta_{Ba} + 4\delta_O)q_{Ba}^2 + (3\delta_{Ti} + 2\delta_O)q_{Ti}^2$$

$$+ (3\delta_{Ba} - 6\delta_{Ti} - 2\delta_O)q_{Ba}q_{Ti}] + [(\tfrac{2}{3}\delta_{Ba}^2 + 0.143\,\delta_O^2 + 0.429\,\delta_{Ba}\delta_O)q_{Ba}^2$$

$$+ (\tfrac{2}{3}\delta_{Ti} + 1.171\,\delta_O^2 + 2.485\,\delta_{Ti}\delta_O)q_{Ti}^2 + (1.314\,\delta_O^2 + \tfrac{4}{3}\delta_{Ba}\delta_{Ti} + 0.429\,\delta_{Ba}\delta_O$$

$$+ 2.485\,\delta_{Ti}\delta_O)q_{Ba}q_{Ti}]\} + \mathcal{O}(\delta^3)$$

(the values of the derivatives used in this calculation are given in table II).

On the other hand,

$$E_{\sigma,\,PE} - E_{\sigma,\,FE} = \frac{1}{\epsilon_0 a}\{\tfrac{1}{3}(q_{Ti} - 2q_{Ba})[(\delta_{Ba} + \tfrac{2}{3}\delta_O)q_{Ba} + (\delta_{Ti} + \tfrac{2}{3}\delta_O)q_{Ti}]$$

$$+ [(\delta_{Ba}^2 + \tfrac{4}{9}\delta_O^2 + \tfrac{4}{3}\delta_{Ba}\delta_O)q_{Ba}^2 + (\delta_{Ti}^2 + \tfrac{4}{9}\delta_O^2 + \tfrac{4}{3}\delta_{Ti}\delta_O)q_{Ti}^2$$

$$+ (\tfrac{8}{9}\delta_O^2 + 2\delta_{Ba}\delta_{Ti} + \tfrac{4}{3}\delta_{Ba}\delta_O + \tfrac{4}{3}\delta_{Ti}\delta_O)q_{Ba}q_{Ti}]\}.$$

Substituting these two equations into (32) we get the contribution to the transition heat in terms of the ionic charges and displacements.

Let us take $q_{Ba} = 2e$, $q_{Ti} = 4e$. Since for $q_{Ti} = 2q_{Ba}$ all the linear terms in the δ's are found to vanish, we have

$$\Delta E = \frac{e^2}{4\pi\epsilon_0 a}(33.51\,\delta_{Ba}^2 + 134.04\,\delta_{Ti}^2 + 13.71\,\delta_O^2 + 134.04\,\delta_{Ba}\delta_{Ti} + 168.71\,\delta_{Ba}\delta_O + 27.44\,\delta_{Ti}\delta_O).$$

Using for the δ's the values obtained by Frazer et al. [17] by neutron diffraction (which actually give the displacements of the nuclei) we have

$$\Delta E = 0.3604\,\frac{e^2}{4\pi\epsilon_0 a} = 1.30\text{ eV} = 29.9\text{ cal/mol}.$$

The experimental value for the transition heat is 50 cal/mol [18].

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