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THE ELECTROSTATIC POTENTIAL IN MULTIPOLE LATTICES

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Synopsis

General expressions for the electrostatic potential in perfect multipole lattices are given as expansions in terms of spherical harmonics. The coefficients occurring in these expansions contain lattice sums of a general type, which have been treated previously. Such expressions are derived for a point charge lattice, a multipole lattice, and finally for a lattice built up from a number of different arbitrary charge distributions.

§ 1. *Introduction.* In many problems of solid state physics, in particular in the theory of ionic crystals, it is desirable to have a description of the electrostatic potential everywhere inside the unit cell of the crystal. In order to be sufficiently general, such a description should take account of the fact that the atoms (or ions) are charge distributions of finite extent, which are deformable in the crystalline field. Although on these grounds one expects the atomic (ionic) charge distributions to contain, besides a net charge and possibly a dipole moment, certain higher multipole moments, these complications are usually left out of consideration. For instance, in calculating the electrostatic binding energy of ionic crystals it is customary to consider the ions as spherically symmetric (point-charge-model) and to correct only for the overlap of these spherical charge distributions. When considering also higher multipole moments, however, one would expect the electrostatic binding energy to deviate from its point-charge-value (Madelung energy), even in the absence of overlap. Other examples where the existence of higher multipoles should manifest itself are in the elastic behavior of crystals (deviations from the Cauchy relations) and in their dielectric properties (modification of the relation of Clausius-Mossotti). A more precise description of the crystalline potential should also be of interest in the theory of ferroelectricity and of colourcenters, to mention a few more examples.

In order to arrive at such a general description of the crystalline electrostatic potential, it seems most natural to expand the potential inside the unit cell into spherical harmonics. We will derive such expansions firstly for lattices of point charges, secondly for lattices of multipoles of higher

order and finally for lattices built up from a number of different arbitrary charge distributions. The coefficients in these expansions turn out to be lattice sums of a rather general type, which have been treated by us in a previous publication[1]) (to be quoted as I). This description of the crystalline potential can be used in any situation where the charge distributions do not overlap the field point. Therefore, although the present derivations in themselves are purely classical, this treatment of the potential might be incorporated into a quantum-mechanical theory, by inserting for the charge distributions those which follow from the ionic wave functions.

In a following paper we propose to investigate which corrections to the electrostatic binding energy and the dielectric constant result from the occurrence of higher multipole moments in the charge distributions of ionic lattices.

§ 2. *The electrostatic potential in a lattice of positive and negative unit point charges.* As a first example we will give an expression for the electrostatic potential in a point lattice with alternately positive and negative unit charges at the lattice points. The potential in a point $\mathbf{R}$ is (the + charge at the origin 0 being omitted)

$$V_{pt}(\mathbf{R}) = \sum\nolimits'_{\lambda} \frac{(-1)^{\lambda_1+\lambda_2+\lambda_3}}{|\mathbf{R}-\mathbf{r}_\lambda|} = \sum\nolimits'_{\lambda} \frac{e^{2\pi i \mathbf{k}_{\frac{1}{2}}\cdot \mathbf{r}_\lambda}}{|\mathbf{R}-\mathbf{r}_\lambda|} \equiv S'(\mathbf{R}|\mathbf{k}_{\frac{1}{2}}, \tfrac{1}{2}) \tag{1}$$

(cf. I, (12) and (22)). Using the expansion

$$|\mathbf{R}-\mathbf{r}_\lambda|^{-1} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} (4\pi/2l+1)\, R^l r_\lambda^{-l-1}\, Y^*_{l,m}(\vartheta, \varphi)\, Y_{l,m}(\theta_\lambda, \phi_\lambda)\ ^*) \tag{2}$$

$R < r_\lambda$ ($\mathbf{R}(R, \vartheta, \varphi)$, $\mathbf{r}_\lambda(r_\lambda, \theta_\lambda, \phi_\lambda)$), we can write for (1)

$$V_{pt}(\mathbf{R}) = \sum_{l,m} R^l Y^*_{l,m}(\vartheta, \varphi)(4\pi/2l+1) \sum\nolimits'_{\lambda} r_\lambda^{-l-1} Y_{l,m}(\theta_\lambda, \phi_\lambda)\, e^{2\pi i \mathbf{k}_{\frac{1}{2}}\cdot \mathbf{r}_\lambda}. \tag{3}$$

This can be abbreviated as

$$V_{pt}(\mathbf{R}) = \sum_{l,m} a_{l,m}\, R^l\, Y^*_{l,m}(\vartheta, \varphi) \tag{4}$$

with

$$a_{l,m} = (4\pi/2l+1) \sum\nolimits'_{\lambda} r_\lambda^{-l-1}\, Y_{l,m}(\theta_\lambda, \phi_\lambda)\, e^{2\pi i \mathbf{k}_{\frac{1}{2}}\cdot \mathbf{r}} \equiv (4\pi/2l+1) S'_{l,m}(0|\mathbf{k}_{\frac{1}{2}}, \tfrac{1}{2}) \tag{5}$$

(cf. I, (39)). This expansion of $V_{pt}(\mathbf{R})$ in terms of spherical harmonics is valid for all points inside a sphere with a radius equal to the nearest neighbour distance (cf. condition for validity of (2)). This, however, does not involve any serious restriction.

The expansion coefficients $a_{l,m}$ are proportional to lattice sums of a type

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*) $Y_{l,m}(\vartheta,\varphi)$ is defined by $Y_{l,m}(\vartheta, \varphi) = (2\pi)^{-\frac{1}{2}} \overline{P_l^m}(\cos\vartheta)\, e^{im\varphi}$, where

$$\overline{P_l^m} = (-1)^m \left\{ \frac{2l+1}{2} \cdot \frac{(l-m)!}{(l+m)!} \right\}^{\frac{1}{2}} \frac{(1-x^2)^{m/2}}{2^l l!} \cdot \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l.$$

Both definitions hold for positive as well as negative m ($|m| \leqq l$) See e.g. Meixner[2]) pp. 160, 197.

discussed in I, § 6. Rapidly converging expressions for these sums are given by I, (44) for $l \neq 0$, while $2\sqrt{\pi}\, S'_{0,0}(0|\mathbf{k}_i, \frac{1}{2})$, the Madelung constant, is given by I, (19). In these expressions a few terms of the sums in ordinary and Fourier space already lead to very accurate results. The advantage of expressing $V_{pt}(\mathbf{R})$, i.e. the potential in an *arbitrary* point $\mathbf{R}$, into the form (4), is that one needs only one set of sums $S'_{l,m}(0|\mathbf{k}_i, \frac{1}{2})$ (which are taken with respect to the origin and not with respect to $\mathbf{R}$) in order to calculate the potential everywhere inside the unit cell by simply applying (4) *). This is the point where the present method distinguishes itself from Ewald's method [4]), which has been most extensively used so far. In the latter method a rapidly converging expression for the sum (1) is derived (to which our expression I, (38) is equivalent) which has the advantage of being valid everywhere in the lattice. But the formulae can only be evaluated with relative ease for special points in the unit cell (viz. such points for which the distances $|\mathbf{R} - \mathbf{r}_\lambda|$ are "lattice vector-like"), while moreover for each point (or rather, each set of crystallographically equivalent points) the sums have to be evaluated anew.

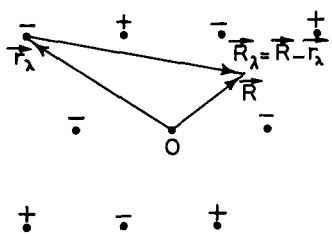

Fig. 1. Lattice vectors in a lattice of positive and negative point charges.

The coefficients $a_{l,m}$ vanish for all odd l as a result of the inversion symmetry of the potential in a Bravais lattice (cf. I, § 6). An additional number of coefficients $a_{l,m}$ (for even l) will vanish on account of the symmetry of the particular lattice considered. This is because only such $Y^*_{l,m}$'s can occur in (4), which are compatible with the particular lattice symmetry. We shall have to consider this problem in a little more detail in the following paper (see also the next section).

We note, combining (1), (4) and (5), the following relation between lattice sums

$$S'(\mathbf{R}|\mathbf{k}, \tfrac{1}{2}) = \sum_{l,m}(4\pi/2l + 1)S'_{l,m}(0|\mathbf{k}, \tfrac{1}{2})\, R^l Y^*_{l,m}(\vartheta, \varphi), \qquad (6)$$

which holds not just for $\mathbf{k}_i$, but for any reciprocal space vector $\mathbf{k}$ and for every $\mathbf{R}$ for which (2) is valid.

*) The authors recently discovered a paper by Kanamori, Moriya, Motizuki and Nagamiya [3]) who also expand the crystalline potential in terms of spherical harmonics. Explicit formulae (equivalent to (4) and (5)) are given for point charge and dipole lattices. Their methods for calculating the expansion coefficients are, however, less satisfactory than the method of I.

§ 3. *Numerical example: the potential in a NaCl-type lattice.* As an application of the formulae (4) and (5), derived in § 2, we will now give numerical expressions for the potential in a cubic lattice with alternately positive and negative unit charges and lattice distance 1.

The cubic symmetry of the potential simplifies its expansion (4) considerably: only terms with l is even and $m = 0$ or a four-fold can occur, while for given l, the $Y^*_{l,m}$'s which do occur must be combined into a linear combination Υ_l which is invariant for the operations of the full cubic group O_h (Υ_l then is the invariant vector in the $2l+1$-dimensional representation space of O_h). The invariant linear combinations Υ_l for $l = 4$, 6, 8 and 10 respectively are (for $l = 2$ no such Υ exists)

$$\left.\begin{aligned}
\Upsilon_4 &= (5/14)^{\frac{1}{2}}\,(Y^*_{4,4} + Y^*_{4,-4}) + Y^*_{4,0}\\
\Upsilon_6 &= -(7/2)^{\frac{1}{2}}\,(Y^*_{6,4} + Y^*_{6,-4}) + Y^*_{6,0}\\
\Upsilon_8 &= (5/3)(13/110)^{\frac{1}{2}}(Y^*_{8,8}+Y^*_{8,-8})+(1/3)(14/11)^{\frac{1}{2}}(Y^*_{8,4}+Y^*_{8,-4})+Y^*_{8,0}\\
\Upsilon_{10} &= -(187/130)^{\frac{1}{2}}(Y^*_{10,8}+Y^*_{10,-8})-6(11/390)^{\frac{1}{2}}(Y^*_{10,4}+Y^*_{10,-4})+Y^*_{10,0}
\end{aligned}\right\}\ *)\quad (7)$$

Using (7) we may write for the potential in this example

$$V_{pt}(\mathbf{R}) = 2\sqrt{\pi}\,S'_{0,0} + (4\pi/9)\,S'_{4,0}R^4\Upsilon_4(\vartheta,\varphi) + (4\pi/13)\,S'_{6,0}R^6\Upsilon_6(\vartheta,\varphi) + \\ + (4\pi/17)\,S'_{8,0}\,R^8\Upsilon_8(\vartheta,\varphi) + (4\pi/21)\,S'_{10,0}R^{10}\,\Upsilon_{10}(\vartheta,\varphi) + O(R^{12}). \quad (8)$$

Knowledge of the invariant linear combinations Υ_l thus makes that, for each l occurring, one only needs to calculate one single lattice sum. Using the values (for a simple cubic lattice with lattice distance 1; z-axis along one of the four-fold axes),

$$\left.\begin{aligned}
(4\pi)^{\frac{1}{2}}S'_{0,0}\ (0|\mathbf{k}_{\frac{1}{4}},\tfrac{1}{2}) &= -1.74756\ \text{(Madelung constant)}\\
(4\pi/9)^{\frac{1}{2}}S'_{4,0}\ (0|\mathbf{k}_{\frac{1}{4}},\tfrac{1}{2}) &= -3.5789\\
(4\pi/13)^{\frac{1}{2}}S'_{6,0}\ (0|\mathbf{k}_{\frac{1}{4}},\tfrac{1}{2}) &= -0.9895\\
(4\pi/17)^{\frac{1}{2}}S'_{8,0}\ (0|\mathbf{k}_{\frac{1}{4}},\tfrac{1}{2}) &= -2.9329\\
(4\pi/21)^{\frac{1}{2}}S'_{10,0}(0|\mathbf{k}_{\frac{1}{4}},\tfrac{1}{2}) &= -1.0114
\end{aligned}\right\}\quad (9)$$

(the accuracy in the latter four being ± 2 in the last significant figure), we can now, from (8), find $V_{pt}(\mathbf{R})$ for any point $\mathbf{R}(R, \vartheta, \varphi)$. As an illustration we give expressions for (8) for three directions, viz. those to a 1^{st} (direction 1), a 2^{nd} (direction 2) and a 3^{rd} nearest neighbour (direction 3) respectively. We find for direction 1

$$V_{pt}^{(1)}(R) = -1.74756 - 3.5789R^4 - 0.9895R^6 - 2.9329R^8 - 1.0114R^{10} + \\ + O(R^{12}), \quad (10)$$

for direction 2

$$V_{pt}^{(2)}(R) = -1.74756 + 0.89473R^4 + 1.6079R^6 - 1.6498R^8 + 0.03161R^{10} + \\ + O(R^{12}), \quad (11)$$

*) The Υ_l's can be determined by group theoretical methods (cf. Altmann [5]) for $l = 4,6$) but also, more easily, from a comparison of certain terms of the related lattice sums $S'_{l,m}$ (cf. following paper).

and finally for direction 3

$$V_{pt}^{(3)}(R) = -1.74756 + 2.3859R^4 - 1.7591R^6 - 0.86900R^8 + 1.5983R^{10} + \\ + 0(R^{12}). \quad (12)$$

These functions are plotted in fig. 2 for values of R inside the unit cube (cube with edge 1 symmetrically around 0); the calculations have been made with (10), (11) and (12). For R-values outside the unit cube the periodicity of $V_{pt}(\mathbf{R}) + 1/R$ can be used to evaluate the potential. A check on these formulae and on the calculations is provided by the fact that due to its periodicity, $V_{pt}(\mathbf{R}) + 1/R$ must be zero on the boundary of the unit cube.

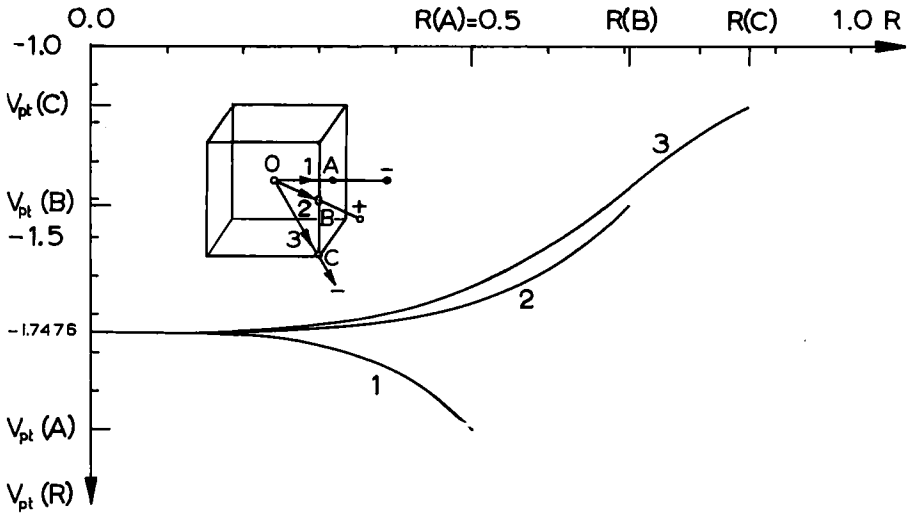

Fig. 2. The potential $V_{pt}(R)$ in a cubic $\pm$ lattice as a function of R, plotted for three different directions. Insert: the unit cube with the three directions.

§ 4. *The electrostatic potential in a lattice of point charges with a neutral basis.* This is a generalization of the case considered in § 2. Let the basis contain γ different point charges q_j ($j = 1,2, \ldots, \gamma$), then the condition for neutrality is $\sum_{j=1}^{\gamma} q_j = 0$. If $\mathbf{r}_\lambda$ gives the position of the cell λ(λ is the cell-index) and $\mathbf{r}_j$ that of the j-th point charge in the basis (j is the base-index), then the lattice vector is $\mathbf{r}_{\lambda,j} = \mathbf{r}_\lambda + \mathbf{r}_j$.

If the origin is placed at the position of one of the point charges q_1, then the electrostatic potential in the lattice, in absence of the point charge at the origin, is given by

$$V(\mathbf{R}) = \sum_\lambda' \sum_j \frac{q_j}{|\mathbf{R} - \mathbf{r}_{\lambda,j}|} + \sum_j' \frac{q_j}{|\mathbf{R} - \mathbf{r}_j|}, \quad (13)$$

the prime on the summations meaning that the terms $\lambda = 0$ and $j = 1$, respectively, are to be omitted. For the same reasons as in § 2, it is advan-

tageous to expand the first term of (13) into spherical harmonics. Then we can write for (13)

$$V(\mathbf{R}) = \Sigma_{l,m} b_{l,m} R^l Y^*_{l,m}(\vartheta, \varphi) + \Sigma'_j q_j/|\mathbf{R} - \mathbf{r}_j|, \tag{14}$$

with $R < r_{\lambda,j}$ $(\lambda \neq 0)$ and where

$$b_{l,m} = (4\pi/2l + 1)\, \Sigma'_\lambda \Sigma_j q_j r_{\lambda,j}^{-l-1} Y_{l,m}(\theta_{\lambda,j}, \phi_{\lambda,j}) \equiv$$
$$\equiv (4\pi/2l + 1)\mathfrak{S}'_{l,m}(0|0, \tfrac{1}{2}). \tag{15}$$

$\mathfrak{S}'$, which is defined by (15), indicates a sum over all the points of the composite lattice (giving different weights q_j to the various points in the

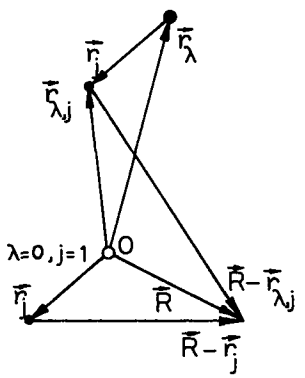

Fig. 3. Lattice vectors in a lattice with basis.

bases) in analogy with S' (cf. (5)) which denotes a lattice sum over a simple Bravais lattice. The sum $\mathfrak{S}'$ can be brought into a rapidly converging form by means of the method developed in I. A straight-forward generalization of that method to the case of a composite lattice sum leads to

$$\mathfrak{S}'_{l,m}(0|0, \tfrac{1}{2}) = \frac{1}{\Gamma(l + \frac{1}{2})}\left[\frac{\Sigma'_\lambda \Sigma_j q_j \Gamma(l + \frac{1}{2}, \pi r^2_{\lambda,j}) Y_{l,m}(\theta_{\lambda,j}, \phi_{\lambda,j})}{r_{\lambda,j}{}^{l+1}} - q_1 \delta_{l,0} - \right.$$
$$- \Sigma'_j \frac{q_j \gamma(l + \tfrac{1}{2}, \pi r_j^2) Y_{l,m}(\theta_j, \phi_j)}{r_j{}^{l+1}} +$$
$$\left. + \frac{i^l \pi^{l-\frac{1}{2}}}{v_a} \Sigma_\lambda G(\mathbf{h}_\lambda) h_\lambda{}^{l-2} \, e^{-\pi h_\lambda^2} \, Y_{l,m}(\vartheta_{\mathbf{h}_\lambda}, \varphi_{\mathbf{h}_\lambda})\right]. \tag{16}$$

$$G(\mathbf{h}) = \Sigma_j q_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) \tag{17}$$

is the *structure factor* of the charge distribution in the basis, $\delta_{l,0}$ is the Kronecker symbol.

For $l = 0$ the sum $\mathfrak{S}'$ is conditionally convergent which means that its value and hence that of $V(\mathbf{R})$, is not uniquely determined but depends on the order of summation. This ambiguity becomes apparent in (16) (for

$l = 0$) because the value of the term $\lambda = 0$ in the last sum depends on the way in which the limit $\mathbf{h} \to 0$ is taken. A similar phenomenon has been discussed recently for the example of the electric field in a dipole lattice [6]).

The origin of the ambiguity in V can be readily found when one expresses the charge distribution in the basis as a series of multipoles and carries out a separate summation of each of these multipoles over the entire lattice, as is done in § 5 and § 6. It is then seen that both the dipole moments ($l=1$) and the quadrupole moments ($l = 2$) of the basis (as defined in § 6) appear in the expression for V as the coefficients of conditionally convergent sums. In a Bravais lattice, however, the dipoles do not contribute to the potential (due to the inversion symmetry), so that the ambiguity in V is essentially due solely to the quadrupole moments. But the latter only give a shape dependent contribution to the potential which is constant throughout the unit cell. Although this term may seem to be of little interest since most physical effects are related to the electric field rather than to the potential, it is precisely this quadrupole contribution to the constant term in the potential which gives rise to the difference in average crystal potential which is found between the Frenkel-Bethe-convention for calculating this average on the one hand, and the Ewald-convention on the other; this difference was discussed recently by Birman [7]).

For cases where one is not interested in this ambiguous but constant contribution to V, the entire difficulty can be resolved just by omitting in (16) the term in the origin of reciprocal space. This procedure, which is equivalent to simply putting $G(0) = 0$ and which is often followed without reference to the above mentioned difficulties, could be argued (though admittedly not in a completely rigorous way) as follows. In the method for the conversion of lattice sums (cf. I) which leads to the expression (16) for $\mathfrak{S}'_{l,m}$, the reciprocal lattice is found as a sum of δ-peaks in reciprocal space, each of which is multiplied by the structure factor $G(\mathbf{h})$ taken in that particular point. Since $G(0) = 0$, no δ-peak will appear in the origin of reciprocal space and the second summation in (16) should therefore be read with a prime. It is for this case that the equivalence of the methods of § 2 and that of § 4 for a two-particle basis, is shown in the appendix.

§ 5. *The electrostatic potential in a lattice with multipoles of equal or alternate sign.* As a preparation for the description of the electrostatic potential in a lattice consisting of a number of arbitrary charge distributions, we will now derive an expression for the potential in a lattice of equal multipoles. These multipoles may all have the same sign, in which case the corresponding inverse power of r ($l + 1$) should be equal or higher than three in order to have convergence, or they may be of alternate sign (valid for arbitrary inverse power of r, cf. § 2).

The potential in a point $\mathbf{R}_\lambda(R_\lambda, \vartheta_\lambda, \varphi_\lambda)$ due to a simple multipole $Q_{l,m}$ (fixed l, m) of order 2^l in the origin may be written as

$$V_{l,m}{}^{(\lambda)}(\mathbf{R}_\lambda) = Q_{l,m} R_\lambda^{-l-1} \, Y^*_{l,m}(\vartheta_\lambda, \varphi_\lambda). \tag{18}$$

The multipole moment $Q_{l,m}$ gives the strength of the pole. The potential in the neighbourhood of a lattice point (where the multipole is thought to be removed) due to all the order multipoles in the lattice is found by summing expressions of the type (18) over the entire lattice

$$V_{l,m}{}^{(\pm)}(\mathbf{R}) = \sum_{\lambda}'((-1)^{\lambda_1+\lambda_2+\lambda_3}) V_{l,m}{}^{(\lambda)}(\mathbf{R}_\lambda). \tag{19}$$

The factor $(-1)^{\lambda_1+\lambda_2+\lambda_3}$ applies for multipoles of alternate sign; for multipoles of equal sign it should be omitted. In order to arrive at a more convenient expression, where $V_{l,m}$ is given in terms of the spherical coordinates of the field point $\mathbf{R}$ (cf. fig. 1), we start out by using the relation

$$\frac{Y^*_{l,m}(\vartheta_\lambda, \varphi_\lambda)}{R_\lambda{}^{l+1}} = \frac{(-1)^{l-\frac{1}{2}m(1\pm1)}}{2\sqrt{\pi}} A_{l,m}\left(\frac{\partial}{\partial X_\lambda} \mp i\frac{\partial}{\partial Y_\lambda}\right)^{|m|}\left(\frac{\partial}{\partial Z_\lambda}\right)^{l-|m|}\left(\frac{1}{R_\lambda}\right),^*) \tag{20}$$

where the upper sign holds for $m \geqslant 0$, the lower sign for $m \leqslant 0$;

$$A_{l,m} = (2l+1/(l+m)!\,(l-m)!)^{\frac{1}{2}}. \tag{21}$$

$X_\lambda, Y_\lambda, Z_\lambda$ are the cartesian components of $\mathbf{R}_\lambda$. Let X, Y and Z be the components of $\mathbf{R}$, then

$$(\partial/\partial X_\lambda)R_\lambda{}^{-1} = (\partial/\partial X)|\mathbf{R} - \mathbf{r}_\lambda|^{-1} \qquad \text{and cyclic.} \tag{22}$$

If we now substitute (22) into (20) and at the same time replace $|\mathbf{R} - \mathbf{r}_\lambda|^{-1}$ by its expansion in terms of spherical harmonics (cf. (2), using μ, ν instead of l, m) we find for (18)

$$V^{(\lambda)}{}_{l,m}(\mathbf{R}) = (-1)^{l-\frac{1}{2}m(1\pm1)}\, 2\sqrt{\pi}\, Q_{l,m}\, A_{l,m} \sum_{\mu,\nu} \frac{Y_{\mu,\nu}(\theta_\lambda,\phi_\lambda)}{(2\mu+1)\, r_\lambda{}^{\mu+1}} \cdot \left(\frac{\partial}{\partial X} \mp i\frac{\partial}{\partial Y}\right)^{|m|}\left(\frac{\partial}{\partial Z}\right)^{l-|m|} R^\mu Y^*{}_{\mu,\nu}(\vartheta, \varphi). \tag{23}$$

A further transformation of (23) is obtained by using the relation

$$\left(\frac{\partial}{\partial X} \mp i\frac{\partial}{\partial Y}\right)^{|m|}\left(\frac{\partial}{\partial Z}\right)^{l-|m|} R^\mu Y^*{}_{\mu,\nu}(\vartheta, \varphi) = = (-1)^{\frac{1}{2}m(1\mp1)}\, B_{l,m;\,\mu,\nu}\, R^{\mu-l}\, Y^*{}_{\mu-l,\nu+m}(\vartheta, \varphi) \tag{24}$$

(upper sign for $m \geqslant 0$, lower sign for $m \leqslant 0$), where

$$B_{l,m;\mu,\nu} = \left(\frac{2\mu+1}{2\mu-2l+1} \cdot \frac{(\mu+\nu)!\,(\mu-\nu)!}{(\mu-l+\nu+m)!\,(\mu-l-\nu-m)!}\right)^{\frac{1}{2}}. \tag{25}$$

Substitution of (24) into (23) gives

$$V_{l,m}{}^{(\lambda)}(\mathbf{R}) = = (-1)^{l-m}\, 2\sqrt{\pi}\, Q_{l,m} A_{l,m} \sum_{\mu,\nu} \frac{Y_{\mu,\nu}(\theta_\lambda, \phi_\lambda)}{(2\mu+1) r_\lambda{}^{\mu+1}} B_{l,m;\mu,\nu}\, R^{\mu-l} Y^*{}_{\mu-l,\nu+m}(\vartheta, \varphi).$$

*) This relation, as well as (24), can be obtained by repeated differentiation of the well-known differentiation formulae for the spherical harmonics. See e.g. Meixner [2]), p. 206.

The μ-summation runs from l up. Further, only such ν's occur for which $|\nu + m| \leqslant \mu - l$. Putting $\mu - l = k$ and $\nu + m = n$, we have $k \geqslant 0$ and $|n| \leqslant k$, hence

$$V_{l,m}^{(\lambda)}(\mathbf{R}) =$$

$$= (-1)^{l-m} 2\sqrt{\pi} Q_{l,m} A_{l,m} \sum_{k,n} \frac{Y_{k+l,n-m}(\theta_\lambda, \phi_\lambda)}{(2k+2l+1) r_\lambda^{k+l+1}} B_{l,m;k+l,n-m} R^k Y^*_{k,n}(\vartheta, \varphi).$$

We can now write for (19)

$$V^{\pm}_{l,m}(\mathbf{R}) = \sum_{k,n} c^{(\pm)}_{l,m;k,n} R^k Y^*_{k,n}(\vartheta, \varphi), \tag{26}$$

where

$$c^{(\pm)}_{l,m;k,n} = F_{l,m;k,n} Q_{l,m} \sum'_\lambda ((-1)^{\lambda_1+\lambda_2+\lambda_3}) r_\lambda^{-k-l-1} Y_{k+l,n-m}(\theta_\lambda, \phi_\lambda) =$$

$$= F_{l,m;k,n} Q_{l,m} S'_{k+l,n-m}(0|^0_{(k_{\frac{1}{2}})}, \tfrac{1}{2}), \tag{27}$$

$$F_{l,m;k,n} = ((-1)^{l-m} 2\sqrt{\pi} A_{l,m} B_{l,m;k+l,n-m})/(2k + 2l + 1). \tag{28}$$

c refers to the case of multipoles of equal sign, the reciprocal space vector $\mathbf{k}$ appearing in the lattice sum S' is then zero. In this case $V_{l,m}$ only exists for $l \geqslant 2$. For $l = 2$ the value of $V_{l,m}(\mathbf{R})$ depends on the order of summation because the sum $S'_{2,-m}$ (appearing in the term $k = 0$) is conditionally convergent. Sums of this type, which for example appear in the expression for the electric field strength in a dipole lattice, were considered in some detail in a separate publication [6]).

$c^{(\pm)}$ refers to the case of multipoles of alternate sign. In that case the reciprocal space vector appearing in S' is $\mathbf{k}_{\frac{1}{2}} = \frac{1}{2}(\mathbf{b}_1 + \mathbf{b}_2 + \mathbf{b}_3)$.

Equation (26) is the desired expansion of $V_{l,m}$ in terms of the spherical coordinates of $\mathbf{R}$.

§ 6. *The electrostatic potential in a lattice containing different types of charge distributions.* Just as in § 2 and § 4, the potential may be expressed in various different ways. First there is the method of direct summation, which is equivalent to the expressions (1) and (7) for the point charge case. If the charge distributions are denoted by $\rho(\mathbf{r})$, then the total potential in the lattice is

$$V(\mathbf{R}) = \sum'_\lambda \int \frac{\rho(\mathbf{r})}{|\mathbf{R} - \mathbf{r}_\lambda - \mathbf{r}|} \, \mathrm{d}_3\mathbf{r}.$$

To obtain better convergence, this expression may be further treated by the method of I, § 5, leading to an expression which, just as the above, is valid everywhere in the lattice. This again is essentially Ewald's method which has been most commonly used so far, e.g. recently by Birman [8]) to evaluate the effect of overlap of the charge distributions on the lattice potential. While having the advantage of being valid for field points which are overlapped by the charge distributions, this method can only be applied relatively easy for

spherically symmetric charge distributions and for selected field points. Moreover, for (crystallographically) different points $\mathbf{R}$, different sums have to be calculated.

A second obvious way to express $V(\mathbf{R})$ would be to adapt the method of § 4 to the case of continuous charge distributions, namely by replacing the summation over the charges in the basis by integrations over the charge distributions. The potential could then again be expressed as an expansion in spherical harmonics, but the coefficients would still be very complicated sums which are not very well suited for numerical computations.

For the problems for which we intend to use this analysis, namely the effect of the finite size of the ions on binding energy and dielectric constant, it seems most profitable to describe the charge distributions in terms of their multipole moments.

Let us consider a lattice containing γ different types of charge distributions (distinguished by the superscripts 1, 2, ..., γ) which occupy γ different sublattices in the lattice.

The potential due to a charge distribution $\rho(r, \theta, \phi)$ in a point outside ρ at the distance $\mathbf{R}_\lambda$ from its center may be written as

$$V_\rho(\mathbf{R}_\lambda) = \sum_{l,m} Q_{l,m} R_\lambda^{-l-1} Y^*_{l,m}(\vartheta_\lambda, \varphi_\lambda), \tag{29}$$

where the multipole moments $Q_{l,m}$ are given by

$$Q_{l,m} = (4\pi/2l + 1) \int \rho(r, \theta, \phi)\, r^l\, Y_{l,m}(\theta, \phi)\, \mathrm{d}_3\mathbf{r}. \tag{30}$$

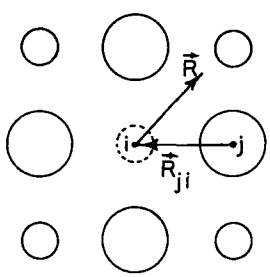

Fig. 4. Lattice consisting of two types of charge distritbutions ($\gamma = 2$).

Let us consider the potential around a lattice point of the i-th sublattice, the charge distribution at the lattice point itself being removed. We have

$$V^{(i)}(\mathbf{R}) = v'_i(\mathbf{R}) + \sum_{j\neq i}^{\gamma} v_j(\mathbf{R}); \tag{31}$$

v'_i is the potential due to the i-th sublattice (central charge distribution removed), v_j that due to the j-th sublattice.

Summing an expression of the type (26) over all the multipoles appearing in the i-th charge distribution, we may write

$$v_i'(\mathbf{R}) = \sum_{k,n} C^{(i)}{}_{k,n} R^k Y^*{}_{k,n}(\vartheta, \varphi), \tag{32}$$

where

$$C^{(i)}{}_{k,n} = \sum_{l,m} F_{l,m;k,n}\, Q^{(i)}{}_{l,m}\, S^{(i)\prime}{}_{k+l,n-m}\,(0|0,\tfrac{1}{2}). \tag{33}$$

$S^{(i)\prime}$ denotes a lattice sum over the i-th sublattice, in which the origin is omitted. In a similar fashion we can write for $v_j (j \neq i)$

$$v_j(\mathbf{R}) = \sum_{k,n} C^{(j)}{}_{k,n}\, R^k\, Y^*{}_{k,n}(\vartheta, \varphi), \tag{34}$$

but now

$$C^{(j)}{}_{k,n} = \sum_{l,m} F_{l,m;k,n}\, Q^{(j)}{}_{l,m}\, S^{(j)}{}_{k+l,m-n}\,(\mathbf{R}_{ji}|0,\tfrac{1}{2}). \tag{35}$$

In $S^{(j)}$ the origin of the j-th sublattice is included in the summation. The complete expression for $V^{(i)}(\mathbf{R})$ is

$$V^{(i)}(\mathbf{R}) = \sum_{k,n} A^{(i)}{}_{k,n}\, R^k\, Y^*{}_{k,n}(\vartheta, \varphi) \qquad (i = 1, 2, \ldots, \gamma) \tag{36}$$

where

$$A^{(i)}{}_{k,n} = \sum_{j=1}^{\gamma} C^{(j)}_{k,n} = \sum_{l,m} F_{l,m;k,n} \{Q^{(i)}{}_{l,m}\, S^{(i)\prime}{}_{k+l,n-m}(0|0,\tfrac{1}{2}) + \\ + \sum_1^{\gamma}{}_{j\neq i}\, Q^{(j)}{}_{l,m}\, S^{(j)}{}_{k+l,n-m}\,(\mathbf{R}_{ji}|0,\tfrac{1}{2})\}. \tag{37}$$

Now, clearly, (37) cannot be used for all values of k and l. Consider for example $A_{0,0}$. The first term ($l = 0$) in this sum, giving the potential in the center due to the monopoles (net charges) at the other lattice points, does not exist since the sums $S'_{0,0}(0|0,\frac{1}{2})$ and $S_{0,0}(\mathbf{R}|0,\frac{1}{2})$ are divergent. Apparently the division of the lattice into sublattices is not appropriate in this situation. However, the potential due to the net charges can be treated by the method of § 2 or § 4. The term $l = 1$ in $A_{0,0}$ gives the contribution of the dipoles at the other lattice points to the potential in the center. If we assume each lattice point to be a center of inversion then all the sums $S_{l,m}$ vanish for odd l (cf. I, § 6); this dipole contribution, therefore, vanishes. The term $l = 2$ in $A_{0,0}$ gives rise to the sums $S'_{2,m}(0|0,\frac{1}{2})$ and $S_{2,m}(\mathbf{R}|0,\frac{1}{2})$ which are conditionally convergent. Their values depend on the shape of the crystal that is being considered (cf. ref. 6). In $A_{1,n}$ the term $l = 0$ vanishes while the terms $l = 1$ give rise to conditionally convergent sums. Finally in $A_{2,n}$ only $l = 0$ gives rise to conditionally convergent sums. All other terms contain absolutely convergent sums.

We can easily modify (37) to include the potential due to the net charges, viz. by simply adding (15) to (37) and by carrying out the summation in (37) over values of l larger than zero,

$$A^{(i)}{}_{k,n} = (4\pi/2k+1)\mathfrak{S}'_{k,n}\,(0|0,\tfrac{1}{2}) + \\ + \sum_{l>0,m} F_{l,m;k,n} \{Q^{(i)}{}_{l,m}\, S^{(i)\prime}{}_{k+l,n-m}(0|0,\tfrac{1}{2}) + \\ + \sum_1^{\gamma}{}_{j\neq i}\, Q^{(j)}{}_{l,m}\, S^{(j)}{}_{k+l,n-m}\,(\mathbf{R}_{ji}|0,\tfrac{1}{2})\}. \tag{38}$$

The equations (36) and (38) give a general and complete description of the electrostatic potential around the lattice points of a composite lattice which

are centers of inversion and for field points which are not overlapped by any of the charge distributions. If overlap occurs it will usually only be of importance between nearest neighbours so that these would have to be excluded from the expansion in (36), while their potential should be added as an extra term. If there would exist considerable overlap of the charge distributions then the crystal should have to be considered as one whole and the introduction of polarizabilities (c.f. following paper) would no longer be possible. But for ionic crystals the assumption of small or no overlap seems to be quite reasonable and will be fulfilled the better according as the ionic character of the binding of the crystal is the stronger.

In actual cases some or all of the sublattices of the crystal will have the same structure. Well-known examples (for $\gamma = 2$) are the NaCl- and CsCl-crystals which have simple cubic (*sc*) and body centered cubic (*bcc*) structures respectively. In the first case both sublattices are face centered cubic (*fcc*), in the second case they have *sc* structure. Crystals with the perovskite structure such as $BaTiO_3$ contain 5 sublattices, all *sc* and with the same lattice constant.

Appendix

Proof of equivalence of the methods of § 2 *and* § 4. The case of the lattice with alternately positive and negative point charges at the lattice points, which was considered in § 2, can also be treated by the method of § 4, e.g. if one considers a base containing two particles. We will here prove the equivalence of both methods for this example.

In I ((38), (44)), we found for the lattice sums occurring in the potential-field expansion (4), (5) of § 2

$$S'_{l,m}(0|\mathbf{k}_{\frac{1}{2}}, \tfrac{1}{2}) =$$
$$= (\Gamma(l+\tfrac{1}{2}))^{-1}\,[\textstyle\sum_\mu{}'(-1)^{\mu_1+\mu_2+\mu_3}\Gamma(l+\tfrac{1}{2}, \pi r_\mu{}^2) r_\mu{}^{-l-1} Y_{l,m}(\theta_\mu,\phi_\mu) - \delta_{l,0} +$$
$$+ i^l \pi^{l-\frac{1}{2}}\, v_\alpha{}^{-1} \textstyle\sum_\mu |\mathbf{h}_\mu - \mathbf{k}_{\frac{1}{2}}|^{l-2}\, \mathrm{e}^{-\pi|h_\mu - k_{\frac{1}{2}}|^2}\, Y_{l,m}(\vartheta_{h_\mu - k_{\frac{1}{2}}}, \varphi_{h_\mu - k_{\frac{1}{2}}})]. \qquad \text{(A.1)}$$

In order to compare this with the corresponding sum obtained by the method of § 4, we have to absorb the second term in the right hand side of (13) into the first one. The sum to be compared to (A.1) then is

$$(\Gamma(l+\tfrac{1}{2}))^{-1}[\textstyle\sum_\lambda \sum_j{}' q_j \Gamma(l+\tfrac{1}{2}, \pi r^2_{\lambda,j})\, r_{\lambda,j}{}^{-l-1} Y_{l,m}(\theta_{\lambda,j}, \phi_{\lambda,j}) - q_1 \delta_{l,0} +$$
$$+ i^l \pi^{l-\frac{1}{2}} v_a{}^{-1} \textstyle\sum_\lambda{}' G(\mathbf{h}_\lambda) h_\lambda{}^{l-2}\, \mathrm{e}^{-\pi h_\lambda{}^2}\, Y_{l,m}(\vartheta_{h_\lambda}, \varphi_{h_\lambda})], \qquad \text{(A.2)}$$

where the prime on the first summation indicates that the term $\lambda = 0, j = 1$ is to be omitted. In the second summation we have omitted the term in the origin (cf. § 4). Now (A. 1) should be equal to (A.2) if in the latter case we have two unit charges (of opposite sign) per unit cell, one in the origin and the other in the center of the cell. In (A.1) we have indicated the index by

μ and the volume of the unit cell by v_α because the Bravais lattices are different from those in (A.2).

Comparing (A.1) and (A.2) we see that the first two terms in both expressions are equivalent; they both are sums over the same (composite) lattice, but written in a different form. It thus remains to be shown that the third terms in (A.1) and (A.2) are equivalent, i.e. that

$$v_\alpha^{-1} \sum_\mu \ldots = v_a^{-1} \sum_\lambda' \ldots$$

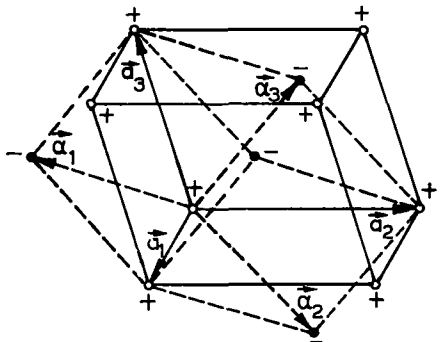

Fig. 5. Two possible unit cells in a lattice of pos. and neg. point charges.

Let $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$ define the unit cell in (A.1) and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ that in (A.2), then it is seen that (cf. fig. 5)

$$\left.\begin{aligned} \mathbf{a}_1 &= \boldsymbol{\alpha}_1 + \boldsymbol{\alpha}_2 \\ \mathbf{a}_2 &= \boldsymbol{\alpha}_2 + \boldsymbol{\alpha}_3 \\ \mathbf{a}_3 &= \boldsymbol{\alpha}_1 + \boldsymbol{\alpha}_3 \end{aligned}\right\}, \tag{A.3}$$

from which follows

$$v_a = \mathbf{a}_1 \cdot (\mathbf{a}_2 \wedge \mathbf{a}_3) = 2v_\alpha. \tag{A.4}$$

Let us next consider the effect of $G(\mathbf{h}_\lambda)$ in (A.2). There are two particles in the basis at the positions $\mathbf{r}_1 = 0$ and $\mathbf{r}_2 = \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$. Since $q_1 = +1$, $q_2 = -1$ we have

$$G(\mathbf{h}_\lambda) = 1 - \exp\{2\pi i \mathbf{h}_\lambda \cdot \tfrac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)\} = 1 - (-1)^{\lambda_1+\lambda_2+\lambda_3},$$

hence

$$G(\mathbf{h}_\lambda) = \begin{cases} 2 \text{ when } \lambda_1 + \lambda_2 + \lambda_3 \text{ is odd} \\ 0 \text{ when } \lambda_1 + \lambda_2 + \lambda_3 \text{ is even.} \end{cases} \tag{A.5}$$

The value 2 of $G(\mathbf{h}_\lambda)$ is compensated by the 2 in (A.4) which enters in the denominator.

Finally we have to show that $\sum_\mu$ is a summation over the same points in reciprocal space (when taken with respect to the point $\mathbf{k}_i$) as $\sum_\lambda'$ (when taken with respect to the origin).

If $\boldsymbol{\beta}_1$, $\boldsymbol{\beta}_2$, $\boldsymbol{\beta}_3$ determine the reciprocal lattice of $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$ and $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ that of $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$, then it is easily verified that

$$\mathbf{h}_\lambda = \lambda_1\mathbf{b}_1 + \lambda_2\mathbf{b}_2 + \lambda_3\mathbf{b}_3 = \tfrac{1}{2}(\lambda_1 - \lambda_2 + \lambda_3)\boldsymbol{\beta}_1 + \tfrac{1}{2}(\lambda_1 + \lambda_2 - \lambda_3)\boldsymbol{\beta}_2 + \\ + \tfrac{1}{2}(-\lambda_1 + \lambda_2 + \lambda_3)\boldsymbol{\beta}_3. \qquad \text{(A.6)}$$

This vector, taken for all values of λ_1, λ_2, λ_3 such that $\lambda_1 + \lambda_2 + \lambda_3$ is odd (i.e., $\lambda_1 = \lambda_2 = \lambda_3 = 0$ excluded), should indicate the same points as

$$\mathbf{h}_\mu - \mathbf{k}_i = (\mu_1 - \tfrac{1}{2})\boldsymbol{\beta}_1 + (\mu_2 - \tfrac{1}{2})\boldsymbol{\beta}_2 + (\mu_3 - \tfrac{1}{2})\boldsymbol{\beta}_3, \qquad \text{(A.7)}$$

when taken for all values of μ_1, μ_2, μ_3 (0 included).

Equating (A.7) to (A.6) gives

$$\left.\begin{aligned} 2\mu_1 - 1 &= \lambda_1 - \lambda_2 + \lambda_3 \\ 2\mu_2 - 1 &= \lambda_1 + \lambda_2 - \lambda_3 \\ 2\mu_3 - 1 &= -\lambda_1 + \lambda_2 + \lambda_3 \end{aligned}\right\}. \qquad \text{(A.8)}$$

It is readily seen that with each set of (pos., neg.) integers for μ_1, μ_2, μ_3 there corresponds just one set of integers λ_1, λ_2, λ_3, of which the sum is odd. The inverse is also true. This completes the proof of the equivalence of (A.1) and (A.2) for the special case under consideration.

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REFERENCES

1) Nijboer, B. R. A. and De Wette, F. W. Physica **23** (1957) 309.
2) Meixner, J., *Hdb. Physik*, Vol. **1**, Springer, Berlin 1956.
3) Kanamori, J., Moriya, T., Motizuki, K. and Nagamiya, T., J. Phys. Soc. Jap. **10** (1955) 93.
4) cf. Born, M. and Göppert-Mayer, M., *Hdb. Physik*, Vol. **24**, part 2, Springer, Berlin 1933, p. 710.
5) Altmann, S. L. Proc. Camb. Phil. Soc. **53** (1957) 343.
6) Nijboer, B. R. A. and De Wette, F. W., Physica **24** (1958) 422.
7) Birman, J. L., Phys. Rev. **98** (1955) 1863, J. Phys. and Chem. Solids **6** (1958) 65.
8) Birman, J. L., Phys. Rev. **97** (1955) 897.