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Note

Calculation of the Coulomb Coefficients and the Madelung Constant in a Face-Centered Cubic Crystal with Additional Charges Located along the (100) Direction

1. Introduction

It is well known that lattice sums are not absolutely convergent. The problem of summing this type of series arose from early calculations in lattice dynamics and was first solved by Ewald [1]. Since this pioneering work, many other papers on the same subject have appeared. They suggest alternative solutions using more sophisticated approaches such as the quite recent papers by Glasser [2].

In the present note we illustrate a practical method for calculating these sums in a fairly complicated crystal structure. This consists of a face-centered cubic crystal (NaCl type) with additional charges located the (100) directions. These charges, to be called overlap charges, arise from the exchange and overlap effects in the case of partially covalent bond, such as in silver halides [3].

The lattice sums considered here are of three types: (1) positive-ion–overlap-charges interactions; (2) negative-ion–overlap-charges interactions; and (3) overlap-charges–overlap-charges interactions. The ion–ion interactions are not included because the corresponding coefficients are well known [4].

Since these coefficients depend on the location of the overlap charges, we have indicated by G the distance of an overlap charge from the closest positive ion divided by the interionic distance r_0, G ranges from 0.1 to 0.5.

Since each ion is surrounded by six overlap charges which do not occupy equivalent positions in the primitive cell, there are in principle 6 interactions of the group (1) or (2) and 36 of the group (3). The coefficients calculated below include all these interactions and the final results given in Fig. 1 were divided by the number of interactions which contribute to the coefficient under consideration. The same procedure was also adopted for the calculation of the Madelung constant coefficients.

2. Theoretical Background

The method of Ewald was used in order to obtain quickly convergent lattice sums. This method is also known as the theta function transformation [4, 5] and allows us to covert sums over the lattice points l into sums over the reciprocal lattice h. Since this method is well known we only recall results for the Coulomb coefficients and the Madelung constant.

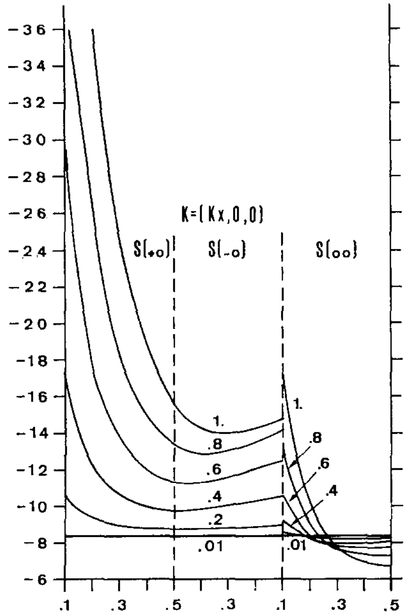

FIG. 1. Plot of the coefficients $S_{xx}(kk')$ in units $1/v_a$ for $\mathbf{k}$ along [1, 0, 0]. Since G is measured from the closest positive ion, for $S_{xx}(_{+0})$ the abscissa corresponds to the actual distance (in units of r_0), whereas for $S_{xx}(_{-0})$ the distance from the closest negative ion is $(1 - G)$ and for $S_{xx}(_{00})$ the shortest distance between two overlap charges is $\sqrt{2}G$.

(a) *Coulomb Coefficients*

We are interested in a sum over the lattice points r_l:

$$S_{xy}(\mathbf{k}, \mathbf{r}) = \frac{\partial^2}{\partial_x \partial_y} \left\{ \sum_l \frac{1}{|\mathbf{r}_l - \mathbf{r}|} e^{2\pi i \mathbf{k}\cdot(\mathbf{r}_l - \mathbf{r})} \right\} e^{2\pi i \mathbf{k}\cdot\mathbf{r}}. \tag{1}$$

By means of Ewald's method this sum can be written [4] as

$$\begin{aligned} S_{xy}(\mathbf{k}, kk') = {} & \frac{4\pi}{v_a} \sum_h \left\{ \frac{(h_x + k_x)(h_y + k_y)}{(\mathbf{h} + \mathbf{k})^2} e^{-(\mathbf{h}+\mathbf{k})^2/4} \right\} \cos \pi(\mathbf{h} \cdot \mathbf{r}_{kk'}) \\ & + 2 \sum_l \left\{ \left[\left(4\pi^2 + \frac{6}{l^2}\right) \frac{l_x l_y}{l^2} - \frac{2}{l^2}\, \delta_{xy} \right] \pi^{1/2} e^{-\pi^2 l^2} \right. \\ & \left. + \left[3\, \frac{l_x l_y}{l^2} - \delta_{xy} \right] \frac{\psi(\pi l)}{l^3} \right\} \cos \pi(\mathbf{k} \cdot \mathbf{l}), \end{aligned} \tag{2}$$

where v_a is the volume of the primitive cell and k labels one of the two sublattices. The distances from the origin are written in the form $l = (l_x, l_y, l_z)\, r_0$ and the reciprocal lattice sites as $h = (h_x, h_y, h_z)/2r_0$ and $\psi(\pi l)$ is the complementary error function.

(b) *Madelung Constant*

For the present lattice we define the Madelung constant as follows:

$$\alpha = \frac{1}{2} \sum_k e_k \sum_{l'k'}{}' e_{k'} \frac{r_0}{r\begin{pmatrix} l' \\ kk' \end{pmatrix}}, \tag{3}$$

where e_k, $e_{k'}$ indicate the types of charges (measured in units of e) and r is the distance of the charge being considered from the origin (at a lattice site). Using the procedure previously described, (3) becomes

$$\alpha = \frac{1}{2} \sum_k e_k \sum_{k'} e_{k'} \left[\sum_{l'} \frac{\psi\left(\pi d \begin{pmatrix} l' \\ kk' \end{pmatrix}\right)}{d\begin{pmatrix} l' \\ kk' \end{pmatrix}} + \frac{2}{\pi} \sum_h \frac{e^{-h^2/4} \cos \pi(\mathbf{h} \cdot \mathbf{d}_{kk'})}{h^2} \right] - \pi^{1/2} \sum_k e_k{}^2$$

$$= \frac{1}{2} \sum_k e_k \sum_{k'} e_{k'} (R_{kk'} - 2\pi^{1/2} \delta_{kk'}). \tag{4}$$

In the present case very few terms constribute to the sums over l, but about 30 terms give an appreciable constribution to those over h. Different procedures were used in calculating these two types of sums. In fact since only one or two indices of the set (l_x, l_y, l_z) are different from zero a simplified calculation technique is sufficient for these sums but not for the sums over h because in this case all indices (h_x, h_y, h_z) may be different from zero.

3. Calculation of the Sums Over l

The set of lattice sites which give a relevant contribution to these sums is given in Table I.

We have adopted the procedure of constructing matrices of the order $3 \times N$ where N can be 3, 6, 12 depending on the number of charges which is either 6 or 12 or 24. In these matrices each row corresponds to one of the allowed permutations (for example for the matrix $b1$ this could be 1, 0, $1 - G$) and the number of rows is one half of the total number of permutations. This is a consequence of the fact that sets l and $-l$ give the same contribution.

TABLE I

Terms in l Contributing to (2) and (4). For the Definition of G See Text. The Matrices of Type a, b, c Are, Respectively, of the Order 3×3, 3×12, and 3×6.

Interactions	Distances	Typical term	Number of charges	Type of matrix
Positive-ion–overlap-charge	G	$G\,0\,0$	6	$a1$
Positive-ion–overlap-charge	$[2(1-G)+G^2]^{1/2}$	$1-G\,1\,0$	24	$b1$
Positive-ion–overlap-charge	$2-G$	$2-G\,0\,0$	6	$a2$
Negative-ion–overlap-charge	$1-G$	$1-G\,0\,0$	6	$a3$
Negative-ion–overlap-charge	$[1+G^2]^{1/2}$	$G\,1\,0$	24	$b2$
Negative-ion–overlap-charge	$1+G$	$1+G\,0\,0$	6	$a4$
Overlap-charge–overlap-charge	$\sqrt{2}G$	$G\,G\,0$	12	$c1$
Overlap-charge–overlap-charge	$\sqrt{2}(1-G)$	$1-G\;0\;1-G$	12	$c2$
Overlap-charge–overlap-charge	$2-G$	$2-G\,0\,0$	6	$a5$
Overlap-charge–overlap-charge	$2-2G$	$2-2G\,0\,0$	6	$a6$
Overlap-charge–overlap-charge	$[4G(G-1)+2]^{1/2}$	$1-2G\,1\,0$	24	$b3$

By means of these matrices the calculation of the terms l_x, l_y in (2) boils down to the multiplication of two elements in the same row of the appropriate matrix, and this can be carried out cyclically, whereas the δ_{xy} are similarly evaluated from the multiplication of the elements of a diagonal matrix.

The contribution of the term (0, 0, 0) is, as is well known [4] is $\frac{8}{3}\pi^{5/2}\delta_{xy}$ and has to be added to the terms in the sum (2), whereas in (4) it has been included.

TABLE II

Set of Coefficients of Type h, Related Number of Permutations and Values of L and M Used to Calculate Them.

h_x h_y h_z	permutations	L	M
0 0 0	1	1	1
h_1 0 0	6	3	2
h_1 h_1 0	12	3	4
h_1 h_2 0	24	6	4
h_1 h_1 h_1	8	1	8
h_1 h_1 h_2	24	3	8
h_1 h_2 h_3	48	6	8

4. Calculation of the Sums Over h

For the calculation of these quantities we have adopted the procedure of carrying out the permutations of the three indiced h_x, h_y, h_z including the negative values. In Table II we give the types of sets that appear in these sums, the number of permutations and the quantities L and M required to carry out the permutations. These were carried out using a computer program (described in the appendix) which includes two loops. In the inner one (that over L) the computer permuted the indices or exchanged them. In the outer one (over M) all indices or part of them were changed in sign according to the value of M in order to obtain a complete set of permutations, including the negative values.

5. Results and Conclusions

In Fig. 1 we plot the Coulomb coefficients (2) for the three types of interactions discussed in Section 1, for **k** along [1 0 0]. The coefficient plotted is S_{xx}, in fact the remaining coefficients satisfy the following relations:

$$2S_{yy} = 2S_{zz} = -S_{xx}, \qquad S_{xy} = S_{xz} = S_{yz} = 0.$$

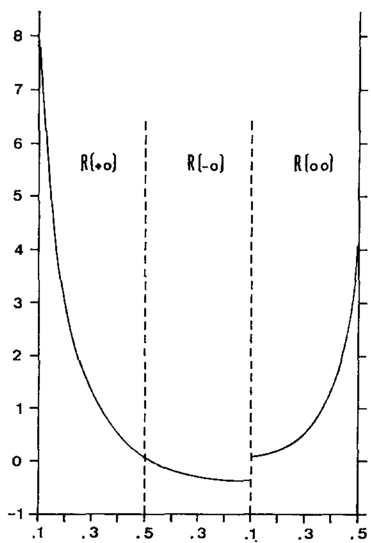

Fig. 2. Plot of the coefficients $R_{(+0)}$, $R_{(-0)}$, and $R_{(00)}$ vs G as in Fig. 1.

The dependence of the results on G when $\mathbf{k}$ assumes values close to π/a is to be expected. In fact for short wavelengths the trigonometric factors which appear in the lattice sums (2) vary rapidly with G. The behavior for $\mathbf{k} \to 0$ is also expected. In fact for small values of $\mathbf{k}$, the coefficients (2) depend only on its direction. Consequently when the overlap charges are displaced (which equivals to changing k') the results are not affected.

In Fig. 2 we plot the coefficients R_{kk} of the Madelung constant (4). There are five such coefficients: (a) ion–ion (of the same type); (b) ion–ion (of different types); (c) positive-ion–overlap charges; (d) negative-ion–overlap charges; and (e) overlap-charges–overlap-charges. The terms (a) and (b) are independent of G, whereas the others depend on G and in the figure are indicated with $R(+\circ)$ $R(-\circ)$ and $R(\circ\,\circ)$ These coefficients increase as the inverse power of the distance when this tends to zero. This behavior which is essentially that of the Coulomb potential arises from the predominant contribution of the sums over l.

Appendix

In this Appendix we give a schematic procedure for the calculation of the sums over h. Each set of indices h_x, h_y, h_z, must have the order given in Table II. For instance the set 4, 0, 2 must be presented as 4, 2, 0, or 2, 4, 0.

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. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
  INTEGER HX, HY, HZ
  READ HX, HY, HZ, L, M
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
  NX=HX, NY=HY, NZ=HZ
  D0 10 M1 = 1, M
  D0 3 L1 = 1, L
  IF (4-L1) 2, 1, 2
1 HX = HY, HY = HX
2 HX = HY, HY = HZ, HZ = HX
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
C COMPUTES THE SUMS USING HX, HY, HZ
. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
3 CONTINUE
  A = M1
  IF (4-M1) 5, 4, 6
4 NZ = -NZ
5 A = M1-4
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  6 A = A/2. 0
    IA = A * 100. 01
    IF(IA-100) 7, 8, 6
  7 NX = -NX, NY = -NY, NZ = -NZ
    GO TO 9
  8 NY = -NY; NZ = -NZ
  9 HX = NX, HY = NY, HZ = NZ
 10 CONTINUE
    . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
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