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Concerning the Work of Polarization In Ionic Crystals of the NaCl Type. I. Polarization around a Single Charge in the Rigid Lattice*

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Previous work is reviewed, and the Mott-Littleton method of treating the rigid lattice case is extended with some modification to higher order approximations. Numerical results are given for their hypothetical monatomic crystal and for NaCl.

QUANTITATIVE calculations of the polarization work which occurs in ionic crystals on removing one or more charges are of great importance in theories of electrolytic conductivity,[1-3] absorption spectra,[4,5] color centers,[6] and electron emission.[4,7] The cases which have been previously considered are (a) the removal of a single charge, treated by Jost,[1] Jost, and Nehlep,[1] and Mott and Littleton;[3] and (b) the removal of two adjacent charges, treated by Klemm[5] and Born.[8] It is the purpose of the present series of papers to review and to extend this work.

FORMULATION OF THE PROBLEM FOR REMOVAL OF A SINGLE CHARGE

If a charge $-e$ disappears at a lattice point, an effective charge $+e$ will tend to polarize the surrounding medium. It is known from Maxwell's equations that when a charge is placed in a dielectric medium, the electrostatic energy,

$$U = (1/8\pi) \int \int \int (\mathbf{E} \cdot \mathbf{D}) dv, \quad (1)$$

is changed by an amount

$$W = \tfrac{1}{2} e\varphi, \quad (2)$$

where φ is the potential field at the charge e (to be taken as origin) due to the polarized medium and W is the polarization work. If the medium is considered to consist of discrete ions, each with a polarizability α and a distance r from the origin,

$$W = -\frac{1}{2} e \sum_i \varphi_i = -\frac{1}{2} e \sum_i \frac{\mu_i}{r_i^2} = -\frac{1}{2} e \sum_i \alpha_i \frac{F_i}{r_i^2}. \quad (3)$$

Here F_i is the component directed along r_i of the total electric field on the ith ion due to the polarizing charge and to the dipoles on all other ions,** and μ_i is the corresponding dipole moment. Only this radial component of μ_i contributes to φ_i and W.

$$\mu_i = \alpha_i F_i = \alpha_i \left[\frac{e}{r_i^2} + \mathbf{F}_d \cdot \frac{\mathbf{r}_i}{r_i} \right]; \quad \mathbf{F}_d = \sum_j{}' \nabla_i \varphi_j,$$

where φ_j is the potential field of the jth ion dipole on the ith ion, and the prime denotes the omission of the origin and the case $i = j$.

$$\varphi_j = -\mathbf{\mu}_j \cdot \nabla_i \frac{1}{|\mathbf{r}'|}; \quad \mathbf{r}' = \mathbf{r}_i - \mathbf{r}_j.$$

Finally,

$$\mu_i = \alpha_i \left[\frac{e}{r_i^2} - \sum_j{}' \nabla_i \left(\mathbf{\mu}_j \cdot \nabla_i \frac{1}{|\mathbf{r}'|} \right) \cdot \frac{\mathbf{r}_i}{r_i} \right]. \quad (4)$$

This is an exact formulation of the problem. However, Eqs. (3) and (4) lead to an infinite set of equations with an infinite number of unknowns, and attempts to obtain exact solutions

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[1] W. Jost, J. Chem. Phys. **1**, 466 (1933); W. Jost and G. Nehlep, Zeits. f. physik. Chemie **B32**, 1 (1936).
[2] W. Schottky, Zeits. f. physik. Chemie **B29**, 335 (1935).
[3] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), Ch. II.
[4] See reference 3, Chapters III and IV.
[5] W. Klemm, Zeits. f. Physik **82**, 529 (1933).
[6] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).
[7] D. A. Wright, Proc. Phys. Soc. **60**, 13 (1948).
[8] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, Teddington, 1935), p. 241.

** The polarization work is sometimes calculated from the expression:
$$W = 1/2 \sum \alpha_i F_i^2.$$
This expression disagrees with Eq. (3) except for the special case: $F_i = e/r_i^2$, which corresponds to neglecting the dipole-dipole interaction.

TABLE I. System of four, seven, and ten simultaneous equations.

$1.00000 = \left(\frac{1}{\beta_1}+2.3713\right)m_1 + 4.5749\,m_2 + 1.2879\,m_3 - 1.4966\,m_4 - 0.22801\,m_5 + 0.31057\,m_6 + 0.085827\,m_7 + 0.068323\,m_8 - 0.15349\,m_9 - 0.043242\,m_{10}$

$0.50000 = 2.2874\,m_1 + \left(\frac{1}{\beta_2}+2.70745\right)m_2 + 2.2993\,m_3 + 0.80873\,m_4 + 0.20265\,m_5 - 0.45988\,m_6 + 0.34349\,m_7 + 0.017680\,m_8 + 0.12157\,m_9 + 0.060969\,m_{10}$

$0.33333 = 0.96593\,m_1 + 3.4499\,m_2 + \left(\frac{1}{\beta_1}+0.76908\right)m_3 + 0.81341\,m_4 + 2.8894\,m_5 + 0.24095\,m_6 + 0.28823\,m_7 + 0.62092\,m_8 + 0.47658\,m_9 + 0.17898\,m_{10}$

$0.25000 = -1.4966\,m_1 + 1.6175\,m_2 + 1.0845\,m_3 + \left(\frac{1}{\beta_2}+0.29642\right)m_4 + 4.7253\,m_5 + 1.8903\,m_6 + 0.57186\,m_7 - 0.98202\,m_8 - 0.85640\,m_9 - 0.030186\,m_{10}$

$0.20000 = -0.057252\,m_1 + 0.10132\,m_2 + 0.89047\,m_3 + 1.1813\,m_4 + \left(\frac{1}{\beta_1}+2.2211\right)m_5 + 3.2005\,m_6 + 0.44497\,m_7 + 1.1560\,m_8 + 0.88219\,m_9 + 0.035975\,m_{10}$

$0.16667 = 0.077641\,m_1 + 0.22994\,m_2 + 0.080318\,m_3 + 0.54486\,m_4 + 3.2005\,m_5 + \left(\frac{1}{\beta_2}+1.7539\right)m_6 + 0.92089\,m_7 + 1.3701\,m_8 + 0.88966\,m_9 + 0.57982\,m_{10}$

$0.12500 = -0.042914\,m_1 + 0.34349\,m_2 + 0.19215\,m_3 + 0.28593\,m_4 + 0.88994\,m_5 + 1.8418\,m_6 + \left(\frac{1}{\beta_1}-0.33343\right)m_7 + 2.8977\,m_8 + 1.2733\,m_9 + 1.0183\,m_{10}$

$0.11111 = -0.030800\,m_1 + 0.071296\,m_2 + 0.010541\,m_3 + 0.82244\,m_4 + 0.90353\,m_5 + 1.1299\,m_6 + 0.92606\,m_7 + \left(\frac{1}{\beta_2}+1.2606\right)m_8 + 2.6658\,m_9 + 1.9870\,m_{10}$

$0.10000 = -0.040085\,m_1 + 0.060785\,m_2 + 0.15586\,m_3 + 0.13653\,m_4 + 0.88219\,m_5 + 0.88717\,m_6 + 0.63065\,m_7 + 2.0749\,m_8 + \left(\frac{1}{\beta_1}+1.2257\right)m_9 + 2.4500\,m_{10}$

$0.09091 = -0.010810\,m_1 + 0.030485\,m_2 + 0.059660\,m_3 + 0.0075464\,m_4 + 0.060325\,m_5 + 0.58065\,m_6 + 0.52108\,m_7 + 1.5982\,m_8 + 2.4500\,m_9 + \left(\frac{1}{\beta_2}+0.67456\right)m_{10}$

$\beta_i = \alpha_i/a^3$

have been unsuccessful. All solutions heretofore obtained represent approximations of various orders.

APPROXIMATE SOLUTIONS FOR THE RIGID LATTICE

One of the simplest approximations that can be made is to neglect the dipole-dipole interaction, as has been done by Landshoff in a paper dealing mainly with another problem.[9] This leads to

$$W = e^2/2\sum\alpha_i/r_i^4, \tag{5}$$

where the summation is of the type evaluated by Jones and Ingham.[10] The polarization work calculated in this manner is certainly too high.

The method of Jost[1] (applied to a rigid lattice) is to consider the hole produced by the removal of an ion from the crystal as a spherical cavity of radius R in a continuous medium of optical dielectric constant κ_0. The polarization work is then given by

$$W = e^2(1-1/\kappa_0)/2R. \tag{6}$$

This method includes the dipole-dipole interactions by way of the dielectric constant concept, avoids the structure sensitive lattice summations, and has the advantage of extreme simplicity. The great disadvantage, however, is the uncertainty in the value to be chosen for R.

Jost and Nehlep[1] have improved somewhat this earlier work by considering the first shell of six ions surrounding the origin in the manner of Eq. (5), and the rest of the crystal in the manner of Eq. (6).

The most nearly exact solution of the problem yet presented is that of Mott and Littleton,[3] which represents a series of approximations of varying order up to the fourth. In their zero-order approximation, in order to include dipole-dipole interactions, the concept of a dielectric constant is employed in calculating the dipole moment on each of the ions, but the crystal is not treated as a continuum. Instead, the total polarization is considered as constituted of an array of induced point dipoles at lattice sites.

$$P = (\mu_1+\mu_2)/2a^3, \tag{7}$$

[9] R. Landshoff, Phys. Rev. 55, 631 (1939).
[10] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. London (A) 107, 636 (1925).

where:

$$P = \text{polarization},$$
$$a = \text{interionic distance},$$
$$2a^3 = \text{volume/ion pair},$$

which leads to

$$\mu_1 = \frac{M_1 a^3 e}{r^2}, \qquad (8)$$

where:

$$M_1 = \frac{2\alpha_1}{\alpha_1 + \alpha_2}\frac{1}{4\pi}\left(1 - \frac{1}{\kappa_0}\right)$$

with similar expressions for μ_2 and M_2. It has been tacitly assumed in the derivation of Eq. (8) that the field F_i at any point is independent of the type of ion at i.

The potential at the origin due to all the induced dipoles is

$$\varphi = ea^3\left[M_1\sum_1\frac{1}{r^4} + M_2\sum_2\frac{1}{r^4}\right]; \qquad (9)$$

the indicated summations are again those evaluated by Jones and Ingham.[10] It will be noted that the polarization work, $\frac{1}{2}e\varphi$, is identical with Eq. (5) if α_i is replaced by $M_i a^3$. The zero-order approximation, Eq. (9), avoids the uncertainty in R inherent in the Jost treatment, but it cannot be stated at this stage that it necessarily yields more exact answers than the latter.

In their higher order approximations, Mott and Littleton consider the first few shells surrounding the origin in a more nearly exact way while continuing to consider the rest of the medium in the manner of the zero-order approximation. In their first-order approximation, for example, the first shell of six ions is considered in detail. The dipole moment, μ_1, on each of these ions is determined as the resultant of three electric fields:

(a) the field resulting from the polarizing charge,
(b) the dipole field of the other five ions in the first shell,
(c) the field resulting from the dipoles on all the ions outside the first shell, the moments of which are given by Eq. (8).

In their second-, third-, and fourth-order approximations, Mott and Littleton repeat this process for the first two, first three, and first four shells of ions, respectively. On comparing the final numerical results for the potential field,

TABLE II. Values of μ and μr^2 in the hypothetical monatomic crystal.*

| | Number of equations solved | | | | |
	$1(M-L)$	$4(M-L)$	4	7	10
μ_1	0.850	0.916	0.932	0.914	0.921
μ_2		0.236	0.220	0.235	0.229
μ_3		0.138	0.170	0.136	0.138
μ_4		0.314	0.406	0.305	0.331
μ_5				0.128	0.126
μ_6				0.097	0.087
μ_7				0.119	0.072
μ_8					0.090
μ_9					0.067
μ_{10}					0.072
$\mu_1 r_1^2$	6.73	7.25	7.37	7.23	7.29
$\mu_2 r_2^2$		3.74	3.48	3.72	3.62
$\mu_3 r_3^2$		3.28	4.04	3.23	3.28
$\mu_4 r_4^2$		9.93	12.9	9.66	10.4
$\mu_5 r_5^2$				5.05	4.97
$\mu_6 r_6^2$				4.60	4.14
$\mu_7 r_7^2$				7.54	4.58
$\mu_8 r_8^2$					6.44
$\mu_9 r_9^2$					5.30
$\mu_{10} r_{10}^2$					6.30

$$\mu r^2 = M a^3 e = 5.02$$

* The units of μ are such that W is in electron volts in the equation $W = (e/2)(\mu/r^2)$ when e has the value 3.7815 and r is in A units.

they find that, except for a slight oscillation, all the values derived from approximations of higher order than the zero are about constant. This leads them to the conclusion that the first-order approximation is a satisfactory one.

It is interesting to compare the values of the dipole moments on all of the ions in the first

TABLE III. Values of μ and μr^2 for ten shells in NaCl.*

	Removal of positive ion		Removal of negative ion	
μ_1	1.09			0.059
μ_2		0.015	0.501	
μ_3	0.246			0.011
μ_4		0.021	0.216	
μ_5	0.194			0.010
μ_6		0.005	0.147	
μ_7		0.003	0.136	
μ_8	0.100			0.005
μ_9		0.005	0.093	
μ_{10}	0.099			0.004
$\mu_1 r_1^2$	8.59			0.46
$\mu_2 r_2^2$		0.24	7.93	
$\mu_3 r_3^2$	5.83			0.25
$\mu_4 r_4^2$		0.67	6.83	
$\mu_5 r_5^2$	7.66			0.38
$\mu_6 r_6^2$		0.25	6.97	
$\mu_7 r_7^2$		0.20	8.62	
$\mu_8 r_8^2$	7.12			0.38
$\mu_9 r_9^2$		0.42	7.32	
$\mu_{10} r_{10}^2$	8.61			0.37

$$\mu_+ r^2 = M_+ a^3 e = 0.36; \quad \mu_- r^2 = M_- a^3 e = 7.29$$

* The units of μ are such that W is in electron volts in the equation $W = (e/2)(\mu/r^2)$, when e has the value 3.7815 and r is in A units.

POLARIZATION IN IONIC CRYSTALS. I.

TABLE IV. Constants for use in Eq. (10).

n, Order of approx.	f_n	g_n	h_n
0	0	10.1977	6.3346
1	6.0000	4.1977	6.3346
2	6.0000	4.1977	3.3346
3	2.6667	3.3088	3.3346
4	1.5000	3.3088	2.9596
5	4.8000	2.3488	2.9596
6	4.0000	2.3488	2.2929
7	1.5000	2.3488	2.1054
8	3.3333	1.9784	2.1054

TABLE V. Values of φ in the monatomic crystal for various orders of approximation.*

n	φ_d	$\varphi_c(J)$	$\varphi_c(M-L)$	$\dfrac{\varphi_d+\varphi_c(J)}{\varphi_0}$	$\dfrac{\varphi_d+\varphi_c(M-L)}{\varphi_0}$	$\dfrac{\varphi}{\varphi_0}(M-L)^3$
0	0.0	2.016	1.326	25.13	16.53	16.53
1	0.699	0.835	0.845	19.12	19.24	18.57
2	0.872	0.641	0.604	18.86	18.40	18.15
3	0.919	0.540	0.533	18.18	18.09	18.03
4	0.981	0.476	0.503	18.16	18.50	18.5
5	1.057	0.430	0.426	18.54	18.49	
6	1.101	0.382	0.372	18.49	18.37	
7	1.115	0.346	0.357	18.21	18.35	
8	1.153	0.327	0.328	18.45	18.46	

$$\varphi_0 = 0.08023$$

* The units of φ are such that W is in electron volts in the equation $W = \frac{1}{2}e\varphi$, when $e = 3.7815$.

four shells calculated in this more exact way with the corresponding μ's obtained from the zero-order treatment. Actually, it is more convenient to compare the values of $\mu_i r_i^2$ as, for the zero-order case, this quantity is a constant equal to $M_i a^3 e$. The $\mu_i r_i^2$ values, which are not listed in reference (3), are contained in the second column of Table II below for a hypothetical crystal with $\alpha_1 = \alpha_2$, $\kappa_0 = 4$, and $a = 2.813$A. It will be seen that the deviations from the zero-order μr^2 value, given at the bottom of the table, are quite pronounced even beyond the first shell. These deviations arise essentially from the irregular change of the number of ions in each shell with distance from the origin, i.e., from the necessity of treating in spherical coordinates a problem where the symmetry is better described by Cartesian coordinates. The μr^2 zero-order value represents an average of these fluctuating values over a very large number of shells. Hence, the justification for considering the first-order approximation as a satisfactory solution resides solely in the numerical constancy obtained in the final potential field results.

Moreover, it will be noted that the value of μ_1 obtained from the first-order approximation (Table II, column 1) is seven percent lower than the more accurate value of μ_1 obtained from the fourth-order approximation. This can probably be accounted for by the fact that the nearest neighbors contribute most heavily to field (c) and that the exact μ_2 and μ_3 values are appreciably lower than the corresponding zero-order values actually used in determining this field, which is depolarizing in the present case. In view of the disparity in the values of μ_1 obtained in these two ways for the monatomic crystal considered, and in view of the large contribution of μ_1 to the potential field, the excellent agreement between the first-($\varphi/\varphi_0 = 18.57$) and fourth-($\varphi/\varphi_0 = 18.5$) order approximations of Mott-Littleton[3] is quite surprising.

In order to gain more insight into the problem, we have carried out higher order approximations in the spirit of the Mott-Littleton method with an important exception. The evaluation by their method of the field corresponding to field (c) is subject to the objection raised in the previous paragraph and also requires performing tedious lattice sums. We have avoided these difficulties by solving Eq. (4) for a convenient number of shells, neglecting the remainder of the crystal in this part of the problem. Consequently, the values of μ for the last few shells will be in error, and they have been discarded in calculating the potential field, $\sum_i \varphi_i$. To obtain the latter, these last few shells and the remainder of the crystal were treated in the manner of the Mott-Littleton zero-order approximation and also, for comparison, in the manner of the Jost approach. The disadvantage of the latter method, namely, the uncertainty in R, becomes less important as R increases because the percentage uncertainty in R decreases and the total contribution of that portion of the crystal considered in this way also decreases.

In the present work a system of ten equations for $m_i = \mu_i/ea$ was derived from Eq. (4). (See Table I for equations and the Appendix for the method of deriving the numerical coefficients.)

These ten equations were applied to the hypothetical monatomic crystal ($\alpha_1 = \alpha_2$, $\kappa_0 = 4$, $a = 2.813$A) and to NaCl ($\alpha_1/\alpha_2 = 20.3$, $\kappa_0 = 2.33$, $a = 2.813$A) for the removal of both a positive

and a negative ion. In addition, the sets of four and seven equations outlined in Table I by solid lines were also examined in the case of the monatomic crystal to gain information as to the uncertainty in the μ's on the ions in the last few shells. Solutions were kindly obtained for us by the R.C.A. Laboratories with the use of their recently developed "Electronic Simultaneous Equation Solver."[11] Final results for μ and μr^2 are shown in Tables II and III.

It will be noted that, as before, appreciable variations in the μr^2 values from the zero-order value still obtain at the larger distances. Also, comparing the third and fourth columns of Table II with the last column, it appears that the last two values of μ obtained from a set of equations are sufficiently in error to warrant their discard.

The total potential at the origin is the sum of the contributions of the shells treated "exactly," φ_d, and of the rest of the crystal, φ_c. A general expression for the potential field at the origin due to all the induced dipoles for the nth order approximation is

$$\sum_i \varphi_i = (f_1\mu_1 + f_2\mu_2 + \cdots + f_n\mu_n)/a^2 + \varphi_{cn}, \quad (10)$$

where, in the spirit of the method of Mott-Littleton,

$$\varphi_{cn}(M-L) = e(g_n M_1 + h_n M_2)/a.$$

M_1 refers to the same type of ion as that in the first shell and M_2 to the type of ion in the second shell. Values of the constants, f, g, and h, for various orders of approximation up to and including $n=8$, are given in Table IV. In the Jost approach

$$\varphi_{cn}(J) = e(1 - 1/\kappa_0)/R_n.$$

We have taken for R_n the distance from the origin to a point halfway between the center of the last shell treated as discrete, and the center of the first shell in the continuum.

The values of φ_d and φ_c obtained for various orders of approximation, using only the μ's on the ions in the first eight shells obtained from the solution of all ten equations, are shown in Table V for the monatomic crystal, and in

[11] E. A. Goldberg and G. W. Brown, J. App. Phys. **19**, 339 (1948).

Tables VI and VII for removing a positive ion and negative ion from NaCl, respectively. Values of φ/φ_0 are included to permit comparison with the Mott-Littleton results. ($\varphi_0 = e(1 - 1/\kappa_0)/4\pi a$.) Finally, in Table VIII are shown the values of the polarization work in NaCl calculated by the various methods discussed.

It will be seen that rapid convergence of the quantity $\varphi_d + \varphi_c(M-L)$ occurs in all cases for approximations of higher order than the third. The convergence in $\varphi_d + \varphi_c(J)$ is less satisfactory, but the eighth-order approximations, where $\frac{1}{2}e\varphi_d$ is roughly 75 percent of the total polarization work, yield closely similar results by both methods.

Tables V, VI, and VII also show that the polarization work calculated by a first-order approximation, using a very nearly exact value of μ_1, is in error by several percent (compare $\varphi_d + \varphi_c(M-L)/\varphi_0$ for $n=1$ and $n=8$). The original Mott-Littleton first-order approximation, which employs approximate values of μ_1, yields excellent results (see Table VIII) because in the cases considered the errors in the μ's

TABLE VI. Values of φ in NaCl for removing a positive ion.*

n	φ_d	$\varphi_c(J)$	$\varphi_c(M-L)$	$\dfrac{\varphi_d+\varphi_c(J)}{\varphi_0}$	$\dfrac{\varphi_d+\varphi_c(M-L)}{\varphi_0}$	$\dfrac{\varphi}{\varphi_0}(M-L)^3$
0	0.0	1.535	1.223	25.13	20.03	20.03
1	0.823	0.636	0.525	23.88	22.07	21.88
2	0.834	0.488	0.508	21.65	21.97	21.83
3	0.917	0.411	0.404	21.75	21.63	21.62
4	0.921	0.362	0.402	21.01	21.66	21.69
5	1.038	0.328	0.290	22.37	21.76	
6	1.041	0.291	0.287	21.81	21.74	
7	1.042	0.263	0.285	21.37	21.73	
8	1.085	0.249	0.242	21.83	21.72	

$\varphi_0 = 0.06106$

TABLE VII. Values of φ in NaCl for removing a negative ion.*

n	φ_d	$\varphi_c(J)$	$\varphi_c(M-L)$	$\dfrac{\varphi_d+\varphi_c(J)}{\varphi_0}$	$\dfrac{\varphi_d+\varphi_c(M-L)}{\varphi_0}$	$\dfrac{\varphi}{\varphi_0}(M-L)^3$
0	0.0	1.535	0.796	25.13	13.03	
1	0.044	0.636	0.761	11.14	13.20	13.21
2	0.424	0.488	0.412	14.94	13.70	
3	0.428	0.411	0.407	13.74	13.67	
4	0.469	0.362	0.363	13.61	13.63	
5	0.475	0.328	0.358	13.14	13.63	
6	0.549	0.291	0.280	13.75	13.58	
7	0.575	0.263	0.259	13.72	13.64	
8	0.577	0.249	0.256	13.53	13.65	

$\varphi_0 = 0.06106$

* The units of φ are such that W is in electron volts in the equation $W = \frac{1}{2}e\varphi$, when $e = 3.7815$.

TABLE VIII. Polarization work in NaCl calculated by various methods, ev.

Removal of	No dip.-dip. Eq. (5)	Jost $R=a/2$	Jost-Nehlep	$M-L$ 0 order	$M-L$ 1st order	$M-L$ 4th order	$\frac{1}{2}e[\varphi_d+\varphi_c(M-L)]$ $n=8$	$\frac{1}{2}e[\varphi_d+\varphi_c(J)]$ $n=8$
Na^+	3.73	2.90	3.20	2.31	2.53	2.50	2.51	2.52
Cl^-	2.43	2.90	1.66	1.50	1.53	—	1.57	1.56
Sum	6.16	5.80	4.86	3.81	4.06	—	4.08	4.08

happen to compensate those in W. It is not certain that in other cases these errors will be mutually compensatory. To be completely certain of accurate results, higher order approximations should be carried out; this can be readily accomplished for other crystals of the NaCl type by the use of Table I and Eq. (10).

ACKNOWLEDGMENTS

APPENDIX

Equation (4) can be written in the form

$$\mu_i = \alpha_i\left[\frac{e}{r_i{}^2} - \sum_j{}' A_{ij}\cdot\frac{\mathbf{r}_i}{r_i}\right],$$

where

$$\mathbf{A}_{ij} = \nabla_i\left(\mathbf{\mu}_j\cdot\nabla_i\frac{1}{|\mathbf{r}'|}\right),$$

and

$$|\mathbf{r}'| = [(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^{\frac{1}{2}}.$$

The summation over all the j ions in the crystal can be rewritten so as to bring out explicitly the summation over each shell individually, and leads to the following equation:

$$\mu_i = \alpha_i\left[\frac{e}{r_i{}^2} - \sum_{k=1}^{\infty}\left(\sum_{\substack{\text{all ions in} \\ k\text{th shell}}}{}' A_{ik}\cdot\frac{\mathbf{r}_i}{r_i}\right)\right],$$

where the index k refers to the number of the shell, $\sum_{k=1}^{\infty}$ represents the summation over all shells, and the $\sum'$ within the parentheses is the sum over all the ions in the kth shell.

Using the simplifying notation,

$$r_i{}^2/a^2 = l_i{}^2+m_i{}^2+n_i{}^2 = p_i,$$

$$r_k{}^2/a^2 = l_k{}^2+m_k{}^2+n_k{}^2 = p_k,$$

$$\mathbf{r}_i\cdot\mathbf{r}_k/a^2 = l_il_k+m_im_k+n_in_k = q,$$

it can be shown that

$$\sum_{k\text{th shell}}{}' \mathbf{A}_{ik}\cdot\frac{\mathbf{r}_i}{r_i} = \frac{\mu_k}{a^3}\sum_{k\text{th shell}}{}' b_{ik},$$

where

$$b_{ik} = \frac{1}{(p_ip_k)^{\frac{1}{2}}}\left[\frac{q(p_i+p_k-2q)+3(p_i-q)(p_k-q)}{(p_i+p_k-2q)^{5/2}}\right].$$

Thus,

$$\mu_i = \alpha_i\left[\frac{e}{r_i{}^2} - \sum_{k=1}^{\infty}\frac{\mu_k}{a^3}\sum_{k\text{th shell}}{}' b_{ik}\right]$$

$$= \frac{\alpha_i}{a^3}\left[\frac{ea}{p_i} - \sum_{k=1}^{\infty}\mu_k\sum_{k\text{th shell}}{}' b_{ik}\right].$$

In the notation of Mott-Littleton,

$$\mu_i = eam_i \quad\text{and}\quad \frac{\alpha_i}{a^3} = \beta_i.$$

Then,

$$m_i = \beta_i\left[\frac{1}{p_i} - m_1\sum_{1\text{st shell}}{}' b_{i1} - m_2\sum_{2\text{nd shell}}{}' b_{i2}\right.$$
$$\left. - m_3\sum_{3\text{rd shell}}{}' b_{i3} - \cdots\right]$$

and

$$\frac{1}{p_1} = \left(\frac{1}{\beta_1} + \sum_{1\text{st shell}}{}' b_{11}\right)m_1 + \sum_{2\text{nd shell}} b_{12}m_2$$
$$+ \sum_{3\text{rd shell}} b_{13}m_3 + \cdots,$$

$$\frac{1}{p_2} = \sum_{1\text{st shell}} b_{21}m_1 + \left(\frac{1}{\beta_2} + \sum_{2\text{nd shell}}{}' b_{22}\right)m_2$$
$$+ \sum_{3\text{rd shell}} b_{23}m_3 + \cdots, \text{ etc.}$$

These are the equations used to derive Table I