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Point Charge Interaction Energy in Ionic Crystals

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The interaction energy of two charges located in an ionic crystal is calculated in a macroscopic way. The ions are considered fixed at the lattice points; only the noninertial polarization component of the crystal is taken into account. The result depends on the sign of the charges and for large separations the interaction is of the Coulomb type. If the charges are localized on neighboring ions, the result differs in the mean from the Coulomb energy by 17-20%. The polarization energy of the crystal due to the field of a point charge located at one of the lattice points is calculated in this same approximation for KCl.

In the works of Pekar and his colleagues[1-3] on the investigation of the local states of the electron in ionic crystals, consideration of the polarization of the crystal in the field of a point charge or ionic vacancy (at an *F*-center) plays a great role. A macroscopic expression for the electronic polarization[1] is determined with the help of the coefficient $C = (1/n^2) - 1/\epsilon$ which appears as the basic parameter of the theory. Since the results are subsequently applied to states with effective radii comparable with the lattice constant or even equal to it, there is interest in an estimate of the admissibility of such a method. This is the more essential, that the basic contribution in the polarizing field is made precisely by the near ions, to the determination of the polarization of which the macroscopic method is less applicable.

The author, on the suggestion of K. B. Tolpygo, has considered the problem of the electrostatic interaction energy of two charges which are located in a crystal, and its dependence on the distance between them. The ions are assumed to be fixed at the lattice points (noninertial polarization). The calculations are carried out by a macroscopic method. The extra electron (or hole), in accordance with the chosen approximation, is considered to be localized on the ions of corresponding sign.

Mott and Littleton[4], and also DuPre and others[5] have computed the work of noninertial polarization, performed in transporting a point charge into the ionic crystal, and also the potential which arises at the point where the charge is located. These authors have shown the great role of these quantities in the theory of electrolytic conductivity[5], absorption spectra, color centers and electron emission. However, the method of successive approximations of Mott and Littleton is not successful in our case. Results computed with accuracy to 10th order do not permit us to determine the limit to which they converge.

In the present work, there is given another, completely independent method for the determination of the above-mentioned quantities, which can also be applied to the calculation of the dipole moments of the ions of the polarized crystal. For numerical calculation, the crystal KCl was chosen, for which all the necessary parameters are known, and which is frequently employed in experimental researches.

1. ARRANGEMENT OF THE PROBLEM AND METHOD OF CALCULATION

We introduce two point charges q_1 and q_2 in the ionic crystal; as a result, the crystal is polarized. If the ions are fixed at the lattice points then only non inertial polarization results, which is connected with deformations of the electron shells of the ions and with the appearance of the electric field E of the polarized ions.

The dipole moment p_s^l of an ion of type s located in the lth cell of the crystal can be represented approximately as the sum

$$\mathbf{p}_s^l = \mathbf{p}_{1s}^l + \mathbf{p}_{2s}^l \qquad (1)$$

of the dipole moments associated with the charges q_1 and q_2 separately. We represent the field similarly:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_1(\mathbf{r}) + \mathbf{E}_2(\mathbf{r}). \qquad (2)$$

The total electrostatic energy U of the crystal as a function of the distance $\mathbf{R}$ between the charges q_1 and q_2, with consideration of Eqs. (1) and (2), will be equal to

$$U(\mathbf{R}) = U_1 + U_2 + U_{1,2}(\mathbf{R}), \qquad (3)$$

where

$$U_1 = \sum_s \sum_l \left\{ \frac{(\mathbf{p}_{1s}^l)^2}{2\alpha_s} - \mathbf{p}_{1s}^l \left[\frac{1}{2} \mathbf{E}_1(\mathbf{r}_s^l) + \frac{q_1 \mathbf{r}_{1s}^l}{r_{1s}^l} \right] \right\} \qquad (4)$$

is the characteristic energy of the charge q_1 (the

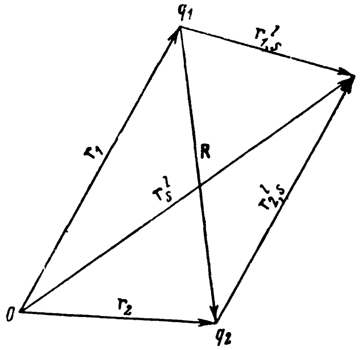

FIG. 1

energy necessary to insert q_1 in the crystal). A similar expression exists for U_2;

$$U_{1,2}(\mathbf{R}) = \frac{q_1 q_2}{R} + 2\sum_s\sum_l \left\{\frac{(\mathbf{p}^l_{1s}\mathbf{p}_{2s})}{2\alpha_s} - \mathbf{p}^l_{1s}\left[\frac{1}{2}\mathbf{E}_2(\mathbf{r}^l_s) + \frac{q_2\mathbf{r}^l_{2s}}{r^l_{2s}}\right] + \mathbf{p}^l_{2s}\left[\frac{1}{2}\mathbf{E}_1(\mathbf{r}^l_s) + \frac{q_1\mathbf{r}^l_{1s}}{r^l_{1s}}\right]\right\} \tag{5}$$

is the interaction energy of charges q_1 and q_2, α_s = polarizability of the ion of type s; for the vector notation, see Fig. 1. Summation in l is carried out over all cells of the fundamental region of the crystal, the number of which we set equal to M. The aim of the present work is the calculation of the energies of Eqs. (4) and (5).

For further calculations, we expand all quantities in Fourier series:

$$\mathbf{p}^l_s = \sum_{\mathbf{k}} \mathbf{p}_{s,\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}^l_s\}; \tag{6}$$

$$\mathbf{E}(r^l_s) = \sum_{\mathbf{k}} \mathbf{E}_{s,\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}^l_s\};$$

$$\frac{q}{r^{l\,3}_s}\mathbf{r}^l_s = \sum_{\mathbf{k}} \vec{\rho}_{s,\mathbf{k}} \exp\{i\mathbf{k}\mathbf{r}^l_s\}.$$

Evidently*,

$$\mathbf{p}^l_s = \alpha_s\left[\mathbf{E}(\mathbf{r}^l_s) + \frac{q}{r^{l3}_s}\mathbf{r}^l_s\right]. \tag{7}$$

It also follows from Eqs (5) and (7) that

$$\mathbf{p}_{s,\mathbf{k}} = \alpha_s[\mathbf{E}_{s,\mathbf{k}} + \vec{\rho}_{s,\mathbf{k}}]. \tag{8}$$

Substituting Eq. (6) in Eqs. (4) and (5), and considering that

$$\sum_l e^{i(\mathbf{k}+\mathbf{k}')\mathbf{r}^l_s} = M\delta_{\mathbf{k},-\mathbf{k}'}, \tag{9}$$

we find U_1 and $U_{1,2}$, expanded in Fourier series.

2. DETERMINATION OF THE FIELD E AND $\vec{\rho}$

The field created by the dipole plane wave

$$\mathbf{p}^l_s = \mathbf{p}_s \exp[i\mathbf{k}\mathbf{r}^l_s - i\omega t],$$

was represented by Ewald[7] in the form of two rapidly converging series which we write out here in view of the presence of a misprint in Ref. 7. The kth component of the field E in Eq. (6) is

$$\mathbf{E}_{\mathbf{k}} = \operatorname{grad}\operatorname{div}\mathfrak{P}_{\mathbf{k}} - \frac{1}{c^2}\ddot{\mathfrak{P}}_{\mathbf{k}}, \tag{10}$$

where $\mathfrak{P}_{\mathbf{k}}$ is the Hertz vector[8]:

$$\mathfrak{P}_{\mathbf{k}}(\mathbf{r}^l_s, t) = \sum_{s'}\sum_{l'}{}' \frac{\mathbf{p}^{l'}_{s'\mathbf{k}}}{|\mathbf{r}^l_s - \mathbf{r}^{l'}_{s'}|} \times \exp\left\{i\omega\left(t - \frac{1}{c}|\mathbf{r}^l_s - \mathbf{r}^{l'}_{s'}|\right) + i\mathbf{k}\mathbf{r}^{l'}_{s'}\right\}$$
$$= e^{i\omega t}\{e^{i\mathbf{k}\mathbf{r}_s}\mathbf{p}_{s,\mathbf{k}}\overline{S}_l(\mathbf{r}^l_s - \mathbf{r}_s) + e^{i\mathbf{k}\mathbf{r}_{s'}}S(\mathbf{r}^l_s - \mathbf{r}_{s'})\}. \tag{11}$$

Here

$$S \equiv S_{\mathbf{k}}(\mathbf{r}) = \sum_{l'} \frac{1}{|\mathbf{r}^{l'} - \mathbf{r}|} \times \exp\left\{i\frac{\omega}{c}|\mathbf{r} - \mathbf{r}^{l'}| + i\mathbf{k}\mathbf{r}^{l'}\right\}, \tag{12}$$

and $\overline{S}_l$ differs from S by the absence of a term with $l' = l$. Ewald transformed S and $\overline{S}_l$ into the rapidly converging series:

$$S(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \times \sum_l e^{i\mathbf{k}\mathbf{r}^l}\int_\varepsilon^\infty \exp\left\{-|\mathbf{r} - \mathbf{r}^l|^2 x^2 + \frac{K_0^2}{4x^2}\right\}dx + \frac{4\pi}{\Delta}\sum_l \frac{\exp\{-(\mathbf{K}_l^2 - K_0^2)/4\varepsilon^2 + i(\mathbf{K}_l\mathbf{r})\}}{\mathbf{K}_l^2 - K_0^2} \tag{13}$$

where the following notation is used: $K_0 = \omega/c$, $\mathbf{K}_l = 2\pi\mathbf{h}_l + \mathbf{k}$, $\mathbf{h}_l$ is the arbitrary vector of the inverse lattice;

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[*] This same relation was proved in Ref. 6 by considering the crystal as a polyelectron problem in the approximation of Heitler-London-Heisenberg.

$$S_l(\mathbf{r}) = S(\mathbf{r}) - i\frac{\sin(K_0|\mathbf{r}-\mathbf{r}^l|)}{|\mathbf{r}-\mathbf{r}_l|} \qquad (14)$$

$$-\frac{1}{2|\mathbf{r}-\mathbf{r}^l|}\left\{e^{iK_0|\mathbf{r}-\mathbf{r}^l|}\,\Phi\left(|\mathbf{r}-\mathbf{r}^l|\varepsilon+\frac{iK_0}{\varepsilon}\right)\right.$$

$$\left.+e^{-iK_0|\mathbf{r}-\mathbf{r}^l|}\,\Phi\left(|\mathbf{r}-\mathbf{r}^l|\varepsilon-\frac{iK_0}{\varepsilon}\right)\right\},$$

Φ = proability integral:

$$\Phi(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt.$$

The result is independent of the choice of ϵ, $\Delta = d^3/4$ is the volume of the elementary cell.

After substitution of Eq. (13) and (14) in Eq. (11), and the result in Eq. (10), we find the components of the expansion of the field E in a Fourier series in the wave numbers k:

$$\mathbf{E}_\mathbf{k}(r_s^l) = e^{-i\omega t+i\mathbf{k}\mathbf{r}_s^l}\left\{\frac{4}{3\sqrt{\pi}}\varepsilon^3\mathbf{p}_s - \frac{4}{\sqrt{\pi}}p_s\sum_{l'\neq l}\int_\varepsilon^\infty x^2\exp\{-|\mathbf{r}^l-\mathbf{r}^{l'}|^2x^2+i\mathbf{k}[\mathbf{r}^{l'}-\mathbf{r}^l]\}\,dx\right.$$

$$+\frac{8}{\sqrt{\pi}}\sum_{l'\neq l}{}'(\mathbf{p}_s[\mathbf{r}^l-\mathbf{r}^{l'}])(\mathbf{r}^l-\mathbf{r}^{l'})\int_\varepsilon^\infty x^4\exp\{-|\mathbf{r}^l-\mathbf{r}^{l'}|^2x^2+i\mathbf{k}(\mathbf{r}^{l'}-\mathbf{r}^l)\}\,dx$$

$$-\frac{4\pi}{\Delta}\sum_{l'}\frac{(\mathbf{p}_s\mathbf{K}_{l'})\mathbf{K}_{l'}}{\mathbf{K}_{l'}^2-K_0^2}\exp\{-(\mathbf{K}_{l'}^2-K_0^2)/4\varepsilon^2\}$$

$$-\frac{4}{\sqrt{\pi}}p_{s'}\sum_{l'}\exp\{i(\mathbf{k}[\mathbf{r}_{s'}^{l'}-\mathbf{r}_s^l])\}\int_\varepsilon^\infty x^2\exp\{-|\mathbf{r}_s^l-\mathbf{r}_{s'}^{l'}|^2x^2\}\,dx \qquad (15)$$

$$+\frac{8}{\sqrt{\pi}}\sum_{l'}(\mathbf{p}_{s'}[\mathbf{r}_s^l-\mathbf{r}_{s'}^{l'}])(\mathbf{r}_s^l-\mathbf{r}_{s'}^{l'})\int_\varepsilon^\infty x^4\exp\{-x^2|\mathbf{r}_s^l-\mathbf{r}_{s'}^{l'}|^2+i\mathbf{k}(\mathbf{r}_{s'}^{l'}-\mathbf{r}_s^l)\}\,dx$$

$$-\frac{4\pi}{\Delta}\sum_{l'}\exp\{-(\mathbf{K}_{l'}^2-K_0^2)/4\varepsilon^2+i\mathbf{q}_{l'}(\mathbf{r}_s-\mathbf{r}_{s'})\}\frac{(\mathbf{p}_{s'}\mathbf{K}_{l'})\mathbf{K}_{l'}}{\mathbf{K}_{l'}^2-K_0^2}$$

$$\left.+\frac{4\pi}{\Delta}\frac{\omega^2}{c^2}\frac{(\mathbf{p}_s+\mathbf{p}_{s'})}{(\mathbf{k}^2-K_0^2)}\exp\{-(\mathbf{k}^2-K_0^2)/4\varepsilon^2\}\right\}.$$

If, in accordance with the above, we set $\epsilon = \sqrt{2}\,\pi/d$, the lattice vectors $\mathbf{a}_1 = (d/2)(j+\mathrm{k})$, $\mathbf{a}_2 = (d/2)(\mathrm{i}+\mathrm{k})$, $\mathbf{a}_3 = (d/2)(\mathrm{i}+\mathrm{j})$, choose the origin of the coordinates in ion K^+, and the radius vectors $\mathbf{r}_s$ and $\mathbf{r}_{s'}$ equal to $\mathbf{r}_1 = 0$, $\mathbf{r}_2 = (d/2) \times (\mathrm{i}+\mathrm{j}+\mathrm{k})$, then, substituting these in Eq. (15), we obtain the expansion coefficients of $\mathbf{E}$ in the Fourier series in k:

$$\mathbf{E}_\mathbf{k} = a^{-3}\Phi_\mathbf{k}\mathbf{P}_\mathbf{k} = 8d^{-3}\Phi_\mathbf{k}\mathbf{P}_\mathbf{k}, \qquad (16)$$

where $\Phi_\mathbf{k}$ is a symmetric matrix of 6th order with elements $\Phi_{ss'xy}$ and $\mathrm{E}_\mathbf{k}$ and $\mathrm{P}_\mathbf{k}$ are six-dimensional vectors with components $E_{\mathbf{k}sx}$ and $p_{\mathbf{k}sx}$ ($s = 1,2$; $x = x, y, z$) which are the totality of two corresponding three-dimensional vectors of the field and the dipole moment, which correspond to the two types of ions.

The elements of the matrix $\Phi_\mathbf{k}$ were considered in Ref. 8 only for eight points of k, which is quite insufficient for further calculations. Therefore, the author has again calculated the matrix $\Phi_\mathbf{k}$ for 29 values of the wave vector k, which makes possible the calculation of the field $\mathrm{E}_{s,\mathbf{k}}$ and the dipole moments $\mathrm{p}_{s,\mathbf{k}}$ at 729 points of the cell of the inverse lattice. The results are given in Table I.

The Fourier components $\vec{\rho}\,^{(j)}_{s,\mathbf{k}}$ of the field of a point charge localized on the ion of type j in the place where an ion of type s is located are considered in similar fashion. Since this calculation has not been performed earlier, we carry it out in some detail.

We obtain from Eq. (6) the kth coeeficient of the series expansion of the field of the point charge q in the usual way. For convenience we temporarily set q at an arbitrary point $\mathbf{r}$ (not at a lattice point). Then

TABLE I. The matrices $\Phi_k \cdot 10^3$

№	$\varkappa_x$	$\varkappa_y$	$\varkappa_z$	φ_{ssxx}	φ_{ssyy}	φ_{sszz}	φ_{ssxy}	φ_{ssxz}	φ_{ssyz}	$\varphi_{ss'xx}$	$\varphi_{ss'yy}$	$\varphi_{ss'zz}$	$\varphi_{ss'xy}$	$\varphi_{ss'xz}$	$\varphi_{ss'yz}$
1	0	0	1/4	1954	1954	—3908	0	0	0	2331	2331	—4662	0	0	0
2	0	0	1/2	1605	1605	—3210	0	0	0	2912	2912	—5825	0	0	0
3	1/4	1	1	—2479	1240	1240	0	0	0	7017	—3509	—3509	0	0	0
4	0	0	1	1083	1083	—2167	0	0	0	3760	3760	—7520	0	0	0
5	0	1/4	1/4	1780	—890	— 890	0	0	—2938	2598	—1299	—1299	0	0	—2576
6	0	1/4	1/2	1343	676	—2019	0	0	—2035	3260	1122	—4382	0	0	—1498
7	0	1/4	3/4	878	934	—1812	0	0	— 991	3948	2270	—6218	0	0	— 592
8	0	1/4	1	677	935	—1612	0	0	0	4242	2650	—6891	0	0	0
9	0	1/2	1/2	669	—335	— 335	0	0	—2132	4140	—2070	—2070	0	0	—1328
10	1/4	1/2	1	— 479	547	— 68	—1222	0	0	4556	526	—5082	618	0	0
11	0	1/2	1	— 394	788	— 394	0	0	0	5493	0	—5493	0	0	0
12	1/8	1/8	1/8	0	0	0	—2052	—2052	—2052	0	0	0	—1943	—1943	—1943
13	1/4	1/4	1/4	0	0	0	—1950	—1950	—1950	0	0	0	—1503	—1503	—1503
14	3/8	3/8	3/8	0	0	0	—1849	—1849	—1849	0	0	0	— 822	— 822	— 822
15	1/2	1/2	1/2	0	0	0	—1808	—1808	—1808	0	0	0	0	0	0
16	1/8	1/8	3/8	1251	1251	—2502	— 559	—1565	—1565	1971	1971	—3941	— 407	—1292	—1292
17	1/8	1/8	5/8	1181	1181	—2363	— 273	— 843	— 843	2955	2955	—5910	— 49	— 555	— 555
18	1/8	1/8	7/8	973	973	—1946	— 219	— 272	— 272	3519	3519	—7039	62	— 148	— 148
19	1/8	3/8	3/8	1096	—548	— 548	— 928	— 928	—2492	2772	—1386	—1386	— 535	— 535	—1803
20	1/8	3/8	5/8	639	456	—1094	— 621	— 689	—1741	3756	510	—4265	— 29	— 258	—1004
21	1/8	3/8	7/8	235	730	— 964	— 556	— 251	— 608	4439	1448	—5886	203	— 60	— 288
22	3/8	3/8	5/8	209	209	— 418	—1495	—1560	—1560	1524	1524	—3047	124	— 402	— 402
23	1/8	5/8	5/8	— 248	124	124	— 602	— 602	—1470	4963	—2481	—2481	77	77	— 669
24	1/4	1/4	1/2	638	638	—1276	—1068	—1720	—1720	1668	1668	—3335	— 387	—1040	—1040
25	1/4	1/4	3/4	640	640	—1281	— 810	— 928	— 928	2766	2766	—5531	149	— 411	— 411
26	1/4	1/4	1	566	566	—1132	— 774	0	0	3167	3167	—6334	315	0	0
27	1/4	1/2	1/2	327	—163	— 163	—1313	—1313	—1966	2876	—1438	—1438	— 230	— 230	— 913
28	1/4	1/2	3/4	— 204	409	— 204	—1206	— 867	—1206	4055	0	—4055	385	0	— 385

$$\rho^{(r)}_{j,\mathbf{k}} = \frac{1}{M}\sum_{l'}\frac{\mathbf{r}_j^{l'}-\mathbf{r}}{|\mathbf{r}_j^{l'}-\mathbf{r}\,|^3}e^{-i\mathbf{k}\mathbf{r}_j^{l'}} \tag{17}$$

$$= \frac{1}{M}e^{-i\mathbf{k}\mathbf{r}_j}\,\nabla\sum_{l'}\frac{e^{-i\mathbf{k}\mathbf{r}^{l'}}}{|\mathbf{r}^{l'}-(\mathbf{r}-\mathbf{r}_j)|^3}\,.$$

But the latter, according to Eq. (12) is equal to

$$\frac{1}{M}e^{-i\mathbf{k}\mathbf{r}_j}\,\nabla S(\mathbf{r}-\mathbf{r}_j)$$

for $K_0 = 0$ (for a static field). Thence, we obtain

$$\vec{\rho}^{\,j}_{j,\mathbf{k}} = q\,\frac{\exp\{-i\,\mathbf{k}\mathbf{r}_j\}}{M}\,\overline{\nabla} S(\mathbf{r}-\mathbf{r}_j), \tag{18}$$

$$\vec{\rho}^{\,j}_{j',\mathbf{k}} = q\,\frac{\exp\{-i\mathbf{k}\mathbf{r}_j\}}{M}\,\nabla S(\mathbf{r}-\mathbf{r}_j),$$

where the upper index refers to the type of ion on which the charge q is placed, and the lower, as usual, denotes the type of ion for which the field is calculated. Carrying out the indicated operations, we get

$$\vec{\rho}^{\,j'}_{j,\mathbf{k}} = \frac{q}{M}\frac{4}{\sqrt{\pi}} \tag{19}$$

$$\times\sum_{l}\Big\{\mathbf{r}^l+\mathbf{r}_j\beta_{jj'}\exp\Big\{-i\,\mathbf{k}\mathbf{r}^l-i\,\mathbf{k}\mathbf{r}_j\beta_{jj'}\Big\}$$

$$\times\int\limits_{\varepsilon}^{\infty}x^2\exp\Big\{-|\mathbf{r}^l+\mathbf{r}_j\beta_{jj'}|^2x^2\Big\}dx$$

$$+\frac{4\pi i}{\Delta}\sum_{l}\frac{\mathbf{K}_l}{K_l^2}\exp\Big\{-\mathbf{K}_l^2/4\varepsilon^2+i\mathbf{q}_l\mathbf{r}_j\beta_{jj'}\Big\}\Big\},$$

where $\beta_{jj'} = 1-\delta_{jj'}$, q_l is the arbitrary vector of the reciprocal lattice, $\mathrm{K}_l = q_l + \mathrm{k}$. As already noted above, ϵ is arbitrary; here we set $\epsilon = \sqrt{2\pi/d}$. The series in Eq. (19) converge rapidly. The charge q was located at the origin of the coordinate system. If the same q were located at a point R, then (see Fig. 1) the entire expression (18) would be multiplied by $e^{i\mathbf{k}\mathbf{R}}$*.

It is also easy to see that the case of holes differs from that of the excess electron by a change of order and also of the signs for $\vec{\rho}_j$: $\rho^{(1)}_{1\mathbf{k}} = -\vec{\rho}^{(2)}_{2\mathbf{k}}$ and $\vec{\rho}^{(1)}_{2\mathbf{k}} = -\vec{\rho}^{(2)}_{1\mathbf{k}}$.

We replace $\rho_{j\mathbf{k}}$ by the dimensionless quantity $\vec{\Psi}_{j\mathbf{k}}$. Then, setting the origin of the coordinates on the ion at which the charge is localized, we get:

1) Field of the extra electron:

$$\vec{\rho}_{j\mathbf{k}} = (8ie/Md^2)\,\vec{\Psi}_{j\mathbf{k}}, \tag{20}$$

2) Field of the hole:

$$\vec{\rho}_{j\mathbf{k}} = -(8ie/Md^2)\vec{\Psi}_{j'\mathbf{k}}, \tag{21}$$

where e is the electronic charge.

The value of Ψ for the 29 values of k were computed by the author and appear in Table II.

3. FOURIER COMPONENTS OF THE IONIC DIPOLE MOMENTS AND THE ENERGY OF THE CHARGES

Substituting Eq. (16) in Eq. (8), we get a system of six equations for the determination of the Fourier coefficients of the dipole moments $p_{j\mathbf{k}}$ of the ions in the external field $\vec{\rho}_{\mathbf{k}}$. In the resultant equations, it is appropriate to transform to the dimensionless quantities $\pi_{j\mathbf{k}}$ and A_j, writing

$$p_{j\mathbf{k}} = (ied/M)\,\pi_{j\mathbf{k}}\,, \tag{22}$$

and

$$\alpha_j = (d^3/8)\,A_j \qquad (j = 1,2).$$

For KCl: $A_1 = 0.02569$ and $A_2 = 0.1087$.

Substituting $\mathrm{p}_{j\mathbf{k}}$ and α_j from Eq. (22) in our set of equations, we finally get

$$\begin{aligned} C_{\mathbf{k}}\vec{\pi}_{\mathbf{k}} &= -\vec{\Psi}_{\mathbf{k}}\ \text{(extra electron)} \\ C_{\mathbf{k}}\vec{\pi}_{\mathbf{k}} &= \vec{\Psi}_{\mathbf{k}}\ \text{(hole)} \end{aligned} \tag{23}$$

where $C_{\mathbf{k}}$ is a 6th order matrix which differs from $\Phi_{\mathbf{k}}$ only in the diagonal elements:

$$-c_{ss'xy} = \varphi_{ss'xy} - (1/A_s)\,\delta_{ss'}\,\delta_{xy} \tag{24}$$

$$(s = 1, 2;\ x = x,\ y,\ z),$$

$\vec{\pi}_{\mathbf{k}}$ and $\vec{\Psi}_{\mathbf{k}}$ are six-dimensional (dimensionless) vectors.

For the determination of the dipole moments $\vec{\pi}_{\mathbf{k}}$ the inverse matrices $C_{\mathbf{k}}^{-1}$ were found by the author for 28 values of the wave vector k. Their values are listed in Table III.

For long waves (limiting case k → 0), the vectors $\vec{\rho}_{\mathbf{k}}$ and the matrix $\Phi_{\mathbf{k}}$ were expanded in a series in k by Tolpygo. The $\vec{\pi}_{\mathbf{k}}$ were determined by him for small k. With accuracy up to terms of order k^2, inclusively.

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* All the $\mathrm{p}_{j\mathbf{k}}$ are multiplied by the same factor, which follows from the linearity of Eqs. (8) and (16).

TABLE II. The vectors $\vec{\Psi}_j \cdot 10^4$

№	Ψ_{1x}	Ψ_{1y}	Ψ_{1z}	Ψ_{2x}	Ψ_{2y}	Ψ_{2z}
1	0	0	—37065	0	0	—39138
2	0	0	—14470	0	0	—17451
3	5613	0	0	— 7756	0	0
4	0	0	0	0	0	0
5	0	—17042	—17042	0	—19341	—19341
6	0	— 5024	—10483	0	— 7901	—13809
7	0	— 1192	— 4466	0	— 4696	— 6873
8	0	— 235	0	0	— 4015	0
9	0	— 4569	— 4569	0	— 8790	— 8790
10	2196	1086	0	— 5299	— 6301	0
11	0	0	0	0	— 5658	0
12	—25165	—25165	—25165	—26345	—26345	—26345
13	—10308	—10308	—10308	—12909	—12909	—12909
14	— 4222	— 4222	— 4222	— 8828	— 8828	— 8828
15	0	0	0	— 7749	— 7749	— 7749
16	— 5738	— 5738	—17515	— 7162	— 7162	—20408
17	— 1426	— 1426	— 8188	— 3224	— 3224	—11145
18	— 210	— 210	— 2367	— 2295	— 2346	— 3612
19	— 2554	— 8277	— 8277	— 4373	—11804	—11804
20	— 469	— 2534	— 4912	— 2925	— 7050	— 8574
21	448	— 208	— 1498	— 2524	— 5498	— 3058
22	— 456	— 456	— 2533	— 6888	— 6888	— 7495
23	703	— 1599	— 1599	— 2881	— 6394	— 6394
24	— 3495	— 3495	— 7749	— 6892	— 6892	—11555
25	— 459	— 459	— 3476	— 4759	— 4759	— 6266
26	409	409	0	— 4301	— 4301	0
27	— 745	— 3149	— 3149	— 5591	— 8257	— 8257
28	1384	0	— 1384	— 5248	— 6657	— 5248

$$\vec{\pi}_j = \frac{A_j}{1-2\pi A/3}\left\{\vec{\Psi}_j - \frac{2\pi}{3}A_j(\vec{\Psi}_j - \vec{\Psi}_{j'}) \right. \quad (25)$$

$$\left. - \frac{2\pi}{1+4\pi A/3}\,\frac{[A_j\vec{\Psi}_j + A_{j'}\vec{\Psi}_{j'}]\vec{\varkappa}}{\vec{\varkappa}^2}\vec{\varkappa}\right\},$$

$$\vec{\Psi}_1 = -\frac{\vec{\varkappa}}{\vec{\varkappa}^2} + 1{,}200\,\vec{\varkappa}, \quad (26)$$

$$\vec{\Psi}_2 = -\frac{\vec{\varkappa}}{\vec{\varkappa}^2} + 0{,}295\,\vec{\varkappa}.$$

Here $\vec{\varkappa}$ is the nondimensional wave vector

$$\mathbf{k} = 2\pi(\varkappa_1\mathbf{b}_1 + \varkappa_2\mathbf{b}_2 + \varkappa_3\mathbf{b}_3) = (2\pi/d)\vec{\varkappa}, \quad (27)$$

where b_1, b_2 and b_3 are the vectors of the reciprocal lattice of the crystal; $A = A_1 + A_2$. The interval of variation of the components of $\vec{\varkappa}$ runs from $-\frac{1}{2}$ to $+\frac{1}{2}$. In the entire work the points of k are designated by $(\varkappa_1, \varkappa_2, \varkappa_3)$ or $(\varkappa_x, \varkappa_y, \varkappa_z)$. The expansion was carried out for the points $\vec{\varkappa}(1/8, 1/8, 1/8)$ and $\vec{\varkappa}(1/4, 1/4, 1/4)$. The deviation from the computed point values did not exceed 2%.

The dipole moments of all ions can now be calculated at will by simple summation of the Fourier series of the three variables.

In Sec. 1 we obtained Eqs. (4) and (5) for the energy of the charges in the crystal. We substitute p and $\vec{p}$ in them. It is easy to show that all the coefficients $\mathbf{E}_\mathbf{k}$, $\mathbf{p}_\mathbf{k}$ and $\vec{p}_\mathbf{k}$ are odd in k, i.e., they change sign upon replacement of k by -k. Keeping this in mind, we obtain, after substitution of Eqs. (23), (19)-(21) and (16) in the expression for U_1, U_2 and $U_{1,2}$ and some simple transformations:

1) Eigenvalue of the energy of each charge $\pm e$:

$$U = -\frac{4e^2}{Md}\sum_s\sum_k(\vec{\pi}_{s,\,\mathbf{k}}\vec{\Psi}_{s,\,\mathbf{k}}); \quad (28)$$

2) Interaction energy of the two charges ($q \equiv e$ = electronic charge):

a) of the same kind

$$U_{1,2}(\mathbf{R}_{1,2}) \equiv U_{1,2}(\mathbf{R}) \quad (29)$$

$$= \frac{e^2}{R} - \frac{8e^2}{Md}\sum_\mathbf{k}\cos(\mathbf{kR})\sum_s(\vec{\pi}_{s,\,\mathbf{k}}\vec{\Psi}_{s,\,\mathbf{k}});$$

TABLE III. Inverse matrices $C^{-1} \cdot 10^4$

№	C^{-1}_{11xx}	C^{-1}_{11yy}	C^{-1}_{11zz}	C^{-1}_{11xx}	C^{-1}_{22yy}	C^{-1}_{22zz}	C^{-1}_{11xy}	C^{-1}_{11xz}	C^{-1}_{11yz}	C^{-1}_{22xy}	C^{-1}_{22xz}	C^{-1}_{22yz}	C^{-1}_{12xy}	C^{-1}_{12xz}	C^{-1}_{12yz}	C^{-1}_{12yx}	C^{-1}_{12xz}	C^{-1}_{12zy}	C^{-1}_{12xx}	C^{-1}_{12yy}	C^{-1}_{12zz}
1	276	276	243	1408	1408	793	0	0	0	0	0	0	0	0	0	0	0	0	89	89	—86
2	276	276	254	1357	1357	862	0	0	0	0	0	0	0	0	0	0	0	0	106	106	—119
3	269	277	277	953	1310	1310	0	0	0	0	0	0	0	0	0	0	0	0	162	—122	—122
4	277	277	277	1291	1291	1001	0	0	0	0	0	0	0	0	0	0	0	0	128	128	—183
5	276	257	257	1381	1098	1098	0	0	—16	0	0	—309	0	0	—60	0	0	—60	97	—11	—11
6	276	265	256	1320	1236	973	0	0	—11	0	0	—221	0	0	—40	0	0	—24	114	46	—94
7	276	268	269	1264	1244	1005	0	0	—5	0	0	—115	0	0	—19	0	0	—2	131	76	—151
8	277	269	277	1242	1237	1037	0	0	0	0	0	0	0	0	0	0	0	0	138	86	—176
9	276	259	259	1237	1116	1116	0	0	—11	0	0	—238	0	0	—22	0	0	—22	134	—50	—50
10	268	261	276	1111	1177	1162	—6	0	0	—147	0	0	1	0	0	12	0	0	126	14	—151
11	276	262	276	1133	1188	1133	0	0	0	0	0	0	0	0	0	0	0	0	158	0	—158
12	263	263	263	1203	1203	1203	—12	—12	—12	—216	—216	—216	—48	—48	—48	—48	—48	—48	27	27	27
13	261	261	261	1186	1186	1186	—12	—12	—12	—205	—205	—205	—37	—37	—37	—37	—37	—37	20	20	20
14	259	259	259	1169	1169	1169	—12	—12	—12	—195	—195	—195	—20	—20	—20	—20	—20	—20	10	10	10
15	258	258	258	1162	1162	1162	—11	—11	—11	—191	—191	—191	0	0	0	0	0	0	0	0	0
16	271	271	251	1319	1319	932	—4	—9	—9	—63	—166	—166	—12	—35	—35	—12	—26	—26	77	77	—76
17	273	273	262	1296	1296	948	—2	—4	—4	—36	—94	—94	—4	—18	—18	—4	—6	—6	103	103	—132
18	274	274	274	1267	1267	1008	—2	—1	—1	—32	—32	—32	—2	—6	—6	—2	0	0	118	118	—173
19	272	257	257	1291	1114	1114	—6	—6	—14	—99	—99	—265	—18	—18	—38	—11	—11	—38	98	—23	—23
20	273	261	262	1232	1190	1056	—4	—4	—9	—74	—73	—194	—7	—12	—25	—2	0	—10	121	21	—106
21	274	264	274	1188	1198	1081	—3	—1	—3	—72	—27	—72	—3	—4	—8	2	2	1	136	46	—159
22	261	261	261	1176	1176	1121	—10	—9	—9	—167	—166	—166	—3	—15	—15	—3	1	1	48	48	—82
23	274	263	263	1142	1154	1154	—3	—3	—8	—66	—66	—176	—5	—5	—6	5	5	—6	144	—71	—71
24	265	265	257	1234	1234	1044	—7	—10	—10	—121	—182	—182	—14	—30	—30	—14	—16	—16	61	61	—75
25	268	268	268	1217	1217	1048	—5	—5	—5	—104	—102	—102	—4	—15	—15	—4	1	1	89	89	—141
26	269	269	276	1203	1203	1072	—5	0	0	—104	0	0	—1	0	0	—1	0	0	98	98	—169
27	267	258	258	1198	1140	1140	—8	—8	—11	—140	—140	—213	—14	—14	—16	—2	—2	—16	91	—35	—35
28	268	260	268	1140	1175	1140	—7	—5	—7	—139	—91	—139	—3	—8	—8	8	8	3	116	0	—116

b) of opposite kind

$$U_{1,2}(\mathbf{R}) = -\frac{e^2}{\mathbf{R}} - 4\frac{e^2}{Md}\sum_{\mathbf{k}} \cos(\mathbf{kR}) \tag{30}$$

$$\times \sum_{s} \{(\vec{\pi}_{e,s,\mathbf{k}} \vec{\Psi}_{q,s,\mathbf{k}}) + (\vec{\pi}_{q,s,\mathbf{k}} \vec{\Psi}_{e,s,\mathbf{k}})\},$$

where the indices q and e refer, respectively, to the hole and to the electron.

In the expression for the energy (29) and (39) there occurs summation over the wave vector k or, what amounts to the same thing, over the nondimensional wave vector $\vec{\varkappa}$. The summation is carried out over the interval $\varkappa_i = \pm 1/2$, in which it has $N = M^{1/3}$ values: $\varkappa_i = 0; \pm 1/N; \pm 2/N; \ldots \pm 1/2$. In view of the large value of N, the summation over $\vec{\varkappa}$ can be replaced by integration over $d\varkappa_1$, $d\varkappa_2 d\varkappa_3$. The integral can be computed by any approximation method. We made use of Simpson's rule.

4. RESULTS OF THE CALCULATION

In view of the tedious nature of the calculation, all the quantities have been found for the minimal R--closest approach of the charges. Like charges are placed on neighboring like ions, with $|\mathbf{R}| = |\mathbf{a}_3| = 2^{-1/2} d$; unlike charges on neighboring ions with $|\mathbf{R}| = d/2$. The results are given in Table IV.

Mott[4] has computed the potential of the field created at the point when the point charge q is located in the crystal polarized by it, and DuPre[5] gave the energy U_q of the charge q in this field.

As would also be expected, on the basis of Eqs. (21) and (22):

$$U_q = qV_q = -q\sum_{s,l} \frac{(\mathbf{p}_s^l \mathbf{r}_s^l)}{r_s^{l3}} \tag{31}$$

$$= -\frac{8e^2}{Md}\sum_{s,\mathbf{k}} (\vec{\pi}_{s,\mathbf{k}} \vec{\Psi}_{s,\mathbf{k}}),$$

i.e., U_q differs only by the coefficient 2 from the eigen energy (28) in the case $q = \pm e$.

The eigen energy (28) was computed, as also $U_{1,2}$, and the results obtained for $d = 6.27 \times 10^{-8}$ cm are given in Table V.

Correspondingly, the potential V_q is expressed by the nondimensional quantity V_q/V_0, for the case $V_0 = (q/4\pi d)(1 - n^{-2})$ is equal to

$$\frac{V_q}{V_0} = -\frac{16\pi}{1 - n^{-2}}\sum_{s}\sum_{\mathbf{k}} (\vec{\pi}_{s,\mathbf{k}} \vec{\Psi}_{s,-\mathbf{k}}). \tag{32}$$

If we set $n^{-2} = 0.4600$ (for KCl), then we get the results of Table VI. It is easy to verify that, when the charges are entirely separated ($R \to \infty$), we get the Coulomb expression

$$U_{1,2}(\mathbf{R}) = e^2/Rn^2.$$

The author considers it his pleasant duty to express his gratitude to K. B. Tolpygo for suggesting the theme and for his lively interest in the work.

TABLE IV. Interaction energy $U_{1,2}(\mathbf{R})$

Charges	Interaction Energy		
	in units of $e^2\sqrt{2}/d$	in ev	in % of Coulomb's law
Electron-electron	0.512	1,665	111
Electron-hole	—0.779	—2.553	120
Hole-hole	0.540	1.756	117
Coulomb's law	0.460	1.469	100

TABLE V. Eigenenergy

Charges	according to Mott, in ev	According to the Author	
		cgs units	in ev
Electron	—2.02	$-0{,}2090(4e^2/d)$	—1.922
Hole	—1.44	$-0.1470(4e^2/d)$	—1.325

TABLE VI. Potential (in arbitrary units)

Charges	According to DuPre et al.				According to the Author
	macroscopic	first approximation	second approximation	third approximation	
Electron	18.96	20.60	20.44	20,27	19.45
Hole	—	—14,69	—	—	—13.69

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[1] S. I. Pekar, *Investigations on the Electronic Theory of Crystals*, Gostekhizdat, Leningrad-Moscow, 1951, Sec. 5.

[2] M. F. Deigen, J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 818 (1948).

[3] G. E. Zil'berman, J. Exptl. Theoret. Phys. (U.S.S.R.) **19**, 135 (1949).

[4] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. 34, 485 (1938).

[5] E. S. Rittner, R. A. Hutner and F. K. DuPre, J. Chem.Phys. **17**, 198 (1949).

[6] T. I. Liberberg and K. B. Tolpygo, J. Exptl. Theoret. Phys. (U.S.S.R.) 26, 35 (1954).

[7] P. P. Ewald, Ann. Physik **64**, 253 (1951).

[8] I. G. Zaslavskaia and K. B. Tolpygo, Trudy Inst. Fiz. Akad. Nauk, Ukrainian SSR 4, 71 (1953).

[9] M. Born and M. Goeppert-Mayer, *Theory of Solids* (Russian translation) ONTI, Moscow-Leningrad, 1938.

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