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Effect of Overlap on Electrostatic Lattice Potentials in Ionic Crystals*

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A calculation has been made of the effect of ionic overlap on electrostatic lattice potentials. The calculation is based on a model which assumes each ion to consist of a core represented by a point charge, and a valence electron density represented by a normalized Gaussian centered at the core site. The contribution of any ion to the potential at a point in the crystal consists of the sum of two terms. One represents the potential due to a neutral configuration (core plus compensating Gaussian); the second the potential due to the unbalanced Gaussian charge of the ion. Upon taking appropriate lattice sums, the lattice potential is obtained in a rapidly convergent form, involving only the usual Ewald sums. The "self-potential" in NaCl and ZnS is evaluated as a function of the half-width α of the assumed Gaussian valence density of the ions. For $\alpha=0$ the result is the well-known "Madelung Potential." The effect of overlap on the potential at an interstitial site in NaCl and ZnS structures is also examined. From the results of the analysis it can be concluded that lattice potentials are sensitive to ionic overlap, so that the effect of overlap cannot in general be neglected.

A table of the available Ewald sums for a cubic lattice is given to aid in the calculation of lattice potentials in cubic crystals.

1. THEORY

FOR many purposes, such as calculation of electronic energy levels at a vacancy,[1] energy band calculations in ionic crystals,[2] calculation of activation energy for impurity or vacancy diffusion,[3] and calculations of the splitting of atomic energy levels of a phosphor activator,[4] it is necessary to know accurately the electrostatic potential $\varphi(\mathbf{r})$ in an ionic crystal. The conventional method of calculating lattice potentials[5] proceeds by shrinking each ion down to a point singularity whose charge equals the net charge of the ion. Depending on the substance concerned, this may or may not be a good approximation; for example there may be less error introduced in assuming that the ions do not overlap in[6] NaCl than in PbS with the same structure where one expects a considerable overlap of the valence electrons.[7] The method which will be described here may be considered as a first step in the direction of accurate determination of lattice potentials in real crystals with overlapping ions, and leads to the convenient evaluation of these lattice potentials in terms of the familiar Ewald sums.

We begin by constructing a "Gaussian" ion, located at the point $\mathbf{r}_{\mathrm{k+n}}=\mathbf{r}_{\mathrm{k}}+\mathbf{r}_{\mathrm{n}}$ where $\mathbf{r}_{\mathrm{k}}=k_1\mathbf{a}_1+k_2\mathbf{a}_2+k_3\mathbf{a}_3$ is a basis vector, and $\mathbf{r}_{\mathrm{n}}=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$ (n_i are integers) is a lattice vector in the cubic crystal space defined by the three orthogonal vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ with $|\mathbf{a}_i|=a$. We divide the electrons of the ion into "inner" (tightly bound) and "valence" electrons; the inner electrons plus the nucleus will be called the core, with net charge q_{k}^c and will be represented as a point density:

$$\rho_{\mathrm{k}}^c(\mathbf{r}-\mathbf{r}_{\mathrm{k+n}})=q_{\mathrm{k}}^c\delta(\mathbf{r}-\mathbf{r}_{\mathrm{k+n}}). \tag{1}$$

The valence electron density will be represented as a Gaussian,[8] normalized to q_{k}^v:

$$\rho_{\mathrm{k}}^v(\mathbf{r}-\mathbf{r}_{\mathrm{k+n}})=(q_{\mathrm{k}}^v/\pi^{\frac{3}{2}}\alpha_{\mathrm{k}}^3)\exp[-(\mathbf{r}-\mathbf{r}_{\mathrm{k+n}})^2/\alpha_{\mathrm{k}}^2]. \tag{2}$$

The net charge of the ions at $\mathbf{r}_{\mathrm{k+n}}$ is $q_{\mathrm{k}}^c+q_{\mathrm{k}}^v$ and the "half width" of the valence electron density is α_{k}.

The contribution to the potential at the field point $\mathbf{r}$ due to the ion at $\mathbf{r}_{\mathrm{k+n}}$ is

$$\varphi_{\mathrm{k+n}}(\mathbf{r})=\int\{\rho_{\mathrm{k}}^c(\mathbf{r}'-\mathbf{r}_{\mathrm{k+n}})+\rho_{\mathrm{k}}^v(\mathbf{r}'-\mathbf{r}_{\mathrm{k+n}})\}d\mathbf{r}'/|\mathbf{r}-\mathbf{r}'|,$$

or:

$$\varphi_{\mathrm{k+n}}(\mathbf{r})=\varphi_{\mathrm{k+n}}^{(1)}(\mathbf{r})+\varphi_{\mathrm{k+n}}^{(2)}(\mathbf{r}), \tag{3}$$

where

$$\varphi_{\mathrm{k+n}}^{(1)}(\mathbf{r})=(q_{\mathrm{k}}^v-q_{\mathrm{k}}^c)\times\int\frac{\exp[-\pi^2\alpha_{\mathrm{k}}^2|\mathbf{n}|^2+2\pi i\mathbf{n}\cdot(\mathbf{r}-\mathbf{r}_{\mathrm{k+n}})]}{\pi|\mathbf{n}|^2}d\mathbf{n}, \tag{3.1}$$

$$\varphi_{\mathrm{k+n}}^{(2)}(\mathbf{r})=q_{\mathrm{k}}^c\{[1-\Phi(|\mathbf{r}-\mathbf{r}_{\mathrm{k+n}}|/\alpha_{\mathrm{k}})]/|\mathbf{r}-\mathbf{r}_{\mathrm{k+n}}|\}, \tag{3.2}$$

where we use the well known transformation of the potential due to a Gaussian, with $\mathbf{n}=\xi\mathbf{b}_1+\eta\mathbf{b}_2+\zeta\mathbf{b}_3$ a running vector in the Fourier space defined by the vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$, reciprocal to $\mathbf{a}_j$, i.e., $\mathbf{b}_i\cdot\mathbf{a}_j=\delta_{ij}$. $\Phi(t)$ is defined as $2\pi^{-\frac{1}{2}}\int_0^t\exp(-x^2)dx$. The contribution to the potential at $\mathbf{r}$ from the unbalanced Gaussian charge of the ion is $\varphi_{\mathrm{k+n}}^{(1)}(\mathbf{r})$, and $\varphi_{\mathrm{k+n}}^{(2)}(\mathbf{r})$ represents the contribution to the potential at $\mathbf{r}$ from the core plus a

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[1] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949); L. Pincherele, Proc. Phys. Soc. (London) **A64**, 648 (1951); T. Inui and Y. Uemura, Progr. Theoret. Phys. (Japan) **5**, 252 (1950).

[2] W. Shockley, Phys. Rev. **50**, 754 (1936); D. Bell *et al.*, Proc. Roy. Soc. (London) **A217**, 71 (1953).

[3] G. J. Dienes, J. Chem. Phys. **16**, 620 (1948).

[4] P. Yuster and C. J. Delbecq, J. Chem. Phys. **21**, 892 (1953).

[5] P. P. Ewald, Ann. Physik, **64**, 253 (1921); M. Born and M. G. Mayer, *Handbuch der Physik* (Springer Verlag, Berlin, 1933), second edition, Vol. 24, Part 2, p. 710.

[6] M. Renninger, Acta. Cryst. **5**, 711 (1952).

[7] See calculations of D. Bell *et al.*, reference 2.

[8] The use of Gaussian wave functions (and densities) for valence electrons in atoms and molecules has been discussed by S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950); R. McWeeney, Nature **166**, 21 (1950); G. F. Neumark, thesis, Columbia University Chemistry Department, 1951 (unpublished).

Gaussian charge which compensates the core charge. For simplicity, we call $q_k^{(1)}=q_k^v-q_k^c$ and $q_k^{(2)}=q_k^c$, so $q_k^{(1)}$ is the net charge of the ion, $q_k^{(2)}$ the core charge.

The total potential at $\mathbf{r}$ due to all ions in the crystal is

$$\varphi(\mathbf{r})=\overset{(\infty)}{\underset{\mathbf{n}}{\mathcal{S}}}\sum_{\mathbf{k}=1}^{p}\varphi_{\mathbf{k}+\mathbf{n}}(\mathbf{r}),\tag{4}$$

where the sums are over the translation lattice $\mathbf{n}$, and over the p points of the basis, $\mathbf{k}$. Using (3), (3.1), and (3.2) in (4), we find

$$\varphi(\mathbf{r};\alpha_1,\cdots,\alpha_p)=\sum\nolimits_{(\mathbf{k})}\{q_{\mathbf{k}}^{(1)}\psi^{(1)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha_{\mathbf{k}})+q_{\mathbf{k}}^{(2)}\psi^{(2)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha_{\mathbf{k}})\},\tag{4.1}$$

with

$$\psi^{(1)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha_{\mathbf{k}})=\mathcal{S}_{(\mathbf{h})}'\exp[-\pi^2\alpha_{\mathbf{k}}^2|\mathbf{b}_{\mathbf{h}}|^2+2\pi i\mathbf{b}_{\mathbf{h}}\cdot(\mathbf{r}-\mathbf{r}_{\mathbf{k}})]/\pi\Delta|\mathbf{b}_{\mathbf{h}}|^2,\tag{4.2}$$

and

$$\psi^{(2)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha_{\mathbf{k}})=\mathcal{S}_{(\mathbf{n})}[1-\Phi(|\mathbf{r}-\mathbf{r}_{\mathbf{k}+\mathbf{n}}|/\alpha_{\mathbf{k}})]/|\mathbf{r}-\mathbf{r}_{\mathbf{k}+\mathbf{n}}|-\pi\alpha_{\mathbf{k}}^2/\Delta,\tag{4.3}$$

where $\Delta=|\mathbf{a}_1\times\mathbf{a}_2\cdot\mathbf{a}_3|$ is the cell volume, and $\mathbf{b}_{\mathbf{h}}$ is a lattice vector in Fourier space. The expression (4.1), then, gives the potential at $\mathbf{r}$ when each different type of ion (labeled by $\mathbf{k}$) has its own characteristic Gaussian half-width $\alpha_{\mathbf{k}}$. In case the ion of the kth sort is considered as composed of a point core plus a sum of Gaussian valence densities,[8] an appropriate modification of (4.1) can be given for the potential, although this will not be discussed here.

The equation analogous to (4.1) for the case of a lattice composed of point ions of net charge $q_{\mathbf{k}}^{(1)}$ is[5]

$$\varphi(\mathbf{r})=\sum\nolimits_{(\mathbf{k})}q_{\mathbf{k}}^{(1)}\{\psi^{(1)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha)+\psi^{(2)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha)\}.\tag{4.1$'$}$$

In all ionic crystals, the basis is neutral, so that $\sum_{(k)}q_k^{(1)}=0$.

The sums (4.2) and (4.3) have been extensively discussed by Ewald,[9] and their physical significance given by him. Thus, $\psi^{(1)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha)$ is the potential at $\mathbf{r}$ due to a lattice of normalized Gaussians centered at $\mathbf{r}_{\mathbf{k}}$ and equivalent points, each of content $+1$, half-width α, the whole immersed in a uniform (compensating) density $-1/\Delta$. $\psi^{(2)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha)$ is the potential at $\mathbf{r}$ due to a simple lattice of point charges of content $+1$ at $\mathbf{r}_{\mathbf{k}}$ and equivalent points, each point charge surrounded by a Gaussian of content -1, and half-width α. If we define

$$\psi(\mathbf{r})=\psi^{(1)}(\mathbf{r};\alpha)+\psi^{(2)}(\mathbf{r};\alpha),\tag{4.4}$$

then $\psi(\mathbf{r})$ represents the "neutralized" potential[5,9] of a lattice of positive point charges, has full cubic symmetry, and is independent of α. If $\psi(\mathbf{r})$ has been found for a particular value of $\mathbf{r}$, either $\psi^{(1)}(\mathbf{r};\alpha)$ or $\psi^{(2)}(\mathbf{r};\alpha)$ but in general not both, needs to be evaluated from the series (4.2), (4.3). [Depending on the value of α, either $\psi^{(1)}(\mathbf{r};\alpha)$ or $\psi^{(2)}(\mathbf{r};\alpha)$ will converge rapidly, so that computational labor is considerably reduced.] Furthermore, when $\alpha_{\mathbf{k}}\rightarrow 0$, we have a lattice of point ions and $\psi^{(1)}(\mathbf{r};\alpha_{\mathbf{k}})\rightarrow\psi(\mathbf{r})$, $\psi^{(2)}(\mathbf{r};\alpha_{\mathbf{k}})\rightarrow 0$. Thus we see how (4.1) goes into (4.11) in this limit of point ions. When $\alpha_{\mathbf{k}}\rightarrow\infty$, $\psi^{(1)}(\mathbf{r};\alpha_{\mathbf{k}})\rightarrow 0$ and $\psi^{(2)}(\mathbf{r};\alpha_{\mathbf{k}})\rightarrow\psi(\mathbf{r})$, so that (4.1) gives a finite value for $\varphi(\mathbf{r};\infty)$. This is as it should be, since the physical situation corresponds to a "crystal" composed of the point cores immersed in a uniform negative electric fluid.

The entire problem of evaluating lattice potentials in a Gaussian ionic lattice is then, merely one of finding the values of the appropriate Ewald sums, $\psi(\mathbf{r})$, $\psi^{(1)}(\mathbf{r};\alpha)$, $\psi^{(2)}(\mathbf{r};\alpha)$. In the Appendix a table of the calculated values of $\psi(\mathbf{r})$ for different $\mathbf{r}$ is given, to aid in calculations based on (4.1) or (4.1′).

In the illustrative calculations presented here α will remain as a parameter; however, it might be assigned to a given ion by fitting the outer part of the appropriate Hartree radial density to a Gaussian.[10] From another point of view, the $\alpha_{\mathbf{k}}$ of the different ions in the crystal are related to their degree of overlap, which can be evaluated exactly for Gaussian ions. Thus, if the two Gaussians are located at $\mathbf{r}_{\mathbf{k}'}$ and $\mathbf{r}_{\mathbf{k}+\mathbf{n}}$, nor-

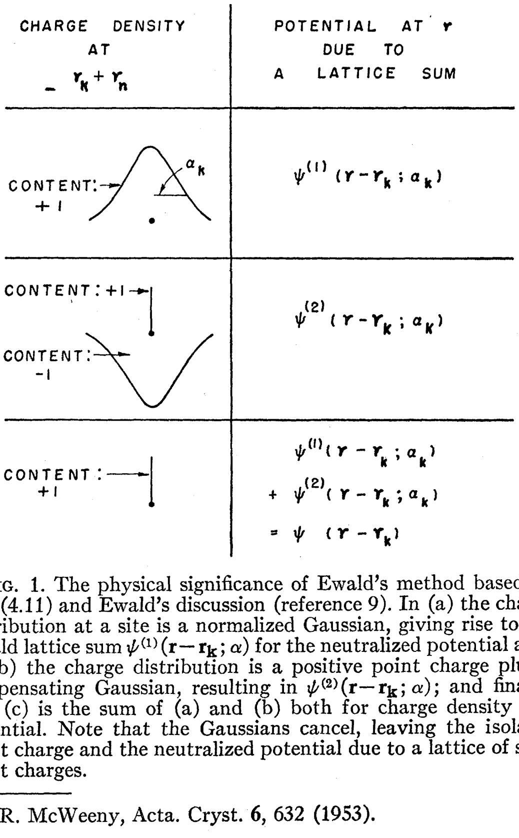

FIG. 1. The physical significance of Ewald's method based on Eq. (4.11) and Ewald's discussion (reference 9). In (a) the charge distribution at a site is a normalized Gaussian, giving rise to the Ewald lattice sum $\psi^{(1)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha)$ for the neutralized potential at $\mathbf{r}$; in (b) the charge distribution is a positive point charge plus a compensating Gaussian, resulting in $\psi^{(2)}(\mathbf{r}-\mathbf{r}_{\mathbf{k}};\alpha)$; and finally, line (c) is the sum of (a) and (b) both for charge density and potential. Note that the Gaussians cancel, leaving the isolated point charge and the neutralized potential due to a lattice of such point charges.

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[9] P. P. Ewald, Nachr. Akad. Wiss. Göttingen, Math. physik. Kl. **3**, 55 (1938). (Independently) F. Bertaut, J. phys. radium **13**, 499 (1952), which has some points in common with the present paper. Also see C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), Appendix B.

[10] R. McWeeny, Acta. Cryst. **6**, 632 (1953).

malized to $q_{k'}$ and q_k, with half-widths $\alpha_{k'}$ and α_k, respectively, we can evaluate their overlap integral:

$$\mathcal{I}(\mathbf{r}_{k'}-\mathbf{r}_{k+n};\alpha_k,\alpha_{k'})\equiv\int\rho_{k'}(\mathbf{r}-\mathbf{r}_{k'})\rho_k(\mathbf{r}-\mathbf{r}_{k+n})d\mathbf{r}$$

$$=q_kq_{k'}[\pi(\alpha_k^2+\alpha_{k'}^2)]^{-\frac{3}{2}}$$

$$\times\exp[-(\mathbf{r}_{k'}-\mathbf{r}_{k+n})^2/(\alpha_k^2+\alpha_{k'}^2)]. \quad (5)$$

To calculate the total overlap between the ion at $\mathbf{r}_{k'}$, and all other ions, (5) must be summed over $\mathbf{n}$ and $\mathbf{k}$. At small values of α_k, the overlap is due to the nearest neighboring ions to the one under consideration, and so the value of (5) may be compared with the overlap integral calculated using Hartree or Thomas-Fermi densities for the ions and considering only nearest neighbor overlap. The α_k can then be chosen to make the Gaussian overlap integral (5) equal to that calculated from these densities.

As can be seen by comparing (4.1) and (4.1′), the present method is intimately connected with Ewald's method—indeed, it involves weighting the two Ewald sums, and recognizing the physical significance of the resulting expression. To illustrate the latter remark, Figs. 1 and 2 show the physical significance of the calculations based on Eqs. (4.1′) and (4.1), respectively. In Fig. 1(a), (b), (c), we show the charge density at the ion site $\mathbf{r}_{k+n}$, and the potential at $\mathbf{r}$ due to a lattice sum of such densities. Thus Fig. 1(a) shows the isolated Gaussian, and the "neutralized" potential $\psi^{(1)}(\mathbf{r}-\mathbf{r}_k;\alpha)$; Fig. 1(b) shows the neutral charge configuration giving rise to $\psi^{(2)}(\mathbf{r}-\mathbf{r}_k;\alpha)$; and the last line, Fig. 1(c), is the sum of the two above it. In Fig. 2(a), (b), (c), we see the result of weighting the charge densities before adding.

TABLE I. Variation of $\psi^{(1)}(\mathbf{r};\alpha)$ with α.

α/a	$a\bar{\psi}^{(1)}(0,0,0;\alpha)$	$a\psi^{(1)}(0,0,\frac{1}{2};\alpha)$	$a\psi^{(1)}(0,\frac{1}{2},\frac{1}{2};\alpha)$	$a\psi^{(1)}(\frac{1}{2},\frac{1}{2},\frac{1}{2};\alpha)$	$a\psi^{(1)}(\frac{1}{4},\frac{1}{4},\frac{1}{4};\alpha)$
0	−2.8373	−0.0959	−0.5825	−0.8019	−0.2005
0.02	−2.8360	−0.0946	−0.5812	−0.8006	−0.1993
0.04	−2.8323	−0.0909	−0.5775	−0.7969	−0.1955
0.06	−2.8260	−0.0846	−0.5712	−0.7906	−0.1892
0.08	−2.8172	−0.0758	−0.5624	−0.7818	−0.1804
0.1	−2.8059	−0.0645	−0.5511	−0.7705	−0.1691
0.12	−2.7921	−0.0507	−0.5373	−0.7567	−0.1553
0.14	−2.7757	−0.0343	−0.5209	−0.7403	−0.1389
0.16	−2.7569	−0.0155	−0.5021	−0.7215	−0.1204
0.18	−2.7355	+0.0058	−0.4807	−0.7001	−0.1002
0.25	−2.6410	+0.0816	−0.3866	−0.6056	−0.0371
0.30	−2.5532	+0.1130	−0.3045	−0.5324	−0.0136
0.40	−2.3373	+0.0978	−0.1503	−0.3199	−0.0009
0.45	−2.2112	+0.0726	−0.0957	−0.2257	−0.0002
0.50	−2.0818	+0.0494	−0.0585	−0.1488	0
0.75	−1.4969	+0.0025	−0.0025	−0.0074	0
1	−1.1285	0	0	0	0
2	−0.5642	0	0	0	0
∞	0	0	0	0	0

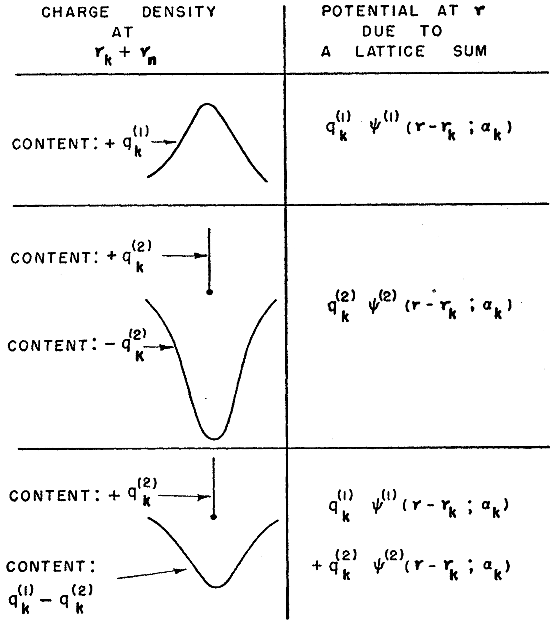

FIG. 2. The physical significance of calculations based on Eq. (4.1). 2(a), (b), (c) are analogous to 1(a), (b), (c). We note that by weighting the charge densities and potentials before adding, the last line corresponds to a "Gaussian" ion.

We emphasize again that the basic physical idea behind the method presented here is that rapid convergence of lattice potentials is obtained if the potential due to any given ion is split into two terms: one representing the contribution due to a neutral configuration (core plus a compensating Gaussian), the second the potential due to the remaining Gaussian charge of the ion.

2. ILLUSTRATIVE APPLICATIONS

To illustrate the calculations based on (4.1) we will evaluate the Madelung potential and the potential at an interstitial site in rocksalt and zincblende structures as a function of the Gaussian half-width of the ions. In this treatment we will assume that each ion is described by a single Gaussian, and we will take the half-widths of the different ions in the same structure to be equal. The values of the Ewald sums needed are given in Table I. Only $\psi^{(1)}(\mathbf{r};\alpha)$ is listed there, as $\psi^{(2)}(\mathbf{r};\alpha)=\psi^{(1)}(\mathbf{r};0)-\psi^{(1)}(\mathbf{r};\alpha)$.

(a) NaCl Structure

This structure consists of cations at (0,0,0) f.c.c.; anions at (0,0,½) f.c.c. We will treat NaCl by taking the ions to have net charges $\pm1|e|$, as is usual. We lump together the point nucleus and inner electrons of sodium to give a point core of charge $+7|e|$; the six $2p$ electrons form the Gaussian valence density. For chlorine we take the core charge $+5|e|$ and the six $3p$ electrons form the valence density. Thus

$$q_{\mathrm{Na}}^{(1)}=+|e|,\quad q_{\mathrm{Na}}^{(2)}=+7|e|;\quad q_{\mathrm{Cl}}^{(1)}=-|e|,$$
$$q_{\mathrm{Cl}}^{(2)}=+5|e|,\quad \alpha_{\mathrm{Na}}=\alpha_{\mathrm{Cl}}.$$

The potential at (0,0,0) is the self-potential or "Madelung Potential" of the lattice, i.e., the potential at (0,0,0) of the entire lattice except the ion at (0,0,0). It is thus the effective potential at the center of a

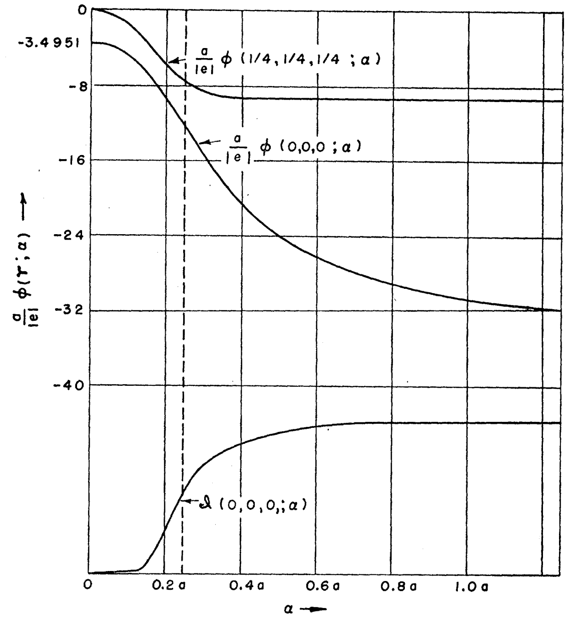

FIG. 3. Variation of lattice potentials and overlap integral with Gaussian half width α, in NaCl. The curve labelled $(a/|e|)$ $\varphi(\frac{1}{4},\frac{1}{4},\frac{1}{4};\alpha)$ shows the variation with α of the potential at an interstitial position, Eq. (7). The following curve gives the variation with α of self-potential, Eq. (6); at $\alpha=0$ this is the standard Madelung potential for point ions. The last curve gives the overlap integral, Eq. (8), in arbitrary units. The dotted line indicates α equal to half the internuclear separation.

positive ion vacancy. The expression for the self-potential is obtained from (4.1) by the usual limiting process.[5] From (4.1), we have

$$\begin{aligned}\varphi(0,0,0;\alpha)=|e|[\bar{\psi}^{(1)}(0,0,0;\alpha)+7\bar{\psi}^{(2)}(0,0,0;\alpha)]\\ +3|e|[\psi^{(1)}(\tfrac{1}{2},\tfrac{1}{2},0;\alpha)+7\psi^{(2)}(\tfrac{1}{2},\tfrac{1}{2},0;\alpha)]\\ +|e|[-\psi^{(1)}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\alpha)+5\psi^{(2)}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\alpha)]\\ +3|e|[-\psi^{(1)}(0,0,\tfrac{1}{2};\alpha)+5\psi^{(2)}(0,0,\tfrac{1}{2};\alpha)].\end{aligned}\quad(6)$$

The functions $\bar{\psi}^{(1)}(0,0,0;\alpha)$ and $\bar{\psi}^{(2)}(0,0,0;\alpha)$ are the limiting forms of (4.2) and (4.3) (see reference 5).

The position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ is an interstitial position in the structure, where, for point ions, the potential is by symmetry, zero.

$$\begin{aligned}\varphi(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)=4|e|[\psi^{(1)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)+7\psi^{(2)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)]\\ +4|e|[-\psi^{(1)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)+5\psi^{(2)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)]\\ =48|e|\psi^{(2)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha).\end{aligned}\quad(7)$$

In Fig. 3 the potentials (6) and (7) are plotted as functions of α (upper 2 curves). At $\alpha=0$, $\varphi(0,0,0;0)=-3.4951|e|/a$ (which is the well-known Madelung constant of NaCl for point ions), and $\varphi(\frac{1}{4},\frac{1}{4},\frac{1}{4};0)=0$. As α increases, both of these potentials fall, reflecting the increase in valence charge density accompanying increasing overlap. Figure 3 also shows the variation with α of the total overlap integral

$$\mathcal{I}(0,0,0;\alpha)=\overset{(\infty)}{\underset{\mathbf{n}}{S}}\sum_{\mathbf{k}=1}^{p}\mathcal{I}(\mathbf{r}_{\mathbf{k}+\mathbf{n}};\alpha).\quad(8)$$

The latter is a measure of the total amount of valence charge overlapping a sodium ions. Since $\alpha=0.25a$ is the half-width equal to half the internuclear spacing (dotted line), we can see that lattice potentials are indeed sensitive to overlap.

(b) Zincblende Structure

This structure consists of cations at (0,0,0) f.c.c., anions at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ f.c.c. We treat ZnS, and take the ions to have net charges $\pm 0.5|e|$.[11] The zinc core will be taken as $+2|e|$, with 1.5 valence electrons in the Gaussian density. For sulfur the core is $+6|e|$, with 6.5 valence electrons in the Gaussian. These net charges may be considered to arise from chemical bonds of mixed (ionic plus covalent) character formed from hybrids of $4s$, $4p$; $3s$, $3p$ orbitals on zinc and sulfur respectively. Thus we have

$$q_{\mathrm{Zn}}^{(1)}=+0.5|e|,\quad q_{\mathrm{Zn}}^{(2)}=+2|e|;\quad q_{\mathrm{S}}^{(1)}=-0.5|e|,$$
$$q_{\mathrm{S}}^{(2)}=+6|e|,\quad \alpha_{\mathrm{Zn}}=\alpha_{\mathrm{S}}.$$

The self potential $\varphi(0,0,0;\alpha)$, and the potential at an interstitial site, $\varphi(\frac{1}{2},\frac{1}{2},\frac{1}{2};\alpha)$ will be evaluated.

$$\begin{aligned}\varphi(0,0,0;\alpha)=|e|[0.5\bar{\psi}^{(1)}(0,0,0;\alpha)+2\bar{\psi}^{(2)}(0,0,0;\alpha)]\\ +3|e|[0.5\psi^{(1)}(\tfrac{1}{2},\tfrac{1}{2},0;\alpha)+2\psi^{(2)}(0,\tfrac{1}{2},\tfrac{1}{2};\alpha)]\\ +4|e|[-0.5\psi^{(1)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)+6\psi^{(2)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)],\end{aligned}\quad(9)$$

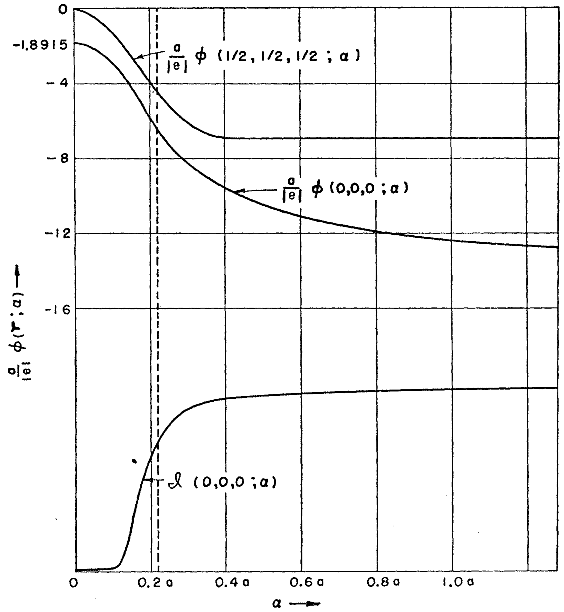

FIG. 4. Variation of lattice potentials and overlap integral with Gaussian half width α, in ZnS. The ions have net charges $\pm 0.5|e|$. The top curve gives the potential at an interstitial position, Eq. (10). The following curve gives the self-potential, Eq. (9); at $\alpha=0$ this is the Madelung potential for point ions. The last curve gives the overlap integral, Eq. (8), in arbitrary units. The dotted line indicates α equal to half the internuclear separation.

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[11] M. Born and E. Bormann, Deutsch. Phys. Gesell. **21**, 733 (1919), and B. D. Saksena, Phys. Rev. **81**, 1012 (1951), more or less agree on an effective charge of about this range. H. D. Vasileff (private communication), of this laboratory, has calculated effective charges of $\pm 0.51|e|$.

and

$$\varphi(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\alpha)=|e|[0.5\psi^{(1)}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\alpha)+2\psi^{(2)}(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2};\alpha)]$$
$$+3|e|[0.5\psi^{(1)}(0,0,\tfrac{1}{2};\alpha)+2\psi^{(2)}(0,0,\tfrac{1}{2};\alpha)]$$
$$+4|e|[-0.5\psi^{(1)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)+6\psi^{(2)}(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4};\alpha)]. \quad (10)$$

The potentials (9) and (10) are plotted in Fig. 4, as the two upper curves. Again, $\alpha=0$ corresponds to the case of point ions, where the Madelung potential for ions of net charge $\pm 0.5|e|$ in zincblende is $\varphi(0,0,0;0) = -1.8915|e|/a$, and $\varphi(\frac{1}{2},\frac{1}{2},\frac{1}{2};0)=0$. We also plot $\mathcal{I}(0,0,0;\alpha)$ [see (8)] as a measure of the total valence charge overlapping a zinc ion. The dotted line indicates the half-width equal to half the internuclear spacing where $\alpha=\sqrt{3}a/8$.

The same characteristic features are apparent in Figs. 3 and 4. Thus, lattice potentials change appreciably when the Gaussian densities begin to overlap, which occurs roughly at a half-width equal to one-fourth of the internuclear separation. However, even at very small overlap the potential is affected by the finite size of the ions. With increasing half-width the potentials rapidly approach their ultimate values, mirroring the rapid approach of the total valence density to its ultimate constant value at $\alpha=\infty$.

3. CONCLUSIONS AND SUMMARY

A method has been presented for calculating electrostatic lattice potentials in ionic crystals composed of "Gaussian" ions. Numerically, the method involves only a slight change in the usual Ewald formulas, and therefore preserves the ease of calculation characteristic of the latter.

TABLE II. Calculated Ewald sums for a cubic lattice.[a]

$a\bar{\psi}(0,0,0) = -2.8373$	
$\mathbf{r}=(x,y,z)$	$a\psi(\mathbf{r})$
0, 0, $\frac{1}{2}$	-0.09593
0, $\frac{1}{8}$, $\frac{1}{8}$	$+2.8825$*
0, $\frac{1}{4}$, $\frac{1}{4}$	$+0.23941$
0, $\frac{3}{8}$, $\frac{3}{8}$	-0.43387*
0, $\frac{1}{2}$, $\frac{1}{2}$	-0.58252
1/24, 1/24, 1/24	$+11.0249$*
1/24, 11/24, 11/24	-0.5714*
1/12, 1/12, 1/12	$+4.1431$*
1/12, 5/12, 5/12	-0.5389
$\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{8}$	$+1.875$
$\frac{1}{8}$, $\frac{3}{8}$, $\frac{3}{8}$	-0.480
$\frac{1}{8}$, $\frac{3}{8}$, $\frac{1}{2}$	-0.5576*
$\frac{1}{6}$, $\frac{1}{6}$, $\frac{1}{6}$	$+0.7885$*
$\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{3}$	-0.4027
5/24, 5/24, 5/24	$+0.1741$*
5/24, 7/24, 7/24	-0.3077*
$\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{8}$	$+0.6178$*
$\frac{1}{4}$, $\frac{1}{8}$, $\frac{3}{8}$	-0.2790*
$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	-0.2005
$\frac{1}{4}$, $\frac{3}{8}$, $\frac{3}{8}$	-0.5912*
$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$	-0.5307
$\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{3}$	-0.5946*
$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$	-0.8019

[a] The values followed by an asterisk are newly computed by the author; the others are given by Hund (reference 12).

The effect of increasing ionic overlap (increasing the Gaussian half-width) upon Madelung and interstitial lattice potentials in NaCl and ZnS was investigated.

The results of the calculation indicate that lattice potentials are sensitive to overlap, contrary to the usual assumption made in treating as equal the lattice potentials of all substances with the same crystal structure and effective ionic charge. Indeed, the calcution shows us that even at very small overlap there may be a significant difference between lattice potentials computed for point ions and the true potential for the given crystal. Since the present paper is intended more to illustrate this point by means of a straightforward calculation based on a simple model rather than to obtain any exact results for a particular substance, no attempt will be made here to fit known densities to Gaussians. As our knowledge of electron densities improves, from x-ray diffraction Fourier analysis and/or accurate quantum mechanical calculations, one expects that more attention must be paid, in evaluating lattice potentials and the quantities which depend upon them, to the actual spatial extent of valence electron densities. The present calculation, therefore, represents a first step in this direction.

4. ACKNOWLEDGMENT

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5. APPENDIX

(a) Ewald Sums for a Cubic Lattice

The available Ewald sums $\psi(\mathbf{r})$ for a cubic lattice are listed in Table II. Those followed by an asterisk (*) are newly computed by the author; the others are given by Hund.[12]

(b) The Hund Identities

Hund[12] has pointed out that various identities exist among the Ewald sums which serve both as a check on numerical work, and as a means of obtaining some unknown values from these already available. Since these identities are of considerable value, we take the liberty of including Hund's justification of them[13] in the present paper. Now $\psi(x,y,z)$ represents the neutralized potential ar $\mathbf{r}=(x,y,z)$ due to a simple cubic lattice of point ions of side 1 unit. If we redefine the cell so that it has side 2 units, introducing thereby an artificial basis, then,

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[12] F. Hund, Z. Physik **94**, 11 (1935).

[13] F. Hund (private communication, August 27, 1951).

for the potential at the same point in crystal space we now have

$$\tfrac{1}{2}[\psi(\tfrac{1}{2}x,\tfrac{1}{2}y,\tfrac{1}{2}z)+\psi(\tfrac{1}{2}x,\tfrac{1}{2}y,\,\tfrac{1}{2}z-\tfrac{1}{2})+\psi(\tfrac{1}{2}x,\,\tfrac{1}{2}y-\tfrac{1}{2},\,\tfrac{1}{2}z)$$
$$+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\,\tfrac{1}{2}y,\tfrac{1}{2}z)+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\,\tfrac{1}{2}y-\tfrac{1}{2},\,\tfrac{1}{2}z)$$
$$+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\,\tfrac{1}{2}y,\,\tfrac{1}{2}z-\tfrac{1}{2})+\psi(\tfrac{1}{2}x,\,\tfrac{1}{2}y-\tfrac{1}{2},\,\tfrac{1}{2}z-\tfrac{1}{2})$$
$$+\psi(\tfrac{1}{2}x-\tfrac{1}{2},\,\tfrac{1}{2}y-\tfrac{1}{2},\,\tfrac{1}{2}z-\tfrac{1}{2}].$$

However, changing the definition of the cell edge changes no physical quantity (e.g., the potential) in the lattice, so that the above expression must equal $\psi(x,y,z)$. By picking particular values of $\mathbf{r}$ and making use of the full cubic symmetry of $\psi(\mathbf{r})$, the equations simplify to those of Hund. Clearly, the same type of argument also holds if the new cell side is any integer.

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Thermal Conductivity of Indium-Thallium Alloys at Low Temperatures*

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The thermal conductivity of a series of homogeneous, solid solution indium-thallium alloys containing up to 50 atomic percent of thallium has been measured as a function of temperature at liquid helium temperatures and as a function of both longitudinal and transverse magnetic fields below T_c, the superconducting transition temperature in zero field. The normal-state results agree quite well with the quasi-free electron theory of metals. The superconducting-state results agree with the hypotheses that electrons in the "superconducting phase" neither transport heat nor scatter phonons.

For pure indium, it was found that $K_{es}/K_{en}=2t^2/(3+t^4)$, where K_{es} and K_{en} are the electronic thermal conductivities at a given temperature when the specimen is superconducting and when it is nonsuperconducting, respectively, and $t=T/T_c$.

For all the alloy specimens the ratio of the lattice thermal conductivities comprised a family of curves such that $t^{-3}<K_{gs}/K_{gn}<t^{-6}$.

A thermal resistivity maximum was found to accompany the isothermal destruction of superconductivity by either a longitudinal or a transverse magnetic field in specimens containing 15 percent Tl or more. When the applied field was reduced to zero, the final thermal resistivity of most of these specimens was greater than would be expected for a simple mixture of superconducting and "frozen-in" normal regions, the concentration of the latter being estimated from magnetic induction measurements. Both this effect and the maxima themselves are thought to be manifestations of an increased lattice thermal resistivity due to alteration of the mean free path of phonons when they approach the boundary between a superconducting and a normal region.

I. INTRODUCTION

THE mechanism of heat conduction in superconductors, like the phenomenon of superconductivity itself, is still very incompletely understood from a quantitative theoretical point of view. However, some progress has been made towards a qualitative understanding of the various physical processes involved particularly in the case of pure metals.[1] In order to indicate the nature of the difficulties involved, it is necessary to discuss briefly the mechanisms of heat transport in nonsuperconductors at low temperatures.

Heat is conducted through nonsuperconducting metals by the motion of conduction electrons and by the direct interactions between atoms. Since these processes can be regarded as heat paths in parallel, it is usual to assume that the separate conductivities are directly additive. For pure metals at low temperatures the electronic thermal conductivity is usually so large that the lattice thermal conductivity is negligible in comparison with it. In this case, Wilson,[2] Makinson,[3] and Sondheimer[4] have shown theoretically that at temperatures below about 0.1Θ, where Θ is the Debye temperature, the electronic thermal resistivity may be expressed in the form

$$1/K_{en}=\alpha T^2+\beta/T, \tag{1}$$

where K_{en} is the electronic thermal conductivity and α and β are constants for a given specimen. The first and second terms on the right represent thermal resistivities due to the scattering of electrons by phonons, and by impurities, respectively; the existence of both types of thermal resistivity is now well established by experiment,[5-9] and there is little doubt that the temperature dependence is close to that predicted theoretically. The experimental values of the coefficient

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