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A New Analysis of Slater's Compressibility Data

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The variation of interatomic forces with interatomic distances in crystals may be determined empirically from compressibility data. The experimentally possible range of variation in interatomic distance is, however, so small that the form of the force function valid for extrapolation to much greater distances cannot be adequately determined. From an analysis of Slater's compressibility data for the alkali halides it appears that for them the interionic forces of repulsion may be derived from a common force function. Because of the relatively large variation of lattice constant between the different alkali halides it is possible to determine a form for this common force function which is valid for relatively large variations in interatomic separation. The force function so found differs but little from the inverse power or from the exponential forms for small displacements from the equilibrium position. It drops off more rapidly, however, for increasing distances and increases more rapidly for decreasing distances. The solution given has the interesting property that of all possible force functions compatible with Slater's compressibility data it is the least favorable for the formation of a secondary structure.

I. INTRODUCTION

THE interionic forces in heteropolar crystals may be either derived quantum-theoretically, or established empirically, mainly from compressibility data. By the former process an exceedingly complicated problem is involved, and it is not strange that although a gratifying agreement as to order of magnitude has been obtained (for instance, in regard to the lattice constant)[1] the results have not been sufficiently precise to be of any great value for practical purposes.

For most purposes it is necessary to employ an empirical method[2] to calculate the interionic forces. By this method the lattice constant, the compressibility, and certain other quantities which can be determined experimentally are taken for granted, and a number of parameters in a more or less arbitrarily assumed force function are adjusted to give an exact agreement with the real force at least over the small region covered by the measurements. In many cases this method is satisfactory, since usually we are interested in the value of the force only over a small region. When extrapolations beyond this region do become necessary, however, the method is open to legitimate objections, because of the arbitrary manner in which the functional form of the force has been chosen. Since such extrapolations are sometimes of theoretical importance, it is a matter of interest that in the present paper some of the arbitrariness of the empirical method of determining the force has been eliminated.

On account of certain relations between the compressibility data for the alkali halides it is possible to relegate a common force function to all the members of this family. The great diversity in lattice constant among these members thus greatly extends the region of validity of the results. Although no attempt is made to justify theoretically the relationship between the alkali halides, the supposition is reasonable that the forces for the different ions have a similar origin. Since the foundations of the present analysis thus are purely empirical, the results are subject to the same limitations and uncertainties as the experimental data on which the analysis is based. Its main advantages over previous analyses are the greater generality in the results as well as in the treatment, and the fact that insofar as assumptions are involved they are physically well defined and reasonable.

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[1] See for instance, E. A. Hylleraas, Zeits. f. Physik **63**, 771 (1930).

[2] In this category must now be placed Born's original theory (M. Born, *Atomtheorie d. festen Zustandes*, Leipzig, Teubner (1923)), as well as recent attempts to make use of an exponential repulsion. (See, for instance, Born and Mayer, Zeits. f. Physik **75**, 1 (1932).)

II. INTERIONIC FORCES IN RELATION TO COMPRESSIBILITY

The change in potential energy per pair of ions, when a crystal is uniformly compressed, may be represented in two different ways as follows:

$$\Delta U=\sum_{n=1}^{\infty}(d^nU/da^n)_{a=a_0}(a-a_0)^n, \tag{1}$$

where a is the central distance between neighboring atoms, a_0 being the value assumed by a in the equilibrium configuration. Or

$$\Delta U=-\int_{V_0}^{V}p(V)dV, \tag{2}$$

where the volume per pair of ions is $V=ca^3$ where c is a constant which depends on the crystallographic arrangement of the atoms.

By Eq. (2) the coefficients in the Taylor expansion (1) may be expressed in terms of the pressure, p, and its derivatives with respect to a, since $d^nU/da^n=d^n(\Delta U)/da^n$. The derivatives of the pressure with respect to a, in turn, may be represented in terms of the compressibility, κ, and its pressure derivatives by the definition $\kappa=-dV/V_0dp$, where V_0 is the initial volume per pair of ions.

Consequently we obtain, in general,

$$\left(\frac{d^nU}{da^n}\right)_{a=a_0}=f_n\left(\left(\frac{d^{n-2}\kappa}{dp^{n-2}}\right)_{p=0},\left(\frac{d^{n-3}\kappa}{dp^{n-3}}\right)_{p=0},\cdots\kappa_{p=0},a_0\right). \tag{3}$$

The quantity dU/da, which represents the central interionic force, therefore is defined as a Taylor expansion around the point $a=a_0$ when the compressibility is known as a function of the pressure.

III. TRANSLATION OF SLATER'S EXPERIMENTAL RESULTS INTO TERMS OF INTERIONIC FORCES

By Slater's measurements[3] the compressibility and its first pressure derivative are known at zero pressure for the alkali halides. Of immediate interest are therefore the three first equations of the general set (3). They are:

$$\begin{gathered}(dU/da)_{a=a_0}=0;\quad (d^2U/da^2)_{a=a_0}=9ca_0/\kappa_0;\\ (d^3U/da^3)_{a=a_0}=27c(2\kappa_0^2+(d\kappa/dp)_{p=0})/\kappa_0^3.\end{gathered} \tag{4}$$

Slater's observations, in conjunction with a determination of the lattice constant, therefore enable us to obtain the three first terms in a Taylor expansion of the central interionic force.[4] For many purposes this information is all that is required,[5] and since our results, so far, are purely empirical and involve no hypothesis, a gratifying degree of rigor is imparted to a group of calculations. When a knowledge of the interionic force is required for a greater range in interionic separation than implied by the three first terms in a Taylor expansion, we must resort to extrapolations. It is the purpose of the following analysis to investigate the possibility of reducing to a minimum the arbitrariness involved in such extrapolations.

For this purpose it is convenient to separate the potential energy of the crystal into two terms, a negative energy of attraction, and a positive energy of repulsion. It has been established by Slater's work[3] that the energy of attraction for the alkali halides is primarily a Coulomb term, although higher order terms are not definitely excluded. We shall, for the present, group these higher order terms with the energy of repulsion, Φ, and therefore bear in mind that Φ may contain negative as well as positive terms. Accordingly the energy per pair of ions is $U=\Phi-Me^2/2a$, where M is the Madelung constant. If now, for simplicity, we write, $d\Phi/da=\frac{1}{2}Me^2F(a,a_0)$, where the force of repulsion F, for reasons which will shortly become obvious, is considered as a function of two variables, Eqs. (4) become:

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[3] J. C. Slater, Phys. Rev. **23**, 488 (1924).

[4] For a somewhat more laborious method of arriving at this same result, see G. A. Tomlinson, Phil. Mag. **11**, 1009 (1931). There appears to be a slight discrepancy, however, between Tomlinson's third term in the expansion and ours.

[5] An important application hereof is given in the paper immediately following this.

$$\begin{aligned} F(a_0, a_0) &= -1/a_0^2, \\ (\partial F/\partial a)_{a=a_0} &= 2/a_0^3 + 18ca_0/Me^2\kappa_0, \\ (\partial^2 F/\partial a^2)_{a=a_0} &= -6/a_0^4 \\ &\quad + 54c(2\kappa_0^2 + (d\kappa/dp)_{p=0})/Me^2\kappa_0^3. \end{aligned} \tag{5}$$

We define the dimensionless quantities,

$$\begin{aligned} p &= \mu a_0 = a_0^3(\partial F/\partial a)_{a=a_0} \\ Q^2 &= -a_0^4(\partial^2 F/\partial a^2)_{a=a_0}. \end{aligned} \tag{6}$$

Their meaning is as follows. If the law of repulsion were the inverse power postulated by Born,[2]

$$F = -(a_0/a)^p/a_0^2, \tag{7}$$

p would be the value of the exponent in this representation. In that case, moreover, we would have,

$$Q^2 = p(p+1), \tag{8}$$

a relation which cannot be fulfilled, since, as we shall see, Q^2 is as nearly as we can tell a constant for the alkali halide group, and μ, and not p, is also approximately a constant for this group.[6] On the other hand, if the law of repulsion were the simple exponential also suggested in the literature,[7]

$$F = -e^{-\mu(a-a_0)}/a_0^2, \tag{9}$$

μ would be the coefficient in the exponent of the exponential function. In this case, moreover, we would have,

$$Q^2 = p^2 \tag{10}$$

a condition very similar to (8), and, as we shall see, almost equally incompatible with Slater's observations.[8] In general, the distinction between an inverse power and a simple exponential law of repulsion, for practical purposes, is a rather fine one. In other words, calculations based on the one would, in most cases, lead to results not far removed from those obtained from the other. Certainly, Slater's observations off hand do not enable us to draw conclusions in favor of the one or the other. Although the relation (10) is more nearly fulfilled, on the average, than the relation (8), the difference between the two on the average, is only about one-third of the discrepancy between Q^2 and p^2. In this light it would be absurd to draw definite conclusions in favor of the exponential law of repulsion. Rather, the conclusion must be drawn, that if the experimental quantity $d\kappa/dp$ is accurate to within the limits claimed, neither the exponential nor the inverse power law represents correctly the real law of repulsion, and neither can be reliable for extrapolations.

TABLE I. *Compressibility data for the alkali halides at 30°C.*

Salt	a_0	p	Q^2	μ	$(p-3)/a_0$
LiF	$2.07 \cdot 10^{-8}$	7.43	98.1	$3.59 \cdot 10^8$	$2.14 \cdot 10^8$
LiCl	2.57	7.80	72.2	3.03	1.87
LiBr	2.74	7.89	71.0	2.88	1.79
NaCl	2.815	8.78	71.2	3.12	2.05
NaBr	2.97	8.91	68.6	3.00	1.98
KF	2.665	8.96	91.1	3.36	2.23
KCl	3.13	9.73	68.9	3.11	2.16
KBr	3.29	9.93	71.5	3.02	2.11
KI	3.525	10.23	69.7	2.90	2.05
RbBr	3.42	9.81	62.6	2.87	1.99
RbI	3.66	10.50	69.4	2.87	2.05
Average			74.0	3.06	2.04
r.m.s.d.			10.1	0.216	0.122
Percent r.m.s.d.			13.7	7.1	6.0

TABLE II. *Compressibility data for the alkali halides reduced to absolute zero.*

Salt	a_0	p	Q^2	μ	$(p-1)/a_0$
LiF	$1.97 \cdot 10^{-8}$	6.9	95.8	$3.50 \cdot 10^8$	$3.00 \cdot 10^8$
LiCl	2.54	9.0	117.2	3.55	3.16
LiBr	2.71	9.7	135.5	3.58	3.22
NaCl	2.76	10.1	117.8	3.66	3.30
NaBr	2.91	10.5	120.8	3.61	3.26
KF	2.63	8.9	95.0	3.38	3.00
KCl	3.08	10.7	97.5	3.47	3.15
KBr	3.23	11.0	105.9	3.41	3.10
KI	3.47	11.5	108.8	3.31	3.03
RbBr	3.36	11.0	97.8	3.27	2.98
RbI	3.58	12.0	114.0	3.35	3.07
Average			110.0	3.46	3.12
r.m.s.d.			12.2	0.123	0.106
Percent r.m.s.d.			11.1	3.56	3.40

The facts to which we have called attention are illustrated in Tables I and II. The former is based on the data as observed at 30°C. The latter is based on these data as reduced by Slater to the absolute zero.[9] The tables illustrate the approx-

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[6] This discrepancy has already been pointed out by Slater. See reference 3.

[7] See reference 4, and also Born and Mayer, reference 2.

[8] Whereas a consideration of more than the next neighbors would slightly modify the function (13), this would not materially affect the conclusions here drawn.

[9] It would have been highly desirable if this discussion had been preceded by a revision of Slater's extrapolation to the absolute zero. In the absence of such a revision,

imate constancy of the quantity μ, which we have already mentioned, and to which attention previously has been called by Tomlinson.[7] It is seen, however, that this constancy refers more nearly to the quantity $\eta=(p-k)/a_0$, where k is a small numerical constant in the neighborhood of 3 for the unreduced data, and in the neighborhood of unity for the data reduced to the absolute zero. Table I also shows that Q^2 is a constant to well within the limits of experimental error, with the exception of the fluorides which appear to form a group by themselves. From Table II, however, it is seen that the trend is for this subgrouping to disappear with decrease in temperature. From Table II it also appears that *the constancies here suggested are improved by reducing the data to absolute zero*, as shown by the root-mean-square deviations from the mean values given at the bottom of the tables. In the case of the quantity Q^2 this is mainly due to the disappearance of the subgrouping of the fluorides. This quantity otherwise behaves somewhat erratically after reduction which undoubtedly can be easily ascribed to the uncertainties of Slater's extrapolations. In the case of the quantities μ and η, on the other hand, the improvement is unmistakable. We are therefore justified in claiming at least an approximate constancy for the quantities η and Q^2 for the alkali halides. In the case of the former the approximation is very good.

IV. ANALYTIC FORMULATION OF THE RESULTS AND A GENERAL SOLUTION

Together with the exact equilibrium condition, the definition (6) lead to the following set of equations:

$$F_{a=a_0}=-1/a_0^2,\quad (\partial F/\partial a)_{a=a_0}=(\eta a_0+k)/a_0^3,\quad (\partial^2 F/\partial a^2)_{a=a_0}=-Q^2/a_0^4. \tag{11}$$

Since Slater's observations indicate that η and Q^2 are constant for the alkali halides, it follows that for them the force of repulsion may be derived from a common force function F by assigning the proper value to a certain parameter, the physical significance of which we do not know, but which depends uniquely on the observed constant of the lattice a_0. In other words the difference between the members of the alkali halide group, in regard to the forces of repulsion, is sufficiently described in terms of a single parameter.[10] Thus, by making F a function of two variables, a and a_0, we have relegated all the members of the alkali halide group to the same force function, the force in any particular case being obtained by assigning the proper value to a_0.

The system of Eqs. (11) admits of an infinite number of solutions. A general solution is

$$F=-a_0^{k-2}a^{-k}\exp\left[-\int_{a_0}^{a}\Gamma(\alpha,a_0)d\alpha\right], \tag{12}$$

where

$$\Gamma(\alpha,a_0)=\eta\exp\left[\int_{a_0}^{\alpha}T(\beta,a_0)d\beta\right] \tag{13}$$

and

$$T(\beta,a_0)=L(a_0)\eta^{-1}\exp\left[\int_{a_0}^{\beta}S(\gamma,a_0)d\gamma\right] \tag{14}$$

$S(\gamma,a_0)$ is an arbitrary function, and

$$L(a_0)=(k+\eta a_0)^2/a_0^2-(Q^2-k)/a_0^2. \tag{15}$$

This general solution, involving an arbitrary function of two variables, represents the maximum information which can be derived from Slater's observations without resort to any hypothesis or additional data. Any theoretical representation of the force, must conform with this general solution to within limits set by the accuracy of Slater's observations. We have already seen that this condition is not fulfilled by either the inverse power or the simple exponential law of repulsion. Similarly it may be shown that a generalized inverse power law, containing reasonable higher order terms of the Coulomb force as well as of the repulsive force, does not withstand this test. Since, however, the probability of such a law is remote in view of recent theoretical developments, we shall not enter into this demonstration. Considerably more probable in this light,[11] is the exponential law or a modification thereof. In the following we shall see that we do,

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however, the contents of the second table must be taken to indicate only a trend, and too much significance should not be assigned to the absolute numerical values of the quantities tabulated.

[10] Although this applies rigorously only at the points $a=a_0$, it seems fair to assume that it applies generally. However, no advantage is taken of this in the following.

[11] See, for instance, reference 1.

in fact, arrive at a law of this type by a functional analysis, based on an assumption of a reasonable and general nature.

V. DERIVATION OF A FIRST APPROXIMATION SOLUTION

Tomlinson,[7] neglecting the discrepancy in Eq. (10), considered the approximate validity of the force function (9) as evidence that the force of repulsion is a result of an interaction at the "boundaries" of the atom, and therefore is essentially a function of the separation of the "atomic boundaries" rather than of the central separation. The validity of this conclusion, based solely on Slater's results, is doubtful. There are, however, other reasons for believing that Tomlinson's conclusion is essentially correct, to some of which we shall return later. For one thing, it is known that the force of repulsion decreases rapidly with increased separation, so that it is reasonable to assume that only proximate parts of the atoms are materially instrumental in the creation and maintenance of this force. In the limit, therefore, *for the most rapidly decreasing force of repulsion*, this force would be a function of the separation of the atomic boundaries only; aside, perhaps, from a "contact area" which might depend on the atomic separation as well as on the atomic dimensions. In mathematical language:

$$F=\Phi(a, a_0)\Psi(a-r), \tag{16}$$

where $(a-r)$ represents the separation of the atomic boundaries. It may be demonstrated, from Eqs. (11), that a "contact area," Φ, is required. If Φ is to be left as an arbitrary function of two variables the problem is no more determinate than the original one. It is reasonable to assume, however, that if Φ depends on the atomic separation (which, as we shall see, it does) the dependency must be slight; i.e., it must be a slowly changing function of a. In other words, it may be expanded into a power series of a where only the first two terms need be retained. That is,

$$\phi(a, a_0)=\Phi_0(a_0)+a\Phi_1(a_0). \tag{17}$$

For self-consistency, moreover, we must impose the condition:

$$|a_0\Phi_1/\Phi(a_0)|\ll 1. \tag{18}$$

We shall later demonstrate that this condition is fulfilled. As we shall see later, moreover, it follows from the assumption (17) that $a_0-r(a_0)$ is also slowly changing, and therefore may be expanded as follows:

$$a_0-r(a_0)=sa_0 \tag{19}$$

where $s\ll 1$. By removing a factor $(a-r)^{-ks}$ from ψ, we may write

$$F=(\Phi_0+a\Phi_1)(a-r)^{-ks}\psi(a-r). \tag{20}$$

Introducing F into Eqs. (9) we obtain

$$\Phi_1(a_0)/\Phi(a_0)=-\psi'(a_0-r)/\psi(a_0-r)-\eta, \tag{21}$$

$$\frac{\psi''(a_0-r)}{\psi(a_0-r)}-2\eta\frac{\psi'(a_0-r)}{\psi(a_0-r)}-2\left(\frac{\psi'(a_0-r)}{\psi(a_0-r)}\right)^2=\frac{H^2}{a_0{}^2}, \tag{22}$$

where $\mathrm{H}^2=Q^2-k(k+1/s)-2k\eta a_0$. We have already noted that Q^2 is a constant. We are equally justified in claiming that H^2 is constant. In fact, the root-mean-square deviation from the average value of H^2 for the alkali halides is somewhat smaller than that for Q^2. With this assumption Eq. (22) may be reduced to the linear form by the substitution:

$$\psi(x)=y^{-1}x^{-\frac{1}{2}}e^{-\eta x}, \tag{23}$$

where, for short, we have written, $a_0-r=sa_0=x$. The differential equation resulting from this substitution is,

$$y''+(1/x)y'-(\eta^2-(s_1{}^2-\tfrac{1}{4})/x^2)y=0, \tag{24}$$

where $s_1=sH$. This is the differential equation of a Bessel function of imaginary argument. For $s_1>\frac{1}{2}$ the order of the Bessel function is also purely imaginary. The solution is,

$$y=Z_{i\nu}(i\eta x), \tag{25}$$

where $\nu=(s_1{}^2-\frac{1}{4})^{\frac{1}{2}}$. Replacing x by $(a-r)$, we obtain by Eqs. (23) and (25) the following functional form for the interaction at the boundaries:

$$\psi(a-r)=(a-r)^{-\frac{1}{2}}e^{-\eta(a-r)}/Z_{i\nu}(i\eta(a-r)). \tag{26}$$

From Eq. (21), moreover, we obtain,

$$\frac{\Phi_1(a_0)}{\Phi(a_0)}=\frac{1}{2sa_0}+i\eta\frac{Z_{i\nu}'(i\eta sa_0)}{Z_{i\nu}(i\eta sa_0)}. \tag{27}$$

The problem is now completely solved aside from the constant s, and a constant of integration implicitly involved in the symbol $Z_{i\nu}$.

We shall first consider the constant s. Its value, insofar as it determines the order of the Bessel function, is of great importance for the interpretation of the results. As noted, the order becomes imaginary for $s_1 > \frac{1}{2}$. The Bessel function of imaginary order as well as argument has the property,[12] that for $0 < z < \nu$, $Z_{i\nu}(iz)$ has an infinity of zeros condensing toward the origin, whereas to the right of the point $z = \nu$, it has *at most* one zero. Thus $\psi(z)$ would have an infinite number of poles for $0 < z < \nu$, whereas by a suitable choice of the constant of integration it can be made analytic throughout the domain $z > \nu$. In the region where observations have been made, the function $\psi(z)$ is finite and continuous. Therefore the region $0 < z < \nu$ must be outside the region of observation. This imposes an upper limit to the value of the constant s, which from the observed range of variability of a_0 may be estimated as

$$s_1 \leqq 1/2^{\frac{1}{2}} \quad \text{or} \quad \nu \leqq 1/2. \tag{28}$$

A lower limit to the value of s_1 can be set by the largest observed lateral contraction by extension of the crystal. Our force function (20) must yield at least as great a lateral contraction as that observed experimentally, say δ. Translated into terms of the separation of the atomic boundaries, this condition becomes, $s \geqq \delta$. If we allow[13] a value of about 6 percent for δ the lower limit becomes, $s_1 \geqq \frac{1}{2}$ or $\nu \geqq 0$ which combined with the inequality (28) gives,

$$0 \leqq \nu \leqq 1/2. \tag{29}$$

Direct estimates of the value of s can be obtained in three independent ways. First on the basis of the data on hand: In zero approximation the force of repulsion should be a function of the separation of the atomic boundaries only. That is,

$$F = F(a - r). \tag{30}$$

Accordingly we attempt to satisfy the first two of the Eqs. (11) by this force function. That is,

$$F(a_0 - r) = -1/a_0^2, \quad F'(a_0 - r) = (\eta a_0 + k)/a_0^3.$$

After differentiation of the first of these equations with respect to a_0, we obtain by division:

$$1 - dr/da_0 = 2/(\eta a_0 + k).$$

The right-hand side is small of the order $2/Q$ within the domain in which we are interested, thus justifying our assumption that $(a_0 - r)$ is a slowly changing function of a_0. This estimate of s, namely $s = 2/Q$, is still too large by a factor of about $2^{\frac{3}{2}}$ to comply with our requirement (28), thus indicating that it may be necessary to insert a factor a^{-q} in the zero approximation representation (30).

A second estimate may be obtained directly from scattering experiments on liquids such as mercury.[14, 15] It is possible from these measurements to calculate the distribution of atoms around a given atom in the liquid. These calculations give a mean separation corresponding roughly to the lattice constant of crystalline mercury (aside from the difference in density of liquid and solid Hg and certain other small factors). For smaller separations the distribution drops rapidly to practically zero. Although this cut-off point depends to some extent on the temperature it must correspond roughly to the point at which the boundaries are in contact.[16] The difference between the separation of two neighboring atoms in the crystal and the cut-off separation should correspond roughly to the separation of the atomic boundaries in crystalline Hg, and presumably, as to order of magnitude, to that separation in any crystal. The separation thus calculated[17] is something less than 10 percent of the lattice constant, and therefore agrees roughly with our previous estimate.

The value of this agreement lies primarily in the contact it establishes with an independent domain of physical measurements. These estimates otherwise are too inaccurate to delimit satisfactorily the order of the Bessel function in our solution (26). On the other hand, a knowledge

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[12] M. Bocher, Annals of Math. **6**, 137 (1892).

[13] In this connection may be mentioned that the inverse power law gives a lateral contraction of about 5 percent. See F. Zwicky, Phys. Zeits. **24**, 131 (1923).

[14] J. A. Prins, Naturwiss. **19**, 435 (1931).

[15] For an account of the theoretical features, see F. Zwicky, Proc. Nat. Acad. Sci. **17**, 524 (1931).

[16] If a physical definition is to be given to the term "atomic boundary" it clearly must be in terms of the gradient of the repulsive potential; that is, where this gradient becomes very large.

[17] Numerical values obtained from P. Debye; Lecture, California Institute of Technology, October, 1932.

of the quantity $a_0{}^5(\partial^3F/\partial a^3)_{a=a_0}$, even though it be to a rather rough approximation, enables us to arrive at a closer estimate. From Slater's compressibility data and its temperature dependence this quantity may be judged to have a value nQ^3, where n is in the neighborhood of unity although it may be larger than this by at most a factor 5. It can be shown that if n has a value approximately 5, the order of the Bessel function in the solution (26) becomes zero. On the other hand, if we let s_1 assume its maximum value given by the inequality (28), the order of the Bessel function becomes $i/2$ which would make the factor n approximately 1.8. The compressibility data indicate that the latter value is more nearly correct, since the best estimate of the quantity $a_0{}^5(\partial^3F/\partial a^3)_{a=a_0}$ leads to a value of n approximately 2. This is also in accordance with the trend indicated by the other two estimates and is, moreover, within the limits indicated in (29).

The fact that the Bessel function is probably of a purely imaginary order is interesting, since, as we have seen, this means that the force function has an infinity of distributed singularities in the region of the boundary of the atom. This perhaps indicates a certain obscurity in the outline of the atom which would not be averse to present ideas.

Although the value of ν probably is nearer to $\frac{1}{2}$ than to 0, we shall for the purpose of illustration employ the latter value. In this limiting case the Bessel function reduces to one of real order and imaginary argument; its properties are well known, and numerous tabulations are available in the literature facilitating numerical calculations.[18] By this choice the singularities of the function $\psi(z)$ are all displaced to the point $z=0$, so that the boundary of the atom becomes clear cut and well defined. The repulsive interaction in that case becomes,

$$\psi(z)=z^{-\frac{1}{2}}e^{-z}/(J_0(iz)+\tfrac{1}{2}ci\pi H_0{}^{(1)}(iz)), \qquad (31)$$

where J_0 is the ordinary Bessel function of zero order, and $H_0{}^{(1)}$ is the Hankel function of the first kind of zero order. Only one constant of integration, c, appears in this solution since the other constant may be included in Φ, which as yet remains to be determined. An estimate of c can be obtained as follows. The ratio (27), by the inequality (18), should be small throughout the range of variation of a_0. By suitably disposing of c we can make this constant zero at one point at least. For this point we may somewhat arbitrarily choose the midpoint of the range of variation, which is given approximately by $\eta a_0=H$. To demonstrate that our solution is self-consistent, however, it will be necessary to show that this ratio is small for the extreme range of variation of the variable a_0.

The condition that $\Phi_1(a_0)/\Phi(a_0)$ shall be zero for $\eta a_0=H$ yields by Eqs. (27) and (31) the result $c=1.81$. It turns out, moreover, that this ratio is not only zero, but it also has a minimum at this point, so that its greatest value in the range of variability of a_0 is quite small. Calculation will show that the ratio is less than 0.3. Our assumption that the function $\Phi(a, a_0)$ is a slowly changing function of a is therefore borne out by the results, and our solution insofar as can be seen is free from contradictions.

In another important respect our solution exhibits a gratifying self-consistency. Our assumption, that the repulsive force was essentially an interaction along the boundaries of the atoms, implied, that it dropped off exceedingly rapidly with increasing separation. That this is so can best be seen by a comparison with the force functions which have found a predominant application in the literature;[2] i.e., the inverse power force, F_P, (Eq. (7)), and the exponential force, F_E, (Eq. (9)). In Figs. 1 and 2 we have plotted the ratios F_S/F_P and F_S/F_E where F_S represents the force resulting from the present theory. For convenience the calculations were made for a lattice constant, $a_0=H/\eta$, corresponding roughly to the middle of the scale of the alkali halides.

In Fig. 1 these ratios are plotted up to a separation corresponding to the position of the second next neighbors in the crystal. It is seen that the force F_S drops off much more rapidly than the others. In fact, whereas the exponential force, $e^{-\mu a}$, drops off more rapidly than the inverse power, the function F_S drops off essentially as $e^{-2\eta a}$ for large values of a; such that for a separation corresponding to the second next neighbors in the crystal the ratio F_S/F_E is only about one-tenth. With the type of force F_S, *it is consequently*

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[18] See, for instance, E. Jahnke and F. Emde, *Funktionentafeln.*

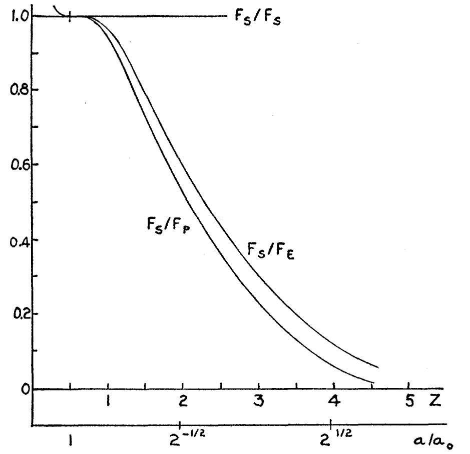

FIG. 1. Comparison of different force functions.

unnecessary to consider more than the next neighbors in calculations involving summations over the infinite lattice of the energy of repulsion or its derivatives. Our solution (20), therefore, refers not only to the crystal as a whole, but in first approximation it also gives the force between two individual ions in the crystal (after division by the number of next neighbors).

From the behavior of the ratio F_S/F_E we can also estimate the integral of the force function F_S, since the integral of F_E is known. In this way we arrive at the result that the energy of repulsion, from the present theory, is something less than 20 percent smaller than the energy of repulsion which would have been obtained from the simple exponential law. The latter, in turn, is smaller numerically than the negative Coulomb energy by a factor $p=\mu a_0$. The total energy in the present case thus would be approximately 2 percent greater than that calculated on the basis of the exponential law of repulsion (which, in turn, is very nearly the same as that obtained from the inverse power law). This difference, however, probably would be too small for experimental verification.

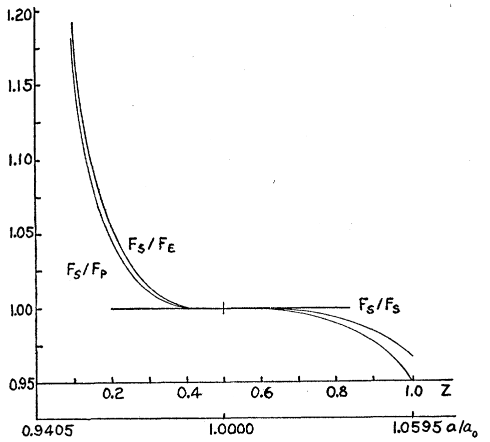

FIG. 2. Comparison of different force functions in the neighborhood of the equilibrium position.

In Fig. 2 the ratios F_S/F_P and F_S/F_E are plotted in the neighborhood of the equilibrium position $a=a_0$. It is seen that, over a region amounting to about 6 percent of the lattice constant around this point, the three functions F_P, F_E, and F_S are within 5 percent of each other, because of course, they have three terms of a Taylor expansion in common. This illustrates our contention that when we are interested primarily in this region it makes very little difference what type of functional form is assumed for the force. The very considerable success of the theory of the solid state, based on the inverse power law of repulsion, might perhaps be explained in this light. Attention is also called to the extremely rapid increase in F_S for separations smaller than the lattice constant, as illustrated by the rapid rise in the ratios F_S/F_P and F_S/F_E in this region. This rapid increase is significant for the remarks which we shall make in the final section, and is moreover in accordance with the assumption on which this analysis was based.

The self-consistency of this first approximation theory is gratifying, as is also the agreement with the independent domains of physical measurement which we have pointed out. The force, F_S, however, remains a first approximation, or perhaps not so much a first approximation as an extreme possibility, in that we have assumed the greatest possible decrease in the force of repulsion with increased separation which is compatible with the compressibility data. No attempt will be made here to improve the order of approximation. In a qualitative way, however, we can off hand point out certain modification possibilities. As to the interaction, $\psi(z)$, the main effect of refinement in the treatment probably would be to replace the distributed singularities in the neighborhood of $z=0$ (that is, near the boundary of the atom), by some array of steep but finite potential walls. This again would lead to a less steep and more smooth force function, particularly for atomic separations less than the lattice constant. For separations greater than this, the effect of the modification should be less marked. Probably, therefore, our result that only the next neighbors need be taken into account in calculating the energy of repulsion of the crystal, would remain valid. The exponential term in the interaction is present in quantum-theoretical derivations of the force,[1] and its retention is otherwise strongly indicated by the experimental data, so that this term is fairly well established.

The failure of the zero approximation (30) to give correctly, except as to order of magnitude, the numerical value of the constant s, indicated that it might be necessary to insert a factor a^{-q} in the right-hand side of Eq. (30), where q probably would have a value k. This would imply that in our final solution (20), the factor $(a-r)^{-ks}$ would be replaced by a factor a^{-k}. This is also borne out by our interpretation of the function $\Phi(a, a_0)$ as essentially a "contact area," not only dimensionally, but also because, as such, it should increase in a general way with a_0. Our choice of the constant of integration, c, in some measure was arbitrary, and might have to be modified. The solution is not much affected, however, by small changes in the value of this constant.

VI. Relation of the Results to the Stability of Heteropolar Crystals

We have shown in a previous paper[19] that, with the inverse power law of repulsion, all crystals of the NaCl- and particularly the CsCl-type are unstable against the so-called φ-variation. Only in the limit when the exponent of the repulsive force becomes infinite are these types definitely stable against this variation. Now of course, any theory of the solid state must explain the stability of crystals against all variations. The failure of the old theory to explain the stability of such crystals as CsCl therefore is a question of fundamental importance. The failure might be ascribed to one or both of the following sources. The forces which we have postulated may be inadequate. In that case the force of repulsion, which is much less firmly established than the Coulomb force of attraction, would come first in line for suspicion. Secondly, our postulated forces may be adequate, but we may have failed to take account of certain "cooperative phenomena,"[20] which arise as a natural consequence of these forces and do not require any new postulates for their explanation.

Here we shall consider briefly only the first possibility. It is significant that the type of crystals mentioned become stable for an infinite exponent of repulsion. The infinite exponent is characterized by the fact that the repulsive effect of all but the next neighbors disappears. This fact is responsible for the discontinuity in the first derivative of the stability curve at the angle, φ, corresponding to the CsCl-type of crystal where the number of next neighbors changes from six to two. This discontinuity again is responsible for the sharp maximum in the stability curve at this point. The repulsive force (20), in general, would not give rise to quite as abrupt a change as this, but it is clear that it would more nearly correspond to this condition than either the exponential or the inverse power law of repulsion. Therefore we can say that this repulsive force would be more favorable to the removal of the "φ-paradox" than either of the other two, and it might even be possible by the adoption of some such law of force to save the situation without calling into play Zwicky's cooperative actions.

These cooperative forces are necessarily based on and accompanied by certain departures from ideal symmetry in the crystal. This slight asymmetry, manifested as a secondary structure, may in turn be produced from the ideal crystal by imposing upon it certain finite but small variations. A necessary (but not sufficient) condition for the thermodynamic stability of this secondary structure is that the energy change by the variation shall be negative. We have shown, at least in a particular case, that the adoption of a force of repulsion, such as (20), may obviate in some measure the necessity of calling into play the cooperative forces to explain the stability of certain crystals. On the other hand, it is of interest to find out what a repulsive force of the form (20) would do to the energy change for variations leading to a secondary structure. This type of

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[19] H. M. Evjen, Phys. Rev. **39**, 675 (1932).

[20] See reference 15, and also a more extensive paper by the same author shortly to be published.

force would make the gain in energy smaller, and therefore would be unfavorable to the formation of a secondary structure, the reason being that almost invariably by any variation leading to a secondary structure, there is an increase in the positive energy of repulsion. It is seen from Fig. 2 that the force of repulsion (20) leads to a greater increase in energy than either the exponential or the inverse power law of repulsion, so that the net gain in energy with a force of this type would be smaller. This is illustrated perhaps most clearly in the case of the variation in which advantage is taken of the gain in energy by the contraction of a single plane from the lattice constant of the crystal to that of the plane.[21] It is obvious from Fig. 2 that such a contraction would be accompanied by a larger increase in positive energy with the force function F_S than with either F_E or F_P. What is more, the amount of contraction would be smaller with the former than with either of the latter, so that not only is there a relative increase in the positive energy, but there is also an absolute decrease in the negative Coulomb energy gained.

It is now pertinent to ask whether from the general solution (12) we could not construct the particular solution which would be *the least favorable to the formation of a secondary structure.* If, with this force function, we should still be able to find variations from the ideal crystal by which the energy would be decreased, the evidence would be more convincing than heretofore that the ideal crystal is not the thermodynamically most stable state. Some of the most legitimate arguments against the theory of the secondary structure would thereby be practically refuted. The evidence is that we have in the force function (20) the solution which is the least favorable to the formation of a secondary structure. This evidence is based on the fact that, of all the solutions which are consistent with the various physical observations to which we have called attention in this paper, the solution (20), by hypothesis, is the steepest in the region $a<a_0$, which is the main criterion as to whether or not the force function is favorable to the formation of a secondary structure. Regardless of whether this solution represents a good approximation to the real force or not, it therefore has considerable theoretical interest on account of its extreme character.

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[21] F. Zwicky, Helv. Phys. Acta **3**, 269 (1930); H. M. Evjen, Phys. Rev. **34**, 1385 (1929).