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ON THE STABILITY OF CERTAIN HETEROPOLAR CRYSTALS

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Abstract

On the basis of the conventional model of heteropolar crystals it is shown that an irregular crystalline behaviour is to be expected in the region of small values of the exponent, p, of the repulsive energy. In the course of this demonstration Madelung's method of obtaining the Coulomb potential for the crystals of the cubical system is justified, and a new, very simple method of calculating the Madelung constant is described. This method is applied to the three crystals of the cubical system and other applications are suggested. The irregular behavior of crystals in the region of small values of the repulsive exponent is shown to be manifested as an instability against various variations by which the geometry of the lattice is altered. In particular, the instability is demonstrated in the case of the "calcite family" of crystals which is evolved by a continuous process from a single parameter ϕ. The NaCl- and CsCl-types of crystals are members of this family, and a continuous mode of transition from one to the other is thus available. These two types of crystals, in general, are unstable against a variation in which the parameter ϕ is changed, (ϕ-variation), and for small values of the exponent, p, all members of the "calcite family" are shown to have a tendency to fall apart into one-dimensional crystals of the Madelung type. Another result of these considerations is that a skew structure, such as that of calcite may be accounted for on the basis of purely central forces. Finally the regions in which respectively one-dimensional and two-dimensional crystals, and the crystals of the cubical system are most stable are calculated. The bearing of these results on the theory of the secondary structure is briefly discussed.

I. Introduction

IN THE following we shall assume that the potential energy of a molecule may be represented thus:

$$U_m = -(ne)^2/r + A/r^p + U_p. \tag{1}$$

The first term is the Coulomb energy of two point charges, $\pm(ne)$, situated a distance r apart; U_p is the energy of polarization which arises as a result of the deformability of the ions, and A/r^p is the potential energy of the repulsive forces between the ions.

This expression for the potential energy is at best a first approximation. In the first place, the term purporting to represent the Coulomb energy, in general, is merely the first member in a power series expansion to which should be added also terms of the nature of homopolar bindings. As we shall see in the course of this discussion, these higher order terms cannot, in general, be neglected. In the second place, the representation of the energy of repulsion is not functionally correct.[1] As redeeming features we have the two

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[1] See, for instance, J. C. Slater, Phys. Rev. **23**, 488 (1924) or G. A. Tomlinson, Phil. Mag. **11**, 1009 (1931).

arbitrary parameters A and p which may be adjusted empirically in such a way as to make our approximate functional representation of the energy closely approach the true representation over the small interval of the independent variable, r, in which we are primarily interested.

The simple hypothesis (1), in the hands of Born,[2] Madelung,[3] and others, has led to fruitful results insofar as the socalled structure insensitive properties of heteropolar crystals have been satisfactorily accounted for. There are reasons for believing[4] that the complete failure of the theory to explain the structure sensitive properties of such crystals is not primarily due to the approximate nature of the fundamental assumption (1), but is due to the presence of a regular secondary structure within the crystal, predicted by Zwicky,[5] and later verified experimentally.[6] The existence of a secondary structure appears to be intimately connected with the existence of the crystal itself,[7] and therefore appears to be, within wide limits, independent of the particular nature of the function by which we choose to represent the potential energy. In particular, it has been shown that secondary structures of various types[8] are not inconsistent with energy functions of the type (1). From this we are led to believe that small inaccuracies in the representation (1) should lead to correspondingly small inaccuracies in any calculated property of the crystal, (as exemplified by the comparatively slight spread between calculated and observed structure insensitive properties); that is to say, if proper account is taken of the secondary structure. This is our justification for considering the simple energy function (1) adequate for our present needs.

II. THE POTENTIAL ENERGY OF AN IDEAL CRYSTAL

In the ideal models with which here we shall be concerned the lattice points are symmetry centers at which the electric vector vanishes. Hence the energy of polarization is zero, and the potential energy per molecule may be represented as,

$$U = -M(ne)^2/\rho + RA/\rho^p \tag{2}$$

where M, which we shall call Madelung's constant, is a summation over the lattice points and depends only on the geometry of the crystal; R similarly represents a summation over the lattice points and depends also on the exponent of the energy of repulsion, p. Eq. (2) involves the assumption that the three different combinations of ions which occur in a crystal are identical in regard to the mutual repulsive forces. This naturally will derogate the

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[2] M. Born, Atomtheorie d. Festen Zustandes, Teubner, 1923; Enz. d. Math. Naturwiss. V3, 4.

[3] E. Madelung, Phys. Zeits. **19**, 524 (1918).

[4] F. Zwicky, Helv. Physica Acta **3**, 269 (1930); and **4**, 49 (1931).

[5] F. Zwicky, Proc. Nat. Acad. Sci. **15**, 816 (1929).

[6] A. Goetz, Proc. Nat. Acad. Sci. **16**, 99 (1930); F. Zwicky, Proc. Nat. Acad. Sci. **16**, 211 (1930); M. Straumanis, Zeits. f. physik. Chem. (B) **13**, 316 (1931); H. Johnson, Journ. Franklin Inst. Oct. (1931). F. Bitter, Phys. Rev. **38**, 1903 (1931).

[7] F. Zwicky, Proc. Nat. Acad. Sci. Sept. (1931).

[8] See references 4 and 5, and also, H. M. Evjen, Phys. Rev. **34**, 1385 (1929).

generality of our results, without, however, seriously impairing their qualitative value. By the usual method we stabilize our model against uniform compression by letting,

$$\frac{\partial U}{\partial \rho} = 0. \tag{3}$$

It is easily seen that for p greater than unity $\partial^2 U/\partial \rho^2$ is always greater than zero, so that the extreme obtained by Eq. (3) is always a minimum.

If we substitute the value $\rho = d$ obtained from Eq. (3) into Eq. (2) we obtain,

$$U = -\,[(p-1)/p]\cdot[M(ne)^2/d] \tag{4}$$

which is always negative, so the crystal is always stable against all variations by which it would fall completely apart. Eq. (4) also may be written,

$$U = -f\left(\frac{M}{R^{1/p}}\right)^{p/p-1} \tag{5}$$

where $f=(p/p-1)[(ne)^{2p}/pA]^{1/p-1}$ is independent of the geometry of the crystal and depends only on the physical properties of the ions involved. The ratio $M/R^{1/p}$ then is a measure of the stability of the crystal.[9] The larger this ratio the more stable the crystal. This ratio we shall call the *stability factor* of the crystal.* The inaccuracies of the hypothesis (1), to which we have called attention, of course detract from the reliability of the stability factor. In particular, Pauling[10] has shown that it is not absolutely reliable in comparing the stability of crystals of different geometrical complexions. In view of Hund's results, however, it may at least be considered as a qualitative guide to the stability of crystals.

The static model obtained by this procedure, as we have seen, is always stable against uniform compression or expansion. The question remains whether it is stable against variations of a different type. In particular, is it stable against variations by which the geometry of the lattice is altered? This has been generally taken for granted. Recently it has been shown, however, that this is not, in general, true. Zwicky[11] has shown that for p less than 6, (5.95 to be more exact) the NaCl-type of crystal is unstable against a "residual-ray variation." The writer[12] similarly has found several variations against which the same type of crystal is unstable; for instance, Poisson's ratio becomes negative for p less than 6.2 and the crystal there becomes unstable against elongation and contraction. Thus there is a considerable variety of variations against which the ideal crystal is unstable in the region of small exponents, p. In the following we shall point out a fact which may be the fundamental cause of this instability.

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[9] F. Hund, Zeits. f. Physik **34**, 833 (1925).

[10] L. Pauling, Zeits. f. Krist. **69**, 35 (1928).

[11] F. Zwicky, Phys. Rev. **38**, 1772 (1931).

[12] To be published shortly.

* Not to be confused with the dynamic stability factor given by the normal modes of vibration of the system.

III. The Coulomb Energy of an Ideal Crystal

In accordance with Eq. (1) the Coulomb energy of an ideal crystal may be written as follows:

$$U_c = -M(ne)^2/d$$

where

$$M = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \frac{(-1)^{\Phi(\alpha,\beta,\gamma)}}{\dfrac{r(\alpha,\beta,\gamma)}{d}}. \tag{7}$$

Several ingenious methods[13] have been devised for evaluating the sum of the series (7). Madelung's method depends for its success and simplicity on the peculiar order in which the potentials of the individual ions are summed. In fact, the ions are collected into groups, each group forming a linear element within the crystal. The potential of one such linear element is calculated, and the potential of the crystal as a whole is then said to be the sum of the potentials due to these linear elements. Such a procedure, in general, is not strictly correct. It is only permissible when the series in question is such that its sum is independent of the order of summation. Although it is not at all obvious, Madelung's method, as we shall see, is justified in the case of the crystals of the cubical system. If, however, his method is applied indiscriminately to a calculation such as that of the change in energy by a "residual-ray variation" the result, in general, will be incorrect, since the order of summation here is not immaterial, and the result of the calculation will depend on the external shape of the region affected by the variation. These difficulties are avoided, and incidentally a new and very simple method of calculating Madelung's constant is obtained, if we remember that the building stones of the crystal are not the individual ions but rather the elementary cells of the crystal. In other words, we propose to sum the potentials of the individual cells rather than those of the individual ions; that is,

$$U_c = +(ne) \sum_{l,m,n} \Psi(l, m, n) \tag{8}$$

where $\Psi(l, m, n)$ is the potential at the lattice point (0, 0, 0) of the cell (l, m, n). We now collect the terms of the series (8) in order of increasing distance of the corresponding cells from the origin. It is then easy to show that the remainder after summing N of these terms approaches the integral,

$$Q = (ne)\cdot\sigma \iiint \psi(x, y, z)\,dxdydz \tag{9}$$

where σ is the number of elementary cells per unit volume, and the integration is to be extended over the volume outside the sphere of radius $R(N)$ to which the direct summation has been carried. In the case of the crystals of the cubical system we may choose for the elementary cell the elementary cube, assigning the weights 1, 1/2, 1/4, or 1/8 to the charges according as they are

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[13] See reference 2 for summary.

situated in the interior, on the face, on the edge, or on the corner of the cube. The total charge of the volume cell then, of course, is zero. The potential of the volume cell, referred for instance to its body center, now may be found by an expansion in terms of Legendre polynomials.[14] If r be the radius vector from the origin to the center of the volume cell, and l_i the radius vector from the center of the volume cell to the i-th ion, e_i, of this cell, we have, in fact:

$$\psi = \sum_{n=0}^{\infty} \frac{A_n}{r^{n+1}} \tag{10}$$

$$A_n = \sum_i e_i l_i^n P_n(\cos\theta_i) \tag{11}$$

and

$$\begin{aligned}\cos\theta_i &= \left(\frac{x}{r}\right)\xi_i/l_i + \left(\frac{y}{r}\right)\eta_i/l_i + \left(\frac{z}{r}\right)\zeta_i/l_i \\ &= (a + b + c)/l_i\end{aligned} \tag{12}$$

where (x, y, z) are the coordinates of the center of the volume cell, and (ξ_i, η_i, ζ_i) the coordinates of the i-th ion with respect to the translated Cartesian coordinate system having its origin at the center of the volume cell. Consequently,

$$\begin{aligned}A_n = \frac{1\cdot 3\cdot 5\cdots(2n-1)}{n!} \sum_i e_i\Big[&(a+b+c)^n \\ &- \frac{n(n-1)}{2(2n-1)} l_i^2(a+b+c)^{n-2} + \text{etc.}\Big]\end{aligned} \tag{13}$$

A_n therefore will depend linearly on terms of the type $(x/r)^\alpha\cdot(y/r)^\beta\cdot(z/r)^\gamma$, where $\alpha+\beta+\gamma=n-2s$. It follows that, if we form the integral over the surface of a sphere:

$$B_n = \int_0^{4\pi} A_n d\Omega$$

$B_{2n+1}=0$. It is therefore sufficient to consider the terms where n, α, β, and γ are even. By a slight transformation of Eq. (13) we obtain:

$$A_{2n} = \sum_{t=0}^{n} L_t^{2n} F_t \tag{14}$$

where L_i^{2n} denotes the t-th coefficient in the Legendre polynomial of degree $2n$.

$$F_t = \sum_{\Gamma} \frac{2(n-t)!}{2p!\,2q!\,2s!} M(p, q, s, t)\left(\frac{x}{r}\right)^{2p}\left(\frac{y}{r}\right)^{2q}\left(\frac{z}{r}\right)^{2s} \tag{15}$$

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[14] See, for instance, M. Mason and W. Weaver, The Electromagnetic Field, p. 15.

where Γ denotes a summation over all the sets of integers $p+q+s=n-t$, and $M(p, q, s, t)$ is a $2n$-th order electric moment of the elementary cell, given by:

$$M(p, q, s, t) = \sum_i e_i l_i^{2t} \xi_i^{2p} \eta_i^{2q} \zeta_i^{2s}. \tag{16}$$

For the three types of crystals of the cubical system we have:
A. NaCl-type (Fig. 1)

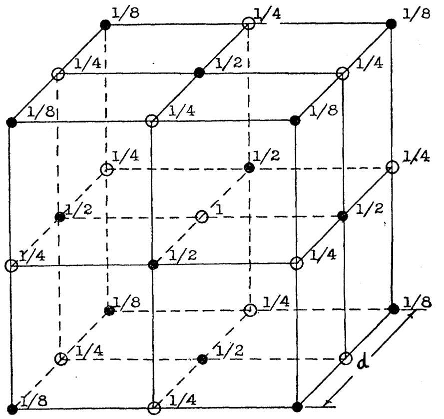

Fig. 1. Elementary cell of the NaCl-type.

$$M(p, q, s, t) = k_1 e(d/2)^{2n} \tag{17}$$

where $k_1 = -3^t + 2^t(0^p + 0^q + 0^s - (0^{pq} + 0^{qs} + 0^{sp})$, and the convention has been adopted:

$$0^m = \begin{cases} 0 \text{ if } m \neq 0 \\ 1 \text{ if } m = 0. \end{cases}$$

Here it is easily seen that $A_{2s+1}=0$, and $A_0=A_2=A_4=0$, so that the first term in the expansion of the potential of the element of an NaCl crystal goes as the inverse seventh power of the distance. This is a significant result since it shows that for a heteropolar crystal of this type the forces of cohesion act almost exclusively between neighboring atoms. In fact, the elementary cube of which an ion is a central member contributes approximately 84 percent to the Coulomb energy of that ion. This may be seen by direct summation with reference to Fig. 1. The contribution of the first elementary cube to the energy of the central ion is:

$$\begin{aligned} U_1 &= [-(6/1)(\tfrac{1}{2}) + (12/2^{1/2})(\tfrac{1}{4}) - (8/3^{1/2})(\tfrac{1}{8})]e^2/(d/2) \\ &= -2.92e^2/d \end{aligned}$$

as against the total energy as calculated by Madelung:

$$U_c = -3.496e^2/d;\ (M_1 = 3.496).$$

This immediately suggests a simple method of calculating the Madelung constant: Sum directly the potentials of the ions over a cube of side *nd* around the origin. The potentials of the ions inside the cube are summed in the ordinary manner, each being given unit weight; the potentials of the ions forming the surface of the cube, however, are given the weights 1/2, 1/4, or 1/8 according as they are situated on a face, an edge, or a corner of the cube. This procedure, of course, is equivalent to summing by cells rather than by ions. If n be increased by unit steps, that is, by adding cubical shells, an extremely rapidly converging series is obtained, which moreover alternates. Narrow limits are therefore obtained between which the Madelung constant must lie. In this way the Madelung constant for the NaCl-type of crystal is obtained to three decimal places by summing over a cube of side not more than three or four times the lattice constant. This must be considered as more than sufficiently close in view of the inaccuracies of the fundamental assumption (1).

B. CsCl-type (Fig. 2)

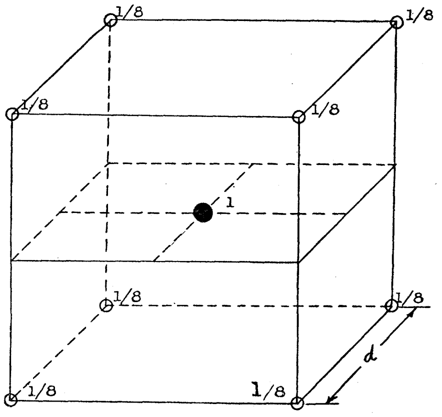

Fig. 2. Elementary cell of the CsCl-type.

For this type of crystal, we have,

$$M(p, q, s, t) = 3^t e(d/2)^{2n}. \tag{18}$$

From Eqs. (14) and (15) we therefore obtain $A_0 = A_2 = 0$, and $B_4 = \int_0^{4\pi} A_4 d\Omega = 0$, so that again the first term in the expansion of the potential of a spherical shell of elementary cells goes as the inverse fifth power of the radius of the shell. If one attempts to evaluate Madelung's constant for this type of crystal by the method outlined above, some difficulty is encountered due to the fact that two different limits seem to be approached according as one stops with a surface containing only positive ions or one containing only negative ions. The two limits, in fact, differ by an amount equal to the potential of a double-layer. This is to be expected, and is due to the fact that we sum over a cube rather than over a sphere. The result for a sphere, in the limit, obviously will be the average between the two limits for a cube. By taking this average after summing 12 distinct terms one obtains:

$$M_2 = 2.034$$

C. ZnS-type (Fig. 3)

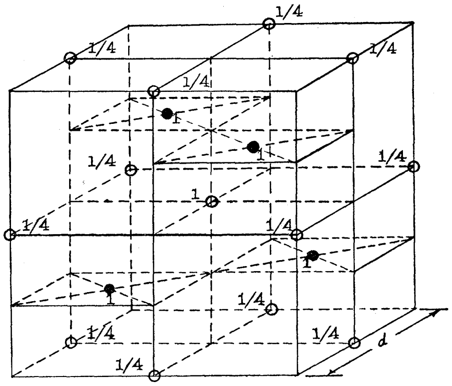

Fig. 3. Elementary cell of the ZnS-type.

The $2n$-th order electrical moment of the elementary cell here is given by:

$$M(p, q, s, t) = k_2 e(d/2)^{2n} \tag{19}$$

where

$$k_2 = 2^t(0^p + 0^q + 0^s) - 4\cdot 3^t(\tfrac{1}{2})^{2n}$$

Eqs. (14) and (15) therefore again yield $A_0 = A_2 = B_4 = 0$, and proceeding as before, one obtains:

$$M_3 = 3.78.$$

As a result of these considerations we can say that the series (8) is absolutely convergent and that its sum is independent of the order of summation for all the three types of crystals here involved. Madelung's method of summing therefore is justified, since his grouping of ions into linear elements may be obtained by a suitable grouping of the elementary cells. In general, the requirement for absolute convergence is $A_0 = A_1 = A_2 = 0$. The first coefficient, A_0, is always zero for electrically neutral matter. The second coefficient, A_1, always can be made to vanish by choosing the point of reference at the center of gravity of the charges of the elementary cell. Thus the most powerful restriction is the requirement that A_2 shall vanish. If A_2 is not zero we may get a conditional convergence if $B_2 = 0$. In general this would mean that the energy of the crystal would depend on its external macroscopic shape, which again might give rise to a type of secondary structure.

The simple method of calculating Madelung's constant which we have pointed out above, needless to say, is no longer of direct practical importance, since this constant has already been calculated for a great number of crystals with great accuracy.[15] The method, however, may be employed in the evaluation of various derivatives of the Coulomb potential; for instance, it may be applied to advantage in the calculation of the elastic constants, and is particularly useful when various irregular variations are imposed on the crystal.[12]

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[15] O. Emersleben, Phys. Zeits. **24**, 73, 97 (1923).

Otherwise the most interesting result of the preceding considerations is the fact, to which we have already called attention, that the first term in the expansion of the Coulomb potential of an element of a cubical crystal goes effectually as the inverse seventh power of the distance. This fact has some important consequences. In the first place, when the exponent, p, of the potential of the repulsive forces is less than seven, the sphere of action of the repulsive forces is greater than that of the Coulomb forces. Consequently we should expect irregularities in the behavior of the crystal at these low values of the exponent p, such as the instability against various variations to which we have already called attention in paragraph 2.

The exceedingly small sphere of action of the Coulomb forces as well as of the forces of repulsion moreover makes it difficult to understand the high degree of regularity over extended regions found by x-ray analysis. This fact seems to lend weight to Zwicky's contention[7] that really a different type of forces is responsible for the existence of crystals. Our consideration of the rapidity of convergence of the series involved may furnish clues as to how such forces can be brought into play, and how the necessary action over great distances can be effected. In the residual-ray variation[11] it is brought about by making the series involved conditionally convergent, but whether or not this is the only possible solution to the problem is a question to which we hope to return later.

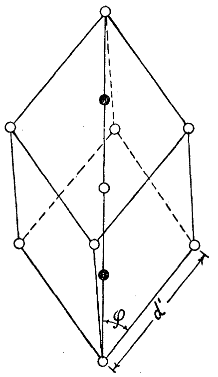

Fig. 4. Elementary cell of the "calcite family"

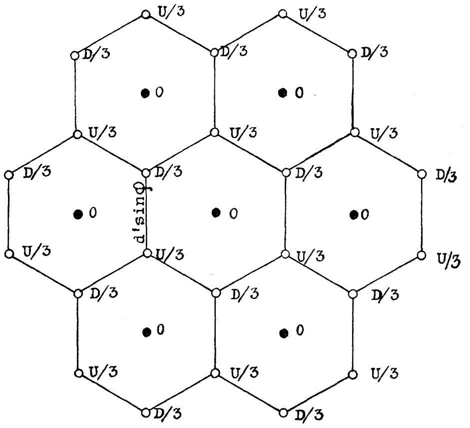

Fig. 5. Projective representation of the "calcite family"

The small radius of action of the Coulomb forces proper also elevates the importance of higher order terms in the expansion giving the Coulomb potential of an ion and also terms of the nature of homopolar bindings. Thus we are not in general justified in leaving out higher order terms in Eq. (1).

We shall now consider some more general evidence of their regular behavior of crystals for small values of the exponent p. This we shall first do in the case of a class of crystals which is evolved by a continuous process from a single parameter ϕ.

IV. STABILITY FACTOR OF THE CALCITE FAMILY OF CRYSTALS

The family of crystals obtained by assigning arbitrary values to the angle ϕ, (See Fig. 4), we shall for convenience call the calcite family of crystals. When the angle ϕ assumes a value approximately 45 degrees we obtain a model which, geometrically speaking, is a replica of calcite. For $\sin\phi = 1/3^{1/2}$ each ion in our model has eight next neighbors, and the model corresponds to the CsCl-type of crystal. On the other hand, for $\sin\phi = 1/3$ each ion has six next niehgbors, and the model becomes synonymous with the NaCl-type of crystal. In addition we obtain a crystal of the hexagonal type for $\tan\phi = 1/32^{1/2}$ with each ion having 12 next neighbors, a crystal, however,which does not appear to be of any interest for our present purposes.

A convenient representation of this family of crystals is given in Fig. 5. The points represent linear, mixed point successions of the Madelung type perpendicular to the plane of the paper. The letters and numerals indicate phase-difference. For instance, $oU/3$ indicates that the nearest positive ion is displaced up one-third of the distance, δ, between successive ions, which is given by:

$$\delta = \tfrac{3}{4}\cdot d'\cdot\cos\phi. \tag{20}$$

With reference to Fig. 5 we can immediately write down the Coulomb energy for this family of crystals, by making use of Madelung's method. It is,

$$U_c = U(0,0) + \sum_{m=0}^{\infty}\ \sum_{n=0}^{\infty}{}'[U_1(m,n) + U_2(m,n)] \tag{21}$$

where $U(0,0) = -8\log 2\,(ne)^2/3\cdot d'\cdot\cos\phi$
and $U_1(m,n) = -16\,(ne)^2/3\cdot d'\cdot\cos\phi$.

$$\cdot\sum_{t=0}^{\infty}K_0\left(\frac{2\pi}{3}\tan\phi(2t+1)(3m^2+(2n-m)^2)^{1/2}\right)\cos\frac{(2t+1)}{3}\pi$$

and $U_2(m,n) = 16\,(ne)^2/3\cdot d'\cdot\cos\phi$

$$\cdot\sum_{t=0}^{\infty}K_0\left(\frac{2(3)^{1/2}}{3}\pi\tan\phi(2t+1)(m^2+3(2n-m)^2)^{1/2}\right)\left[1+\cos\frac{(2t+1)}{3}\pi\right].$$

The energy of the repulsive forces may be most conveniently determined by direct summation. It is,

$$u = u_1 + u_2 \tag{22}$$

where

$$u_1 = 2^pA/(d'\cdot\cos\phi)^p$$

$$\cdot\sum_{t=-\infty}^{\infty}\ \sum_{m=-\infty}^{\infty}\ \sum_{n=-\infty}^{\infty}[3t^2+(2m-t)^2+(3n+1)^2\cot^2\phi/4]^{-p/2}$$

and

$$u_2 = (4/3)^{p/2}[A/(d'\cdot\cos\phi)^p](S_1 - S_2)$$

where

$$S_1 = \sum_{t=-\infty}^{\infty}\ \sum_{n=-\infty}^{\infty}\ \sum_{m=-\infty}^{\infty}{}'\,[t^2+3(2m-t)^2+n^2\cot^2\phi]^{-p/2}$$

and

$$S_2 = \sum_{t=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} [t^2 + 3(2m - t)^2 + (3n + 1)^2 \cot^2 \phi/12]^{-p/2}.$$

A sufficient accuracy here is attained by summing about ten distinct terms directly, after which the summation may be replaced by an integration. The modified Hankel functions $K_0(x)$ appearing in Eq. (21) will be found tabulated in the literature.[16] In conjunction with Eq. (2) the Eqs. (21) and (22) enable us to calculate the stability factor for this family of crystals. Points of contact with previously calculated results are obtained for the angles $\sin^{-1}(1/3^{1/2})$ and $\sin^{-1}(1/3)$.

In Fig. 6 we have plotted the stability factor for this family of crystals for three different values of the exponent p, namely, 5, 9, and infinity. The stability factor for an infinite exponent, of course, must be found by a limiting process. For this exponent the repulsive effect of all but the next neighbors disappears, which is responsible for the discontinuity in the first derivative at arcsin (1/3) where the number of next neighbors changes from six to two.

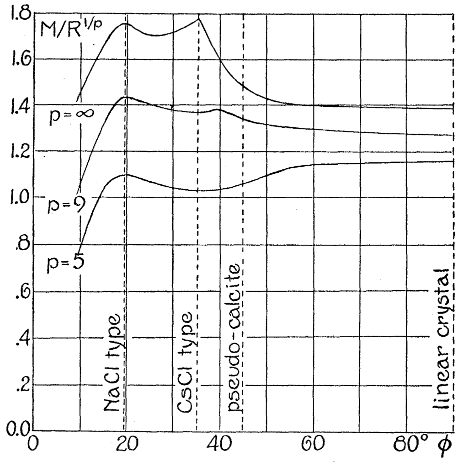

Fig. 6. Stability factor for the "calcite family."

For an infinite exponent the most stable members of this family crystals are seen to be the CsCl-type and the NaCl-type, in the order mentioned. As the exponent decreases the maximum in the neighborhood of the NaCl-type becomes more prominent than that in the neighborhood of the CsCl-type, and finally the NaCl-type becomes more stable than the CsCl-type. This is not the only effect of decreasing the exponent, however; a more startling effect is afforded by the shifting of the angles of maximum stability. The equilibrium position in the neighborhood of the NaCl-type of crystal is shifted only slightly, that in the neighborhood of the CsCl-type, on the other hand, quite appreciably, until finally the maximum occurs at an angle of 90

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[16] E. Jahnke and F. Emde, Funktionentafeln, p. 135 (1928).

degrees which corresponds to a linear crystal. For still smaller exponents the linear crystal becomes even more stable than the NaCl-type.

In general, therefore, our models of the NaCl-type and the CsCl-type of crystals are unstable against the ϕ-variation. The instability of the NaCl-type would lead to a somewhat skewed structure, which, however, would be so slight as to make definite pronouncements hazardous in view of the inaccuracies of the fundamental assumption (1). The instability of the CsCl-type, on the other hand, is unmistakable, the maximum being shifted more and more toward the structure which we have called "pseudo-calcite". It is of interest to note that such a structure could be accounted for on the basis of purely central forces. Of interest is also the mechanism of transition, which here we have found, between the NaCl-type of crystal and the CsCl-type. The energy maximum separating the two types will be seen, in all cases, to be small compared to the total energy.

Finally attention is again called to the evidence of the irregular behaviour in the region of small values of the exponent p exhibited by Fig. 6. It will be noticed that all members of the calcite family of crystals are less stable than the linear crystal in this region. To further illuminate this point we have in the following extended Hund's theory[9] to include linear and planar crystals.

V. EXTENSION OF HUND'S THEORY

In the paper by Hund,[9] to which we have repeatedly referred, he calculates the stability factor for a number of different types of crystals. In view of the tendency of our calcite family of crystals to fall apart into mixed linear point successions of the Madelung type for small values of the exponent p, it is of interest to extend Hund's work to include such linear crystals. Also, for the sake of generality, we shall include two-dimensional or planar crys-

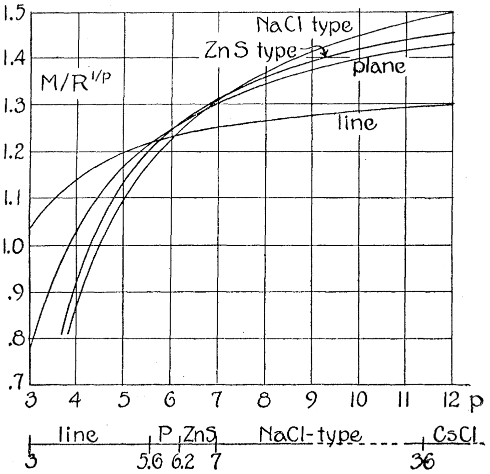

Fig. 7. Stability factor for the one-dimensional, two-dimensional, ZnS, and NaCl types of crystals.

tals, such as are obtained by isolating a 100-plane in the NaCl-type of crystal. The calculations closely parallel those of Hund and no further explanation is required except to say that wherever numerical series occur, the summation either has already been carried out in the literature, or it may be carried out to more than sufficient accuracy by direct summation of a few terms followed by the evaluation of an approximate integrated remainder.

Fig. 7 shows the result of these calculations together with the stability factors of the NaCl- and ZnS-types of crystals. The scale at the bottom of the figure indicates the regions in which each model is most stable. In spite of the idealized background of this diagram, its trend is so unmistakable that it seems permissible to draw some physical conclusions. The apparent instability of the ZnS-type, in particular, for an exponent five,[17] for instance, may not be real in view of the assumptions involved in Eq. (1), but it does not seem very probable that a modification of the energy function (1) could save the situation in general. In the various types of secondary structures, on the other hand, we have a source of energy which, in all cases, is ample to restore the stability of such a crystal as the one mentioned.[8,11]. Of these types of secondary structures the one based on a residual-ray variation[11] appears to be most suitable for the purpose of lining up the scale, Fig. 7, with observations, which is, however, a question to which we hope to return later.

The diagram 7 also appears to show some evidence in favor of the earlier type of secondary structure[8] which essentially consisted of a crystal within the crystal, that is, a regular network of two-dimensional crystals within the three-dimensional one. We are referring to the stability factor of the plane which will be seen to be nowhere very far below those of the three-dimensional crystals, and sometimes above. In order to establish the stability of this type of secondary structure it is, therefore, only necessary to devise a mechanism, such as the utilization of the energy of polarization, by which the comparatively small amount of energy separating the plane from the crystal may be gained without a corresponding loss. Such a mechanism has already been found by Zwicky,[8] and the success of his theory in accounting for the various structure sensitive properties is well known.

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[17] Calculated on the basis of compressibility data. See, for instance, reference 2, p. 746.