

A Contribution to the Theory of Heteropolar Crystals

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It is shown that the failure of theories of the solid state to account for the stability of ideal crystals cannot be due to inadequacy of the force postulate. A number of existing crystals, if ideal, would be dynamically unstable, with respect to certain variations, for any force postulate compatible with the compressibility data. These crystals cannot be ideal. A possible type of departure from the ideal state is suggested which involves a change of energy comparable with the heat of fusion (in agreement with Zwicky's theory). The change in volume at the melting point may be accounted for. Evidence from the photoelectric properties of these crystals indicates that this

proposed type of departure may have physical reality although undoubtedly accompanied by asymmetries. A consideration of the changes necessary in the energy function to permit the existence of secondary structure indicate that such secondary may exist even in crystals apparently dynamically stable. It is conjectural whether any crystal is thermodynamically stable in the ideal state. A working hypothesis that all crystals have a secondary structure leads to a rational explanation of the doublet nature of residual rays in cubic crystals and to an improved form of Lindemann's law.

I. INTRODUCTION

ANY theory of the solid state must explain the stability of existing crystals. Zwicky¹ and the writer² have shown that variations exist for which the conventional crystalline model³ is not stable, whereas the real crystal is definitely stable. As we have pointed out,⁴ the failure of the theory must be ascribed either to an inadequacy of the force postulate, or to failure to take account of certain "cooperative actions."⁵ The latter, arising as a natural consequence of the forces already postulated, would not require any new hypothesis.

In the present paper we shall demonstrate that modifications of the force postulate alone cannot save the situation,⁶ and that therefore we have here new evidence that Zwicky's cooperative

actions, (and consequently the secondary structure which, however, may be deformed into a mosaic structure),⁷ are necessary accompaniments to any theory of the solid state.

In the paper immediately preceding this we examined the experimental background of the force postulate. We saw that extrapolations beyond the immediate neighborhood of the equilibrium configuration are uncertain because the functional form of the force of repulsion is arbitrary. This uncertainty might be responsible for the failure of the ideal model to explain the stability of crystals. We pointed out, however, two different ways in which this uncertainty might be eliminated. By one method we constructed the force of repulsion, compatible with the experimental data, which would be the least favorable to the formation of a secondary structure. By the other, we confined attention to the neighborhood of the equilibrium position of the atoms, where the force is given experimentally, and where thus no hypothesis in regard to the functional form of the force is required. The latter method is more direct and requires less analysis, but the former has a wider field of

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¹ F. Zwicky, *Helv. Phys. Acta* **3**, 269 (1930); **4**, 49 (1931); *Phys. Rev.* **38**, 1772 (1931).

² H. M. Evjen, *Phys. Rev.* **34**, 1385 (1929); **39**, 675 (1932).

³ M. Born, *Atomtheorie d. Festen Zustandes*, Teubner, 1923.

⁴ See paper by Evjen immediately preceding this.

⁵ F. Zwicky, *Proc. Nat. Acad. Sci.* **17**, 524 (1931); *Phys. Rev.* **43**, 270 (1933).

⁶ Although it is not immediately apparent, our demonstration will also cover the possibility that the forces have a noncentral component, at least insofar as the next

neighbors are concerned. (See particularly Eq. (12a) and its implications.) This possibility has been suggested by L. Brillouin, *Scientia*, p. 206, March, 1932.

⁷ F. Zwicky, *Phys. Rev.* **40**, 63 (1932).

application, in that it is suitable when extrapolations are involved. Since, however, the former method is available for the purpose of the present paper, it will be employed. The problem which will be considered is that of obtaining the change in energy when a variation of the "residual ray" type⁸ is imposed on the crystal.

II. THE RESIDUAL RAY VARIATION

By this variation the negative lattice is displaced as a whole, over certain regions, with respect to the positive lattice. For convenience, the energy of the crystal may be divided into a negative energy of attraction and a positive energy of repulsion. Beyond reasonable doubt⁹ the energy of attraction for the heteropolar crystals, with which we shall be mainly concerned, is essentially a Coulomb term. The energy remaining after this term has been subtracted will be called the energy of repulsion. It is easily demonstrated that, because of the conditional convergence of the series involved, the change in Coulomb energy for the residual ray variation depends on the macroscopic shape of the region affected. We shall consider only the possibility that the shape of this region is either a needle or a thin slab, the relative displacement of the negative lattice being in the former case along the axis of the needle, in the latter, parallel to the boundary planes of the slab. These shapes can be shown to give rise to the greatest negative change in Coulomb energy. By subdividing the crystal, in a regular manner, into regions of these shapes, such that the displacements in neighboring regions are always in opposite directions, it is of course possible to have all the ions in the crystal take part in the variation. The manner of subdivision, however, is related to the geometry of a possible secondary structure, the discussion of which we shall defer.

The change in Coulomb energy per pair of ions by the relative displacement of the negative lattice against the positive lattice in a needle shaped or slab shaped region may be most easily found by considering the electric field in which the displacement takes place. Since this relative displacement is mathematically equivalent to a superposed dipole lattice, it turns out that the

electric field is in a direction to assist in the displacement, and is given by¹⁰

$$E = 2\pi e\Delta/3a_0^3(1 - 4\pi\alpha/3a_0^3),$$

where e is the individual electric charge of the ions, a_0 is the central separation of two neighboring ions, and Δ is the relative displacement. For generality the possibility also has been considered that the ions are deformable, the average polarizability of the two ions present being α . The change in Coulomb energy¹¹ consequently is given by:

$$W_c = - \int_0^\Delta eEd\Delta = -\pi e^2\Delta^2/3a_0^3(1 - 4\pi\alpha/3a_0^3). \quad (1)$$

Previous considerations⁴ have indicated that in calculating the energy of repulsion the effect of all but the next neighbors may be neglected. If we do consider more than the next neighbors, the gain in energy by the residual ray variation is actually somewhat greater. The error therefore is such as not to invalidate the main conclusion which is to be drawn, namely, that the ideal crystal is not always a dynamically stable state.

The change in energy of repulsion then may be represented in terms of the first nonvanishing term in a Taylor expansion, as follows

$$W_r = \frac{1}{2} \sum_{i=1}^m \frac{1}{m} \frac{\partial^2 \phi}{\partial x_i^2} \Delta^2,$$

where m is the number of next neighbors and x_i is the x -coordinate of the i th next neighbor. In our previous notation,⁴ if we limit ourselves to crystals of the NaCl-type, this may be rewritten as

$$W_r = (1/12) M e^2 \Delta^2 \{ (\partial F / \partial a)_{a=a_0} + (2/a_0) F_{a=a_0} \},$$

where

$$(\partial F / \partial a)_{a=a_0} = p/a_0^3, \quad \text{and} \quad F_{a=a_0} = -1/a_0^2.$$

¹⁰ H. F. Herzfeld, Phys. Rev. **29**, 701 (1926); and reference 8.

¹¹ The force of electric origin exerted during the displacement is actually,

$$f = eE + \alpha E(dE/dx)_{\Delta=\text{const.}}$$

namely, the force on the ion plus the force on the induced dipole. It can be shown, however, that so long as we are interested in infinitesimal displacements only, $(dE/dx)_{\Delta=\text{const.}}$ vanishes, so that the latter term drops out.

⁸ F. Zwicky, Phys. Rev. **38**, 1772 (1931).

⁹ J. C. Slater, Phys. Rev. **23**, 488 (1924).

Finally,

$$W_r = M(p-2)e^2\Delta^2/12a_0^3, \quad (2)$$

where p may be determined from the compressibility, κ , of the crystal, as follows $p = 2 + 18ca_0^4/Me^2\kappa$.

The total change in energy, by Eqs. (1) and (2), consequently is,

$$W = (M(p-2) - 4\pi/(1 - 4\pi\alpha/3a_0^3))e^2\Delta^2/12a_0^3. \quad (3)$$

This change in energy will be negative if,

$$M(p-2)(1 - 4\pi\alpha/3a_0^3) < 4\pi. \quad (4)$$

The least favorable condition for the fulfillment of this inequality is $\alpha = 0$. In this case, the inequality reduces to,

$$p < 2 + 4\pi/M \quad (5)$$

or, expressed in terms of the compressibility, $\kappa > 9Ga_0/2\pi N\rho e^2$, where G is the gram molecular weight, N is the Loschmidt number, ($6.06 \cdot 10^{23}$), and ρ is the density of the crystal.

The inequality (5) is not quite fulfilled for any available crystal. There is, however, no known reason why this inequality never should be fulfilled, so that, even in this extreme case, the ideal crystal is not always stable against the residual ray variation.

The more general condition (4), which would have to be used to test the stability of real crystals, can be rewritten in a more convenient form by means of the Lorenz-Lorentz law¹² for a non-absorbing medium. For crystals of the NaCl-type this law may be written,

$$4\pi\alpha/3a_0^3 = (n^2 - 1)/(n^2 + 2), \quad (6a)$$

where n is the index of refraction, so that the inequality (4) becomes:

$$n^2 > (3M(p-2)/4\pi) - 2 \quad (6)$$

or, expressed in terms of the compressibility,

$$n^2 > (27a_0G/2\pi N\rho e^2\kappa) - 2.$$

The latter form has the advantage that it

¹² See, for instance, P. Debye, *Handb. d. Radiologie*, VI, p. 597. If so desired, Eq. (6a) may be considered as a definition of n , and the most reliable determinations of α may be inserted into this equation for the purpose of obtaining n . See Born and Bolinov, *Handb. d. Physik* 24, 449.

contains nothing but well-known constants and directly measurable quantities. In its derivation we have limited ourselves to crystals of the NaCl-type. Before we apply this test to real crystals, however, we shall consider somewhat more in detail the possibilities involved if the inequality (6) should happen to be satisfied.

III. SECONDARY STRUCTURE

It was shown by Zwicky⁸ that the instability of an ideal crystal against the residual ray variation would lead to a secondary structure, since the variation, in order to be effective in decreasing the energy of the crystal, must take place over discrete regions of definite geometrical shape. This much is indubitable. Somewhat more doubtful is the question of the dimensions of the secondary structure. Zwicky⁸ estimated the dimensions by considering the lateral displacement which accompanies the variation. On account of the resulting strains, stresses are set up along the boundaries of the regions affected by the variation which ultimately may delimit the dimensions of the secondary structure. It can be shown that the lateral as well as the longitudinal change in lattice constant, accompanying the residual ray variation, are of a higher order. That is, if the latter is infinitesimal of the order Δ , the former will be of the order Δ^2 . Correspondingly the energy changes will be of the order respectively Δ^2 and Δ^4 . If therefore we start with the ideal crystal, there will be no change in lattice constant, either lateral or longitudinal, at the outset of the residual ray variation; and at this stage of the development these secondary effects play no part in the energetic equation. On the other hand, along the boundaries of the regions affected by the variation, the ions will find themselves in different surroundings from those prevailing in the interior of these regions, and the energy change here, whereas in general different from that in the interior, is of the same order of magnitude. If the gain in energy along the boundaries is smaller than that in the interior, we should expect as few boundary planes as possible. In this case the dimensions of the secondary structure evidently would be determined by considerations analogous to those of Zwicky's, or else we would get macroscopic

electric moments such as exhibited by electrets, as also suggested by Zwicky. On the other hand, if the gain in energy should be greater along the boundaries of the polarized regions, other things being equal, we should expect as many boundaries as possible. In the limit, the secondary structure would be reduced to dimensions not far removed from those of the elementary cell of the primary structure.

To settle some of these questions we have in the following calculated the change in energy of ions at the boundaries of various polarized configurations. It should be noticed that the change in energy of these ions depends on the manner in which the adjoining regions are polarized. If the negative lattice in one region is displaced in one direction, that in the adjoining region in the opposite direction, such that the entire positive lattice remains undisplaced, the electric field at the positive boundary ion is different from that at the negative ion. On the other hand, if the negative lattice in one region is displaced in one direction, and the positive lattice in the adjoining

region in the same direction, the electric field at the positive boundary ion is the same as that at the negative ion. In general, it appears that the latter "boundary condition," that is, the symmetrical one, gives the more favorable energy change. We therefore give the results only for this condition. Likewise we have omitted the results for slabs of minute thickness which, in general, appear to be energetically less favorable than very thin needles.

The calculation of the change in Coulomb energy, wherever possible, has been carried out by two or more methods, simplest and most direct of which is the method involving the change in energy by the displacement of an ion against a Madelung line.¹³ These calculations, although somewhat tedious, are quite straightforward and no further comment is required.

The most important results of the calculations in terms of the index of refraction and the quantity p are summarized in the following four equations, where, for the sake of completeness, we have also repeated a statement of Eq. (3).

Change in energy per pair of ions by the residual ray variation

- (1) Interior ions in needles or slabs.

$$W_1 = [M(p-2) - 4.1888(n^2+2)]e^2\Delta^2/12a_0^3.$$

- (2) Boundary ions of these needles or slabs.

$$W_2 = \left\{ M(p-3/2) - \frac{4.5168 \cdot 12.5664(n^2+2)}{(12.8944 - 0.328n^2)} \right\} e^2\Delta^2/12a_0^3.$$

- (3) Needles of four ions cross section.

$$W_3 = \left\{ M(p-1) - \frac{4.8120 \cdot 12.5664(n^2+2)}{(13.1896 - 0.6232n^2)} \right\} e^2\Delta^2/12a_0^3.$$

- (4) Madelung lines polarized alternately in opposite directions.

$$W_4 = \left\{ Mp - \frac{5.3536 \cdot 12.5664(n^2+2)}{(13.7312 - 1.1648n^2)} \right\} e^2\Delta^2/12a_0^3. \quad (7)$$

From these equations it is seen that when $W_2 < W_1$, or $n^2 > 1.95$, the gain in energy of the boundary ion is greater than that of the interior ion, so that the tendency would be for as many boundary planes as possible. If $W_3 < W_2$, or $n^2 > 2.05$, the tendency would be for the needles

to have a cross section of four ions or less. Similarly the tendency would be for a cross section of a single ion if $W_3 < W_4$, that is, $n^2 > 2.10$. Finally, it is seen that for $n^2 > 11.8$ the

¹³ E. Madelung, Phys. Zeits. 19, 524 (1918).

polarizing force in the Madelung lines becomes infinite so that the atoms would be stripped of an electron. This may be contrasted with Herzfeld's condition,¹⁰ which, based essentially on the first of these equations, gives the same result only for an infinite index of refraction. It should be noticed that the facts to which we have called attention refer only to the tendency at the outset of a variation which starts from the ideal crystal. For reasons which we shall shortly point out, we are not justified in drawing conclusions about the state of affairs which will prevail at the end of the variation.

All that can be said with certainty is that if any one of the energy changes W_1 to W_4 should turn out to be negative, the ideal state would be dynamically unstable. In Fig. 1 we have mapped,

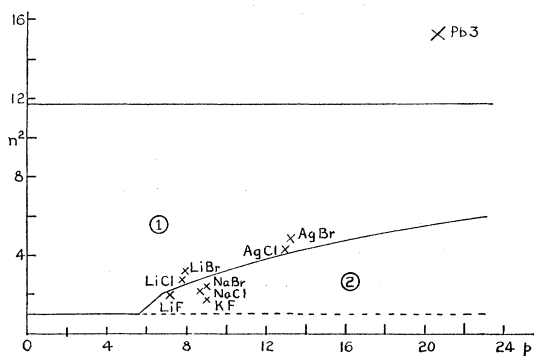


FIG. 1. Regions of dynamic stability and instability of the ideal state. (1) Ideal state dynamically unstable in regard to the residual ray variation. (2) Ideal state dynamically stable but not necessarily thermodynamically stable.

in terms of n^2 and p the region in which this would be true. In the preparation of this map the benefit of any doubt has been given to the ideal crystal. Otherwise it entails no hypothesis of any kind, and only directly measurable quantities are required to give the position of a real crystal in the map. Now, it may be that for reasons unknown to us, all real crystals would fall in the region assigned to the ideal crystal. If, on the other hand, we should find some crystals, having such properties that they would fall in the region where the ideal state is dynamically unstable, the evidence would be overwhelming that non-ideal states have real physical significance.

IV. INTRODUCTION OF THE REAL CRYSTAL

In the preparation of the map, Fig. 1, we have limited ourselves to crystals of the NaCl-type. In our search for non-ideal crystals we shall therefore be limited to crystals of this same type. Among the well-known alkali halides we find crystals which are definitely unstable in regard to the residual ray variation. Whereas LiF must be classified as doubtful,¹⁴ LiBr and LiCl fall well outside the region in which the ideal state is stable. For these crystals, therefore, the ideal state is not even pseudostable, and the existence of a secondary structure may be considered as well established. The silver halides likewise appear to be definitely unstable in the ideal state. PbS, on the basis of values obtained from the *Critical Tables*, appears to fall in the region of infinite polarizing fields, and therefore should have the properties of a metal by our modified Herzfeld condition. This result, however, is not conclusive, since the fact that PbS is definitely not ideal ruins the premises of our calculations. For this same reason, and also because higher order terms have not been considered, we can draw no definite conclusions about the ultimate nature and dimensions of the secondary structure which will result when the ideal crystal is dynamically unstable. All that can be said with certainty is that a secondary structure of some kind will come into existence. There are, however, indications that the present variation has a real physical significance with perhaps minor modifications, relating mainly to a redistribution of atoms at the boundaries of the polarized regions.

By Zwicky's general theory of the solid state⁵ the secondary structure with its cooperative actions is not only to be considered as a slight modification of the ideal state; it is, in fact, supposed to be responsible for the very existence of the crystal. By this theory the energetic aspects of the ideal state are already roughly realized in a statistical manner in the melt. It follows that the heat of fusion of the crystal should be roughly the same as the gain in energy

¹⁴ In Section V we shall see that there is good reason to believe that LiF is at least *thermodynamically* unstable in regard to the present variation. This is of interest in view of the direct experimental evidence obtained by Johnson for a secondary structure in this salt. See Thomas H. Johnson, J. Frank. Inst. **212**, 507 (1931).

by a variation leading from the ideal state to the secondary structure. We can estimate fairly well the gain in energy by a variation of the present type. A simple calculation, the details of which we shall not include, will show that for such crystals as AgBr and LiCl this gain in energy is in good agreement with the heat of fusion. Likewise, from more general considerations, to which we shall return in the last paragraph of this paper, it appears that the change in volume at the melting point may be accounted for in this same way. From this we can probably conclude that the secondary structure in these crystals depends in some essential manner on a variation of the present type.

Further evidence that the present type of departure from the ideal state has physical reality is furnished from the field of non-metallic electronic conduction. The residual ray variation, in its essence, involves a partial liberation of electrons, implied by the deformation of the ions. On this idea, in its extreme of course, is based Herzfeld's theory of metals,¹⁰ the difference being that in the present case the polarizing fields are not sufficient completely to strip the ion of an electron. If the departure from the ideal state here described has physical reality, the individual ions of the crystal would be in a state of deformation depending on their polarizability as well as on the polarizing fields. It is therefore not unreasonable that a correlation should exist between the liberation of conduction electrons by say photoelectric means and the existence of a secondary structure of the present type. Such a correlation does in fact appear to exist. We are referring to the photoelectric output maxima characterized by their presence at the lower limit of the ultraviolet region of absorption.¹⁵ An examination of the photoelectric data available does indeed indicate that these output maxima can occur only in crystals which, in the ideal state, are definitely unstable in regard to the residual ray variation. Empirically this condition has found expression in the rule that these output maxima can occur only in crystals having an index of refraction greater than 2.¹⁵ It is otherwise not unreasonable that these particular photoelectrons should originate in a secondary

structure of the present type. On the one hand, an exhaustive review of the field has led Gudden¹⁵ to believe that nonmetallic conduction electrons, whether liberated photoelectrically or thermally, never originate in the ideal lattice. On the other hand, the strong dependence of these photoelectric and related phenomena on impurities and the past history of the sample brands these as structure-sensitive properties, which by Zwicky's theory¹ are closely related to the existence of a secondary structure. Finally the residual ray type of secondary structure is distinguished from other proposed structures in that it is essentially a volume effect. The presence of impurities therefore should have a smaller effect with this type than with the two-dimensional type¹ where the relative abundance in the secondary network may be quite considerable even though the total amount of impurities is vanishingly small. It is a characteristic of the particular photoelectric output maxima with which we here are concerned that they are less influenced by impurities than other such maxima.¹⁵

From the preceding calculations and considerations we now summarize: Crystals exist which are definitely unstable in the ideal state. Consequently these crystals cannot be ideal. Although the exact manner in which these crystals will depart from the ideal state is not accessible to calculations there is evidence to the effect that the secondary structure depends in some essential manner on the so-called residual ray variation. In the cases where the ideal state is a real minimum and not a saddle point in regard to this variation the question is still open whether or not the ideal crystal is thermodynamically stable. In the following paragraph we shall attempt to show that the ideal state in these cases should not always be expected to be thermodynamically stable.

V. ENERGY OF RESIDUALLY DISPLACED HETEROPOLAR CRYSTAL, AND A DERIVATION OF LINDEMANN'S LAW

In the preceding pages has been demonstrated the possibility that real crystals have a secondary structure of the residual ray type. In general, therefore, we are not justified in writing the energy of the crystal in the con-

¹⁵ B. Gudden, *Phys. Zeits.* **21**, 825 (1931).

ventional manner as $U = U_c(a) + U_r(a)$, where the Coulomb energy and the energy of repulsion both are considered as functions of the single variable, a , or the atomic separation. To include the possibility that the crystal may be residually displaced, we must now write the energy of the crystal as follows:

$$U = U_c(a, \Delta) + U_r(a, \Delta). \quad (8)$$

To replace the simple conventional equilibrium condition, $[dU/da]_{a=a_1} = 0$, we now obtain the two equations:

$$\begin{aligned} [\partial U / \partial a]_{(a=a_0) / (\Delta=\Delta_0)} &= 0; \\ [\partial U / \partial \Delta]_{(a=a_0) / (\Delta=\Delta_0)} &= 0, \end{aligned} \quad (9)$$

where, to exclude saddle points and maxima, we must impose the additional restrictions:

$$[\partial^2 U / \partial a^2]_{a_0, \Delta_0} > 0, \quad [\partial^2 U / \partial \Delta^2]_{a_0, \Delta_0} > 0. \quad (10)$$

Furthermore, the function U is no longer tied up with the compressibility, κ_0 , in the simple manner,⁴

$$d^2 U / da^2 = 9ca_1 / \kappa_0. \quad (11)$$

The correlation now becomes:

$$\partial^2 U / \partial a^2 - \frac{[\partial^2 U / \partial a \partial \Delta]^2}{\partial^2 U / \partial \Delta^2} = 9ca_0 / \kappa_0.$$

The phenomenological theory of the interatomic forces in heteropolar crystals thus needs revision. A general quantitative treatment will not be attempted in the present paper. We shall, however, attempt to demonstrate that a revision may be required also in the cases when the ideal state is dynamically stable. For this demonstration certain simplifying assumptions are permissible. In the first place, all terms of order higher than Δ^2 will be neglected in the Coulomb and polarization energies. Since all higher order terms are negative, this neglect favors the ideal crystal. In the second place, only the next neighbors will be considered insofar as the energy of repulsion is concerned. This also favors the ideal crystal. Finally we shall only consider the Madelung line case, which for finite displacements, Δ , is undoubtedly less favorable energetically than Zwicky's secondary structure. *With three perpendicular sets of such lines, intersecting to form a secondary structure of mini-*

mal dimensions in the crystal, Eq. (8) may be written:

$$U = Me^2 \left(-\frac{1}{2}a - g\Delta^2/a^3 + \phi(a+\Delta) + \phi(a-\Delta) \right), \quad (12a)$$

where, by Eq. (7),

$$g = \frac{5.3536 \cdot 12.5664(n^2+2)}{4M(13.7312 - 1.1648n^2)}.$$

Eqs. (9) similarly become:

$$\begin{aligned} \frac{1}{2}(\phi'(a+\Delta) + \phi'(a-\Delta)) &= -1/a^2 - 6g\Delta^2/a^4, \\ \frac{1}{2}(\phi'(a+\Delta) - \phi'(a-\Delta)) &= 4g\Delta/a^3. \end{aligned} \quad (12)$$

The latter of these equations is satisfied identically for $\Delta=0$. The corresponding solution of the first equation is say, $a=a_1$. This solution does not always represent a real minimum, however; for when $p = a_1^3 \phi''(a_1) < 4g$, the second one of the inequalities (10) is not satisfied, so that the solution represents a saddle point. This is the case which we have already considered, namely the case when W_4 in Eq. (7) is negative, and the ideal state is dynamically unstable. We are now interested in the case when the ideal state is apparently dynamically stable, that is, $p > 4g$. For the sake of argument it is assumed that the real crystal is ideal in this case, so that Eq. (11) is applicable. Calculations demonstrate that Eqs. (12) ordinarily have real solutions other than $\Delta=0$, $a=a_1$, satisfying the inequalities (10). The question whether these other minima represent lower energies than the ideal state, requires knowledge about the functional form of the energy of repulsion. For functions such as the exponential or the inverse power,⁴ it appears that when a condition, $(p-4g)/p < s$ is fulfilled, where s is of the order 1/5 to 1/10, energy states exist which are lower than that of the ideal state. In other words, the boundary in Fig. 1, to the left of which the ideal state is dynamically unstable, is more or less paralleled by another boundary, to the left of which the ideal state is thermodynamically unstable. An exact calculation of this second boundary is hardly worth the trouble in view of the uncertain nature of the premises of the calculations. It should be noted, however, that in these premises the benefit of any doubt has been given to the ideal crystal. It is therefore significant that, for any reasonable

functional form of the energy of repulsion, the maximum ratio, s , for which the ideal state is thermodynamically unstable, is definitely positive. We are therefore justified in believing that a number of the real crystals which are dynamically stable in the ideal state will be thermodynamically unstable. The number of such crystals cannot be calculated without hazardous extrapolations. It is as yet conjectural whether any crystal exists that is thermodynamically stable in the ideal state.

From these considerations it is permissible to adopt, as a working hypothesis, the view that the secondary structure here implied is a general phenomenon, since there is no evidence definitely negating its existence even in crystals which are apparently dynamically stable in the ideal state. The existence of such a general type of secondary structure would be highly desirable from the aesthetic point of view, and even may be said to be phenomenologically suggested. The following experimental evidence, supporting this view, is presented:

In the first place, Professor F. Zwicky called the attention of the writer to the doublet nature¹⁶ of the so-called residual rays (Reststrahlen) in cubical crystals which appears to be a quite general phenomenon. Such a doublet nature is apparently inconsistent with the cubical symmetry of the ideal state¹⁷ but, as pointed out by Zwicky, is exactly what we should expect if the crystal is submicroscopically slightly tetragonal as implied by the residual ray secondary structure. In the second place, if we assume that this type of secondary structure is a general phenomenon which, in accordance with Zwicky's theory of the solid state,⁵ is responsible for the existence of the solid phase, the so-called Lindemann's law may be satisfactorily accounted for and even improved upon.

Lindemann's law¹⁸ connects the residual ray frequency with the melting point, T_s , of the crystal, and was first derived by Lindemann on the basis of an improbable model. Independently

of this derivation dimensional analysis¹⁹ yields,

$$\nu = CR^{\frac{1}{2}}N^{\frac{1}{3}}(T_s/MV)^{\frac{1}{2}},$$

where R is the gas constant, $N=6.06 \cdot 10^{23}$, M the molecular weight, and $V=M/\rho$ the specific volume per mol. C is dimensionless and was found by Lindemann to be approximately constant for a number of crystals. The law otherwise has found no satisfactory theoretical explanation.

On the basis of the present hypothesis, however, this same law may be easily derived. If we disregard the volume contraction, which, as we have seen, would accompany the residual displacement, the change in energy by the displacement is given by the following expansion:

$$\Delta U = -c_1\Delta^2 + c_2\Delta^4,$$

where terms of the order six and higher in the displacement have been neglected. Equilibrium will be reached when, $\partial\Delta U/\partial\Delta=0$ or $\Delta_0^2=c_1/2c_2$ and consequently the maximum gain in energy will be, $\Delta U_0=-\frac{1}{2}c_1\Delta_0^2$. By carrying out this variation in three mutually perpendicular directions we arrive, as we have previously seen, at a secondary structure; and by the argument previously advanced, the total gain in energy by this variation should form a substantial fraction, say β , of the heat of fusion, h , of the crystal, the remainder being furnished mainly by a contraction corresponding to the change in volume at the melting point. We can therefore write,

$$c_1 = 2\beta h/3\Delta_0^2 = (2^{5/3}/3)(N/V)^{\frac{2}{3}}(a/\Delta_0)^2\beta h,$$

where $\beta < 1$ may be expected to be roughly constant for different crystals. For convenience this result may be expressed in terms of the melting point by the following relation: $Nh/RT_s = 4.19\alpha/8.31$, where α has been shown by J. W. Richards²⁰ to be roughly constant for a number of crystals. For the alkali halides α ranges in the neighborhood of 5.

The residual ray frequency, by a well-known elementary theory,²¹ may be expressed as follows:

$$2\pi\nu = (\lambda(m_1+m_2)/m_1m_2)^{\frac{1}{2}},$$

¹⁶ Karl Korth, *Göttinger Nachrichten*, p. 576, 1932.

¹⁷ See, however, attempt by M. Born and M. Blackman, *Zeits. f. Physik* **82**, 551 (1933), to reconcile this doublet nature with the ideal state (an article which appeared after the preparation of this manuscript).

¹⁸ F. A. Lindemann, *Phys. Zeits.* **11**, 609 (1910).

¹⁹ A. Einstein, *Ann. d. Physik* **35**, 689 (1911). E. Grüneisen, *Ann. d. Physik* **39**, 257 (1912).

²⁰ A. Eucken, *Lehrb. d. Chem. Phys.*, p. 220, Leipzig, 1930.

²¹ See, e.g., reference 3, p. 740.

where m_1 and m_2 are the masses of the two ions of the heteropolar crystal. If we disregard the slight tetragonality, introduced by the secondary structure, which as we have seen would give rise to two characteristic frequencies, the quantity λ is given by,

$$\lambda = (\partial^2 \Delta U / \partial \Delta^2)_{\Delta = \Delta_0} = 4c_1.$$

Consequently the residual ray frequency becomes,

$$\nu = 0.465(\alpha\beta)^{\frac{1}{2}}(a/\Delta_0)R^{\frac{1}{2}}N^{\frac{1}{2}}(T_s/\overline{M}V^{\frac{2}{3}})^{\frac{1}{2}}, \quad (13)$$

where $\overline{M} = 4M_1M_2/(M_1 + M_2)$.

This result is essentially Lindemann's law with the exception that \overline{M} has replaced M . In Table I we have tabulated the data employed by Lindemann to test the validity of his formula. It is seen that the substitution of \overline{M} for M , generally speaking, improves the representation. This is particularly noticeable in the case of *KI* where the discrepancy between \overline{M} and M is particularly great.

TABLE I. Comparison of Lindemann's formula with ours.

Crystal	$\lambda_{\text{obs.}}$	$\lambda_{\text{Lind.}}$	λ_{ours}
KCl	63.4	(63.4)	(63.4)
KBr	82.3	85.6	84.0
KI	96.7	112.2	95.4
NaCl	51.7	49.8	48.8

To see whether our formula (13) gives reasonable values for the ratio Δ_0/a we shall employ more recent and more accurate determinations¹⁶

of the residual wave-lengths. In Table II we have tabulated essentially this ratio, calculated from the shorter of the two characteristic frequencies.

TABLE II. Residual displacement predicted by the theory.

Crystal	$\lambda_{\text{obs.}}$	$(\Delta_0/a)(\alpha\beta)^{-\frac{1}{2}}$
KCl	45.5	0.061
NaCl	38.0	0.066
NaF	24.0	0.064
LiF	16.8	0.068

The quantity $(\alpha\beta)^{\frac{1}{2}}$ is of the order of unity, so that this result is reasonable, and is consistent with estimates of the residual displacements arrived at in independent ways.⁸ The approximate constancy of the ratio $(\Delta_0/a)(\alpha\beta)^{-\frac{1}{2}}$ is interesting, and it can be shown that this is also consistent with the theory. For this demonstration it is necessary to consider the problem thermodynamically, which will not be here attempted. We shall, however, indicate the result of a preliminary statistical treatment. For an exponential law of repulsion the following equation represents a first approximation:

$$(\Delta_0/a)(\alpha\beta)^{-\frac{1}{2}} = 1/(3^{\frac{1}{2}}p).$$

With the values of p , previously tabulated,⁴ we obtain for KCl, 0.0595, for NaCl, 0.0656, and for LiF, 0.077. This is in excellent agreement with Table II, and is encouraging evidence for the general occurrence of the residual ray type of secondary structure.