

WHY CRYSTALS EXIST

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§ 1. *Introduction.*—After the discoveries of Laue and Bragg the physics of crystals progressed very rapidly, both experimentally and theoretically. Taking the existence of regular arrangements of atoms in lattices for granted, Laue, Madelung, Born and others developed the theory of ideal crystals. This theory met with great success as far as certain special properties of crystals are concerned. However, at the same time it became apparent that its foundations were not broad enough to provide for a general scheme in which all the phenomena related to the crystalline state could be incorporated. The purpose of this paper is to show that this failure of the theory may have its origin in the fact that nobody seems to have considered seriously the question why crystals do exist at all. A tentative answer to this question will be given in the following. To obtain this answer it will be found that special emphasis must be laid on the problem of arriving at a clear understanding of the nature of the transitions gas-liquid, and liquid-crystal. The suggested solution also throws new light on the problem of the primary and the secondary (mosaic) structure in crystals.

§ 2. *Difficulties of the Theory of Ideal Crystals.*—One of the greatest puzzles in the physics of solids is the existence of structure sensitive phenomena in single crystals. As an illustration I mention a few of the difficulties which are related to the problem of the mechanical strength of single crystals. (See figure 1.)

(a) The yield point, where a plastic deformation first sets in, lies well within the region of the validity of Hooke's law. It seems fairly obvious that for an ideal lattice a reversible strain-stress curve must be expected, showing deviations from Hooke's law, long before the crystal is actually destroyed.

(b) The yield point in general is much too low inasmuch as a real crystal can be destroyed by forces which are often 100 to 10,000 times smaller than those calculated from the theory of ideal atomic lattices.

(c) The crystals after yielding very often become stronger, sometimes as much as a hundred-fold. This phenomenon, known as cold hardening, constitutes a paradox as it seems impossible to understand why an ideal crystal lattice should become stronger after it has been actually destroyed.

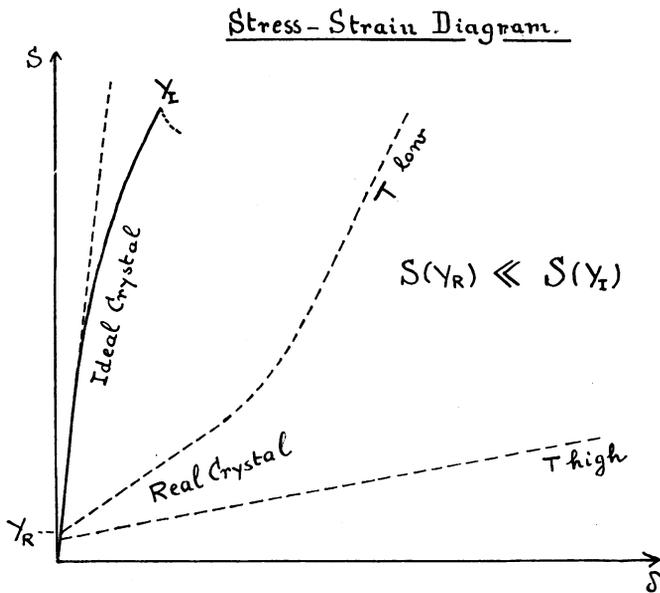
The discussion of difficulties of this kind and the problem of the structure-sensitive properties of solids in general have constituted the main subject of some of my recent publications. I advanced the suggestion that

crystals, geometrically speaking, are not completely characterized by their primary structure alone.¹ On top of the primary structure there appears in general a secondary structure which may be thought of as a crystal within the crystal. The correlation with crystal properties which I have proposed may roughly be characterized by this scheme:

Primary structure———structure insensitive properties

Secondary structure———structure sensitive properties

The idea of the secondary structure provides a satisfactory solution for many of the difficulties encountered by the older theory. Also, a con-



siderable number of new phenomena have been discovered, checking predictions made by the new theory. Nevertheless it seems to me that the considerations from which the existence of a secondary structure has been inferred need to be generalized. Indeed, the difficulties mentioned above are of a very general nature and with a few exceptions do not depend on the particular nature of the crystals involved. It appears therefore that a solution of the problem must be found from an understanding of the most general characteristics of a crystal. Now one of the most fundamental properties of a crystal is undoubtedly its existence. The real problem therefore seems to be to understand why crystals exist.

§ 3. *On the Reasons for the Existence of Crystals.*—If we wish to find the physical justification for the existence of crystals we have first to

formulate some of the more outstanding peculiarities of the crystalline state. I think that the following points are important.

(A) There is a sharp melting point which marks the transition from the crystal to the melt. The transition takes place within a very narrow region of temperature. In other words, the crystal and the liquid represent two different phases, thermodynamically speaking. The existence of such a sharp transition point with pressure and temperature constant and only the total internal energy of the system changing, is really a paradox because of the fact that statistical mechanics in general requires a gradual dissociation of atomic complexes with temperature. Indeed, if a system can be in two energy states, E_1 and E_2 , the relative probability of the two states is proportional to $e^{(E_2 - E_1)/KT}$, a function which is gradually changing with temperature. It will therefore be necessary to investigate which particular circumstances may cause the dissociation (melting) to take place abruptly. In order to find a solution of this problem we shall have to introduce considerations involving the simultaneous action of great numbers of particles.

(B) Atoms in crystals are lined up over great distances, often to a very high degree of accuracy. This fact is surprising because it is known that the action radii of atoms usually extend over a few Angstroms only. The persistence of direction in a crystal is still more surprising if we remark that it is very little affected by the introduction of relatively large amounts of impurities which certainly change almost completely the fields of force of the atoms making up the original substance. An important consequence of the presence of impurities is that it causes a peculiar co-existence of perfection and imperfection in single crystals. Consider for instance a Zn-crystal. Then, due to the impurities, the slipping strength (yield point) may vary considerably if we progress along the hexagonal axis, whereas the direction of this axis apparently stays unmolested. No similar behavior is known for individual atoms or molecules. Perfection and imperfection seem to appear simultaneously only for larger assemblies of elementary particles.

(C) The transition liquid-crystal is apparently of an entirely different type from the transition gas-liquid. This latter transition can be brought to disappear by a suitable change of pressure. However, nobody has succeeded so far in producing a continuous transition from the crystal to the melt. According to G. Tammann's views such a process is impossible. This is because of the fact that the crystalline state either forms a closed region in the phase diagram or that the melting curve extends to infinity.

Our problem then is to find a conception of the crystalline state which satisfies the requirements A, B and C. We first ask how, from the standpoint of statistical mechanics, it is possible to deduce a sharp transition

point without making use of any trick properties of a special model. It appears that the only relevant phenomena of sufficient generality are those involving the simultaneous coöperation of many particles. If two energy states are involved the Boltzmann factor $e^{-E_1/KT}$ for one state can then be made very large on account of small E_1 and its *a priori* probability very small, whereas for the other state the reverse conditions can be supposed to hold. If we make the total probabilities of the two states equal by choosing a suitable value for the temperature we actually obtain a sharp transition point.

Now there is practically only one possibility to make the (negative) energy of a particular state very large, namely, by choosing coördinates for the different particles which are nearly alike. In other words we must bring the atoms near together. This can, of course, be done both in regard to position and in regard to direction. Suppose that we bring many atoms simultaneously in close contact regardless of any lineup. We then get a very low energy state because of the action of the general cohesive forces. The resulting large Boltzmann factor compensates for the large *a priori* probability which characterizes the substance in the gaseous state. This consideration therefore suggests that the transition gas-liquid is caused by the simultaneous agreement of many atoms to stay close together. It is evident that a transition point of this kind may be made to disappear by a change in pressure which sufficiently cuts down the *a priori* probability of the gaseous state.

The second alternative is to have a great number of articles coöperate not only about their proximity in space but about their lineup as well. If actions of this kind can be found it is very suggestive to make them responsible for the existence of crystals. Such actions would, indeed, satisfy all our three requirements A, B and C. Namely (A), as coöperative actions of many atoms they produce a sharp melting point, (B) they exert an influence over distances which are much larger than the usual atomic dimensions, and therefore are not greatly disturbed by small amounts of impurities and (C), they cannot be essentially influenced by a change of pressure, as this process has no directional characteristics. There is therefore no continuous transition from the crystal to the melt.

On the strength of the above considerations we adopt the following working hypothesis. Sharp transition points and the existence of phases in general are to be attributed to some type of simultaneous coöperation of many elementary particles. If this coöperation refers to the relative mutual distances in space alone, we obtain the transition from the gas to the liquid. If this coöperation refers to the lineup in space also we obtain the transition liquid-crystal.

It is clear that our whole scheme would be worthless unless we can actually find coöperative phenomena in atomic assemblies satisfying the

above requirements. Section 5 will be devoted to a short discussion of some of the more promising possibilities. However, before we go into that, I wish to point out a few general conclusions which are suggested by the previous considerations.

§ 4. *Consequences of the Proposed Hypothesis.*—It appears from the previous section that the usual cohesive forces which act only over atomic distances are essential in effecting the transition from the gaseous to the liquid state. However, a new type of force, extending over many atoms simultaneously, must be investigated in order to arrive at an understanding of the change from the liquid to the crystal. To state it very paradox-

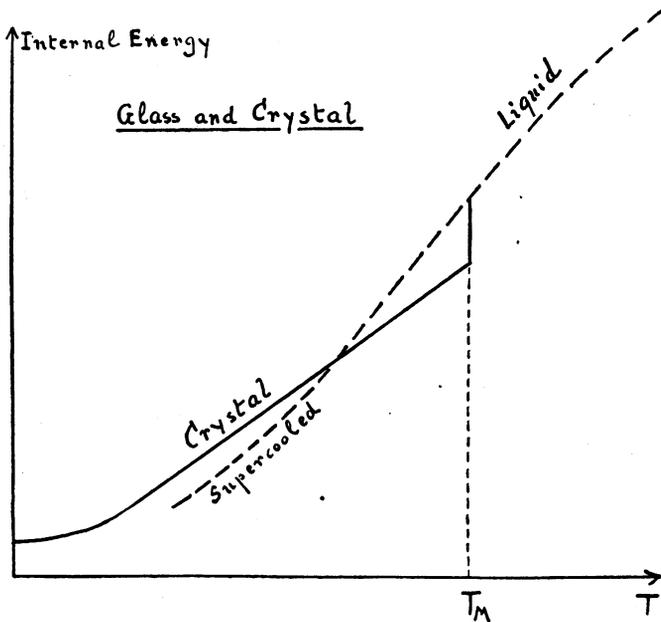


FIGURE 2

ically, we might say, that those forces which determine the primary structure of a crystal are not at the same time responsible for the crystal formation itself. For instance, the primary structure of NaCl is such that each Na^+ ion is surrounded by six Cl^- ions and vice versa. On the other hand in CsCl a Cs^+ ion is surrounded by eight Cl^- ions and vice versa. Our claim is that these arrangements involving six and eight neighbors, respectively, are realized in the melts of the two salts already, at least statistically speaking. These primary arrangements therefore can hardly be made responsible for the crystal formation, inasmuch as they would produce a crystal only at the absolute zero point. If this view is correct it should be possible to find supercooled liquids which

represent configurations of lower energies than crystals of the same substance at the same temperature. The energy diagram of such a substance would be of the type shown in figure 2. We can hope for the realization of this case only if the heat of fusion is very small. Fortunately data for certain glasses are available which prove that liquids may in fact be in a lower energy state than the corresponding crystal.² Although only a few cases of this type are known, they are very significant as a support for our point of view.

It follows further that those forces which form the crystal represent an additional amount of energy which must appear in the heat of fusion. Certain deviations of the specific heat curve from Dulong-Petit's law at high temperatures may have their origin here also.³

The most interesting conclusion which we can draw from our considerations is that crystals in general must show a secondary structure which is superposed on the primary structure. Indeed, if those simultaneous actions which line up the atoms do not possess the same type of symmetry as the primary structure it will be impossible to obtain a geometrically ideal crystal. How this results in the formation of a secondary structure will be better understood from some examples given in the next section. At any rate we arrive at the conclusion that those elementary phenomena which are responsible for the crystalline state in general also demand the existence of a secondary structure.

We go on to discuss some of the phenomena which involve the simultaneous coöperation of many particles and which therefore represent actions over large distances.

§ 5. *Effects Depending on the Mutual Action of a Great Number of Elementary Particles.*—This is a very brief survey of some phenomena which might be of importance in regard to crystal formation. A more detailed discussion will appear in the *Physical Review*.

(a) Permanent Electric Polarization in Crystals.—It is possible to take Herzfeld's theory⁴ of the reasons why certain elements are metals and generalize it to cases where not only the polarizability of the atoms is considered but the dielectric properties of atomic or ionic lattices as well. One finds that certain cubic lattices satisfy the requirement of minimum energy only if they are in a state of permanent electric polarization. The criterion whether this will happen or not is furnished by a certain theoretical relation between the exponents by which the distance enters into the expressions for the attractive and the repulsive forces, respectively. The type of secondary structure which may result if the described effect is present will be discussed in another place.

(b) Permanent Magnetic Polarization in Crystals.—This phenomenon which characterizes ferromagnetic substances is well known. It causes in iron, cobalt, etc., what might be called a magnetic secondary structure.

This structure is essentially of tetragonal symmetry which in iron is superposed on a cubic primary structure. The elementary particles whose coöperation results in ferromagnetism are electron spins on the one hand and completely saturated blocks containing some hundred thousands of atoms on the other hand.⁵ This leads to a rather complicated structure of ferromagnetic crystals inasmuch as one must expect at least two different types of secondary structures which are interwoven with the primary structure. There is some experimental evidence which supports this view.

(c) Dehlinger's "Verhakungen."⁶—Suppose that a great number of atoms are arranged on a straight line at mutual distances, d , which configuration we assume to be in equilibrium. We then put this assembly into a field whose potential energy has maxima and minima in regular distances, d , parallel to our stright line. There are two types of equilibrium configurations. The first is the same as above with the atoms at regular

I Regular Arrangement II Verhakung

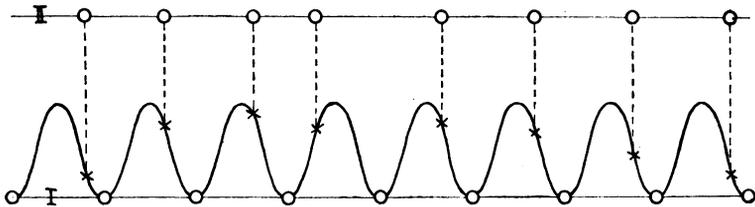


FIGURE 3

distances, d . The second equilibrium configuration is obtained by moving two atoms into the same "groove," leaving another groove empty as shown in figure 3. This Dehlinger calls a "Verhakung." It is very important that one such "Verhakung" is dynamically unstable if for the forces involved one assumes values as they actually occur in atomic physics. If, however, one introduces a number of "Verhakungen" successively along the straight line in regular distances D or closer than they stabilize each other. Thermal agitation makes this whole assembly collapse at a definite temperature. In other words there exists a melting point for this assembly.

(d) One- and Two-Dimensional Crystals.—There may be other cases than that discussed under (A) where a systematic distribution of electric fields is important. I refer to some of my recent publications (1) which have dealt with the problem of the secondary structure. The essential points were, firstly, the tendency of certain planes or lines of atoms to contract or to expand when isolated, and secondly, the formation of electric fields by assemblies of atoms.

(e) Other Types of Secondary Structures.—Finally I wish to mention a few well-known phenomena which suggest the existence of several more types of secondary structures.

In the first place we immediately think of super-conductivity. It seems very tempting to identify the critical point with the melting point of a "crystal within the crystal."

In the second place our attention is drawn to certain transition points which cannot be detected by x-rays. These transitions are nevertheless characterized by markedly abrupt changes of thermal and electrical properties. Such transition points may well turn out to be melting points of certain secondary structures.

In the third place impurities must be considered. If a secondary structure already exists in a pure crystal, the concentrations of foreign atoms must be different for the ideal parts and the regions marking the secondary structure, respectively. But it is also thinkable that the foreign atoms themselves are operative in building up a secondary structure in a given crystal. Foreign atoms can, for instance, exhibit a tendency to form plane crystals or two dimensional lattices which will be stabilized by the original lattice and vice versa. Analogous phenomena on crystal surfaces are well known and have been definitely brought to light by electron diffraction experiments.

§ 6. *Concluding Remarks.*—The purpose of the above considerations was to find a picture of the crystalline state which will allow us to understand the relation between structure sensitive and structure insensitive properties. The following scheme is tentatively proposed.

(1) The ordinary cohesive forces whose action radii are of the order of atomic dimensions are responsible for the condensed states of matter. But they are not characteristic for the crystalline state.

(2) The transition from the liquid to the crystal can only be effected by the simultaneous coöperation of a great number of atoms in regard to a definite directional arrangement.

(3) Several directional phenomena which depend on the coöperation of many particles are briefly described in § 5.

(4) The coöperative phenomenon which is responsible for the stability of a certain crystal will not in general have the same symmetry character as the primary structure. It follows that the crystal as a whole cannot be represented by an ideal crystallographic lattice. A secondary structure must be introduced. The peculiar coexistence of perfection and imperfection which we find in most crystals can easily be derived.

It may be interesting to mention that an analogous persistence of perfection in spite of great external fluctuations is characteristic for living organisms.

¹ F. Zwicky, *Proc. Nat. Acad. Sci.*, **15**, 816 (1929); *Helvetica Physica Acta*, **3**, 269 (1930) and **4**, p. 49 (1931).

² E. Berger, *Forschungen und Fortschritte*, p. 184 (1931).

³ F. M. Jaeger and E. Rosenbohm, *Proc. Amsterdam Acad. Sci.*, **33**, No. 5, 1930, and **34**, No. 1, 1931.

⁴ K. F. Herzfeld, *Phys. Rev.*, **29**, 701 (1927).

⁵ F. Bitter, *Ibid.*, 91 (1931).

⁶ U. Dehlinger, *Ann. Physik*, **2**, 786, 1929.

ON THE AIR RESISTANCE OF PROJECTILES

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1. *Introductory*.—In making this study, the author had in mind its applications to the problem of meteoric impact. The different laws of resistance, heretofore proposed, contain too many empirical or hypothetical elements to permit a safe extrapolation to cosmic velocities. A more thorough investigation into the theoretical aspects of the problem seemed, therefore, desirable. It is known from the experimental results of aeronautics and hydraulics and from their theoretical analysis, that, for moderate velocities, already, the influence of viscosity is small compared with that of inertia. It seems, therefore, permissible to neglect the viscous terms altogether even in the range of velocities attained by ordinary projectiles. The problem is reduced, by this remark, to finding solutions of Euler's equations of hydrodynamics for velocities higher than the velocity of sound. While looking about for a simple case in which the solution could be carried through, it occurred to the author that in the two-dimensional case certain well-known integrals of Euler's equations due to Riemann,¹ Prandtl² and Th. Meyer³ permit a rigorous solution of the problem for polygonal contours. For simplicity, we take a quadrangle symmetrical with respect to one of its diagonals and moving in the direction of this diagonal (Fig. 1). We shall find the rigorous expression for the resistance of such a body in section 7. For lower velocities the formulae are rather involved, but for the limit of very high velocities they are reduced to the very simple expression (28) which remains valid for contours with curved sides and for three dimensional bodies. The properties of our solution and its relation to some laws of ballistic resistance proposed by others and to experiment are discussed in section 8.

2. *Some Mathematical Aspects of the Problem*.—The case of high velocity is in some respects simpler than that of low velocity. The front point