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On the Physics of Crystals. Part I

F. ZWICKY, *California Institute of Technology*

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A. GENERAL

§1. Introduction

THIS review on the physics of crystals is divided into a number of parts. The first parts deal with the experimental aspects of the problem of the solid state. In the last part a general solution of this problem will be proposed and developed.

The experimental facts which distinguish the solid state, particularly those which have not been explained on the basis of the theory of ideal crystallographic lattices will be selected. It is our contention that these obnoxious observations are peculiar to the solid state and to incorporate them into the theory constitutes the present *problem of the solid state.*

In the following sections, the mechanical, thermal, electrical and other properties will be treated separately. In this treatment the successes and failures of the classical theory of ideal lattices will be indicated. We shall then discuss the requirements of a more general theory of the solid state and in the last part give our own solution, introducing *cooperative phenomena* and discussing their influence on the formation of *secondary structures.*

The last part in many respects is still speculative. Even the earlier parts, however, may be more speculative than they appear at first sight. In the physics of solids, and to some extent in any branch of physics, a "fact" may be not just a fact, but a highly complicated combination of observations and interpretations not free from speculations. For instance, if one describes the properties of a crystal, one should not omit to state how the crystal was grown, what impurities it contains, how it has been treated since formation, etc. Experts often differ as to the nature of experimental control and sometimes the same observation has been used to support conflicting theories. The selection of facts in this and any other paper is therefore determined by the author's opinion as to what is important.

§2. The theory of ideal lattices

We shall often use the terms *ideal crystals, perfect crystals, real crystals,* and occasionally the term *mosaic crystals.* To distinguish clearly between these different notions we shall define them.

An *ideal crystal* is essentially a geometrical model. The elementary building stones (atoms, ions, molecules) are located in a discrete set of points which constitute an ideal geometrical point lattice. The spacing (lattice constant) is such that the crystal is in an extremum of energy; the extremum may be a minimum, a saddle point or a maximum. The ideal crystal may not have a real counterpart existing in nature. The existence of such a crystal is possible only if the ideal crystal represents a *statically stable* configuration. To exist as a *thermodynamically stable* configuration at the absolute zero point of temperature, the energy of the ideal crystal must be an absolute minimum.

To allow for the kinetic energy, we extend the notion of an ideal crystal by saying that the average positions of the building stones coincide with the points of the ideal lattice. For an ideal crystal to be thermodynamically the most favored configuration, it must be *dynamically stable* and its free energy an absolute minimum. The stability of a lattice built up of atoms (electrical charges) must of course be dynamic. (Law of Earnshaw.)

The elementary cell of an ideal crystal has dimensions d_1, d_2, d_3 of the order 10^{-8} cm, that is of the order $\delta = h^2/me^2$. An essential feature of the theory of ideal crystals is that the time averages of conditions in all the elementary cells of a free crystal are in every respect identical.

A *real crystal* is a crystal as it actually exists in nature. Real crystals always contain imperfections of various kinds and therefore crystals of the same substance often exhibit different physical properties.

A *perfect crystal* is a real crystal in its thermodynamically stable configuration. If it is a *free crystal*, i.e., one imbedded in its own vapor or melt at constant temperature in a field free space, the free energy is a minimum.

By *mosaic crystal* we mean a real crystal composed of tiny crystal fragments of varying size which are slightly displaced or inclined relative to each other. The idea of a mosaic crystal was first introduced by C. G. Darwin to explain certain features of reflection of x-rays. The term mosaic crystal was introduced by Ewald.

The question whether or not a perfect crystal is identical with an ideal crystal is one of the major issues of the problem of the solid state. On the basis of data furnished by x-rays, this identity has been assumed in the past. Recently various samples of crystals have been found to have different physical properties although x-ray analysis indicated no difference in the crystals. Evidently by such analysis one is not able at present to determine whether or not the perfect crystal is identical with the ideal crystal.

For the study of the theory of ideal crystals the reader is referred to treatises on this subject.[1] This theory has been generally successful in correlating the so-called structure-insensitive properties of crystals with their fundamental building stones (atoms, ions, etc.). Structure-insensitive properties are the space lattice and density, total energy per mol, specific heat, elastic constants, thermal coefficient of expansion, the ordinary electrical and thermal conductivities, the dielectric constant, etc. These properties, in order of magnitude, are the same for single crystals and polycrystalline material. They change very little on plastic deformation, annealing or introduction of small amounts of impurities. The theory is most successful in regard to the properties of ionic crystals such as rocksalt.

Real crystals also possess many physical characteristics which are structure-sensitive. They are the inset of plastic deformation, the rupture strength, the electrical breakdown strength, internal damping for elastic and optical waves, internal diffusion, superconductivity, etc. The classification into structure-sensitive and insensitive properties, is mainly due to A. Smekal.

It should be emphasized that the distinction between structure-sensitivity and insensitivity is only one of degree. All the physical properties are more or less affected by method of growth, by annealing, quenching, etc. Also it may happen that properties which are structure-sensitive at low temperatures may become insensitive at high temperatures.

An example is the critical shearing stress causing plastic deformation (yield point), which at high temperatures becomes independent of previous working.

Such phenomena are probably related to the general fact that low temperatures tolerate the existence of thermodynamically pseudo-stable configurations much more readily than do high

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[1] M. Born, First and second edition of the Handbuch der Physik XXIV.

temperatures. From this point of view, the study of properties of crystals at temperatures near the melting point is desirable.

§3. Imperfections in real crystals

The interpretation of structure-sensitive properties is difficult or impossible in terms of an ideal crystal. There have been many attempts in recent years to correlate structure-sensitivity with the ever-present accidental imperfections in real crystals. In our review we shall consider as imperfections deviations from the ideal lattice which are of an accidental nature, and not characteristic for the thermodynamically stable state.

Imperfections may be of a macroscopic or of a microscopic nature. The latter are more difficult to study but are of interest because of the attempts made by some workers to ascribe many of the discrepancies between the theory of ideal crystals and experiment to such imperfections.

We here list the most common types of imperfection:

(a) Mechanical distortions are common and occur in the form of fissures, crevices, slip lines, twin formations, mosaic formation, lineage, etc. If they are of macroscopic magnitude (greater than $\mu/10$) they may be detected by direct observation, or with the aid of the microscope. Mechanical distortions may be produced during or after the formation of a crystal.

(b) Most real crystals exhibit permanent *accumulations of stresses*. The fact is revealed by observation on transparent crystals in the polarizing microscope and undoubtedly such stresses exist also in opaque crystals. Such stresses in metal crystals can be detected by the so-called thermal and magnetic analyzers.

(c) Inclusion of impurities in crystals can hardly be avoided. In the purest materials there is perhaps one foreign atom per million of the mother substance. Impurities may go into the same space lattice as the mother atoms, replacing them at random as Ag in Au. Or the impurities may form lacunes or layers in crystals. These lacunes may consist of eutectics, or only of impurities, or they may be physical or chemical combinations of impurities with the mother atoms and may be crystalline or amorphous in character. Sometimes the impurities are precipitated out in the form of more or less regular layers, or in the form of dendrites. In Chart I some examples of imperfections are shown.

(d) Surfaces of crystals may have a very complex nature. We shall say little about this subject. We hope that a comprehensive review may come from some other pen.

B. ELASTICITY OF CRYSTALS

§4. Definitions and experimental facts

We assume that we are dealing with crystals in their thermodynamically most stable states. Various macroscopic portions in such a crystal then must exhibit identical macroscopic behavior if we disregard surface effects. Individual microscopic variations such as Brownian movement, exchange of place of the building stones (Platzwechsel) etc. exist, of course, but it is *assumed* that in the first approximation they do not affect the macroscopic behavior. If we now distort a stable crystal by application of various sufficiently small external loads the crystal will be deformed. The characteristics of this deformation are called the elastic properties of the crystal. In most cases real crystals of sufficient perfection may be obtained such that on removal of the loads the crystal returns into its initial state and exhibits the initial macroscopic properties of the crystal in the free state. For this case for which the isothermal application of small loads does not cause any hysteresis effects the following analysis applies. In this analysis we essentially follow the assumptions and notations used by Voigt in his classical book on the physics of crystals.

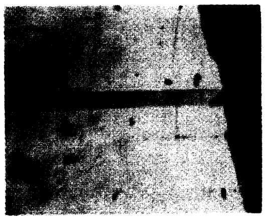
The displacement of a given point P with the cartesian coordinates x, y, z is a vector whose components are $u(x, y, z)$, $v(x, y, z)$, $w(x, y, z)$. The state of strain at P is characterized by the six quantities

$$\begin{gathered} x_x=\partial u/\partial x; \qquad y_y=\partial v/\partial y \quad \text{etc.,} \\ y_z=z_y=\partial v/\partial z+\partial w/\partial y \quad \text{etc.} \end{gathered} \tag{1}$$

It can be shown that the matrix

$$\begin{pmatrix} x_x & x_y/2 & x_z/2 \\ y_x/2 & y_y & y_z/2 \\ z_x/2 & z_y/2 & z_z \end{pmatrix} \tag{2}$$

1



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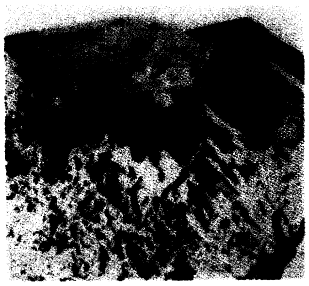

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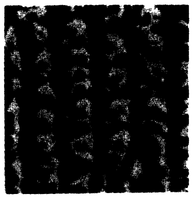

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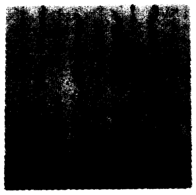

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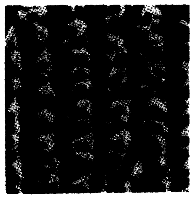

CHART I.

represents a symmetrical tensor of the second rank which is called the ***strain tensor***. The components of this tensor are by definition identically equal to zero for a free crystal at the absolute temperature $T = 0$.

The state of *stress* at a given point P in a solid is known if the stress vectors $\mathbf{S}_n$ are known for all the ∞^2 plane surface element of unit area which contain the point P. $\mathbf{S}_n$ is the force which must be applied on a surface element whose normal is $\mathbf{n}$ if we wish to restore equilibrium after a very thin layer of matter has been removed on the $+\mathbf{n}$ side of our surface element. Under special assumptions, which will be formulated, it can be proved that the state of stress at a point P is completely described if the stress vectors $\mathbf{S}_x$, $\mathbf{S}_y$, $\mathbf{S}_z$ are known, which represent the reactions from the adjoining parts of the solid on three surface elements whose outer normals are in the x, y and z direction. The three stress vectors have the following components

$$\begin{aligned} \mathbf{S}_x &\rightarrow X_x, \quad Y_x, \quad Z_x, \\ \mathbf{S}_y &\rightarrow X_y, \quad Y_y, \quad Z_y, \\ \mathbf{S}_z &\rightarrow X_z, \quad Y_z, \quad Z_z. \end{aligned} \tag{3}$$

DESCRIPTION OF THE PHOTOGRAPHS OF CHART I

FIG. 1. Twin in calcite. At the edge one sees that the cleavage planes in the twin are of a different orientation from those of the whole crystal. Twins in calcite are very frequent and often show remarkable constancy of thickness over their entire length which may be several centimeters. (Magnification ×41.)

FIG. 2. Cleavage surface of calcite with the tracings of two crossing twins, T_1 and T_2. (Magnification ×41.)

FIG. 3. Stepped cleavage surfaces on calcite. The twin T appears displaced at every step, the displacements being proportional to the height of the steps. The existence of permanent stresses in the neighborhood of the twin is apparent from the cleavage contours. (Magnification ×41.)

FIG. 4. Cleavage face (010) of gypsum with precipitates arranged in two sets of planes (111) left and (001) right. Notice the curved surfaces which form the transition between these two sets of planes. (Specimen from the collection of Mr. H. Abraham in Pasadena.) (Magnification ×1.1.)

FIG. 5. Quartz crystal with needle shaped inclusions of Sillimanite $Al_2\ SiO_5$. The needles show no apparent relation to any low indices direction in the crystal. (Specimen from the collection of Dr. Sinclair Smith, Mt. Wilson Observatory.) (Magnification ×1.2.)

FIG. 6. Alloy of iron with 6.33% boron and 0.41% carbon. Notice the regularly spaced precipitations. (Magnification ×735.)

FIGS. 7, 8, 9, 10 are photographs by Professor M. Straumanis in Riga. They represent sections of a single crystal of Zn containing small amounts of Cd. The individual pictures are,

(7) Section parallel to (1120) through single crystal of Zn+0.25 percent Cd. (Magnification ×17.)

(8) Surface of the same crystal as in (7). (Magnification ×17.)

(9) Crystal of Zn+1 percent Cd. (Magnification ×17.)

(10) Single crystal of Zn+0.2 percent Cd+0.05 percent Ni. (Magnification ×14.)

For an account of the solubility of Cd in Zn see M. Straumanis, Metallwirtschaft XII, 1933 and Zeits. f. physik. Chemie **A148**, 112 (1930).

Here we wish to call attention only to the remarkable single and double periodicities of the precipitation of Cd in Zn. The problem of whether all such periodicities are caused by the growing conditions exclusively or whether some of them are intrinsically characteristic for the crystalline structure will occupy us later.

For excellent photographs of other types of imperfections, such as slip lines in metals, Wiedmannstätten figures and striations which are caused by permanent stresses (in diamond), see the publications (24), (26), (27), respectively.

If the crystal is in mechanical equilibrium it follows that the matrix on the right side represents a tensor of the second rank, which is called the *stress tensor*, provided that

$$\lim_{V=0} \mathbf{F}/V = \text{constant vector}, \tag{4}$$

where **F** is the total volume force acting on the matter contained in the volume V. If the moment **M** of the volume forces acting on the volume V satisfies the condition

$$\lim_{V=0} \mathbf{M}/V = 0 \tag{5}$$

it follows that $X_y = Y_x$ etc., so that in this case the stress tensor is symmetrical.

Under the above circumstances the observations indicate that for sufficiently *small* deformations the components of the stress tensor are linear combinations of the components of the strain tensor so that we may write (Hooke's law)

$$\left.\begin{array}{l} X_x = c_{11}x_x + c_{12}y_y + c_{13}z_z + c_{14}y_z + c_{15}z_x + c_{16}x_y \\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ Y_z = c_{41}x_x + c_{42}y_y + c_{43}z_z + c_{44}y_z + c_{45}z_x + c_{46}x_y \\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ \cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \end{array}\right\} . \tag{6}$$

The 36 constants c_{ik} are called the *elastic constants* of the crystal. Provided that crystals are *homogeneous* these constants do not depend on the choice of the point P.

In the ordinary theory of elasticity it is further *assumed* that crystals are holonomous systems and that the forces are all of a conversative nature such that for $T=0$ a *potential energy* ω per cm^3 can be ascribed to the deformed crystal. It is

$$\left.\begin{array}{r} 2\omega = c_{11}x_x^2 + c_{22}y_y^2 + c_{33}z_z^2 + c_{44}y_z^2 + c_{55}z_x^2 + c_{66}x_y^2 \\ +2[c_{12}y_y + c_{13}z_z + c_{14}y_z + c_{15}z_x + c_{16}x_y]x_x \\ +\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ +\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ +\cdot\;\cdot\;\cdot\;\cdot\;\cdot \\ +2c_{56}x_y z_x . \end{array}\right\} \tag{7}$$

If $T \neq 0$, the quantity ω represents the change in *free energy* caused by the deformation. The stresses are obtainable from ω by differentiation

$$X_x = \partial\omega/\partial x_x; \qquad Y_z = \partial\omega/\partial y_z \quad \text{etc.} \tag{8}$$

The existence of a potential energy of deformation implies therefore

$$c_{ik} = c_{ki} \tag{9}$$

and only 21 constants (instead of 36) are necessary to describe the elastic behavior of the most general (triclinic) crystal.

For lattices satisfying special symmetry conditions the number of these constants may be reduced still further. I reproduce here only the schemes for hexagonal (5 constants) and cubic crystals (3 constants).

For hexagonal crystals, we obtain the matrix (c_{ik})

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ & c_{11} & c_{13} & 0 & 0 & 0 \\ & & c_{33} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & (c_{11}-c_{12})/2 \end{array} \tag{10}$$

if the hexagonal axis is chosen as z axis. We also have

$$\begin{array}{l} 2\omega = c_{11}(x_x^2+y_y^2) + c_{33}z_z^2 + c_{44}(y_z^2+x_z^2) \\ \quad + (c_{11}-c_{12})x_y^2/2 + 2c_{12}x_x y_y + 2c_{13}(x_x+y_y)z_z . \end{array} \tag{11}$$

For *cubic* crystals the scheme is

$$\begin{array}{cccccc} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ & c_{11} & c_{12} & 0 & 0 & 0 \\ & & c_{11} & 0 & 0 & 0 \\ & & & c_{44} & 0 & 0 \\ & & & & c_{44} & 0 \\ & & & & & c_{44} \end{array} \tag{12}$$

and the potential energy

$$2\omega = c_{11}(x_x^2+y_y^2+z_z^2)+2c_{12}(y_yx_x+z_zy_y+x_xz_z) +c_{44}(y_z^2+z_x^2+x_y^2). \quad (13)$$

For isotropic non-crystalline solids and for liquids the number of the elastic constants reduces to two and one, respectively.

Very often instead of the relation (7), the strain components are expressed as linear combinations of the stress components with introduction of the *elastic* moduli (s_{ik}). Experimentally one usually determines the elastic moduli first, and not the elastic constants.

The c_{ik} are to be obtained from the s_{ik} by the following relations. Cubic crystals:

$$\begin{aligned} &c_{11}=(s_{11}+s_{12})/s, \\ &c_{12}=-s_{12}/s, \qquad s=(s_{11}+2s_{12})(s_{11}-s_{12}). \quad (14) \\ &c_{44}=1/s_{44}. \end{aligned}$$

Hexagonal crystals:

$$\begin{aligned} &c_{11}+c_{12}=s_{33}/s, \quad c_{11}-c_{12}=1/(s_{11}-s_{12}), \\ &c_{13}=-s_{13}/s, \quad c_{33}=(s_{11}+s_{12})/s, \quad c_{44}=1/s_{44}, \quad (15) \\ &\qquad s=s_{33}(s_{11}+s_{12})-2s_{13}^2. \end{aligned}$$

It must be noted that if the s_{ik} are observed directly and if the probable errors of this determination are of the order Δ, then, because of the relative smallness of $s_{11}+2s_{12}$, the elastic constants c_{11} and c_{12} of a cubic crystal may be easily afflicted with a probable error of 5Δ or more.

Before discussing the experimental values of the coefficients c_{ik} we summarize the assumptions which must be made regarding the nature of real crystals in order for the above scheme of interpretations to be justified.

(α) We assume that it is justified to work with time and space averages of the stresses on surface elements sufficiently small to make the rules of the differential calculus applicable.

(β) The tensor character of the stress rests on the validity of Eq. (5).

(γ) The symmetry of the stress tensor rests on the validity of Eq. (6).

(δ) We assume that no hysteresis effects occur, so that a potential energy of deformation exists.

(ϵ) If in addition we require absolute homogeneity of the crystal (ideal crystal) then Eq. (4) for the *free* crystal is replaced by the more rigorous requirement

$$\lim_{V=0} \vec{\mathbf{F}}/V=0 \quad (4')$$

and the divergence of the stress vectors $\mathbf{S}_x$ etc. is equal to zero. That means that in the free homogeneous crystals the stresses are zero throughout.

We may mention already here that in many cases the ordinary theory of elasticity can be applied successfully in spite of the fact that the above condition (δ) is not rigorously satisfied. For instance, all vitreous substances (glasses) fall into this class. Glasses indeed flow, regardless of how small the stresses are. We may, for a given state of homogeneous stresses σ_{ik} define a critical time of flow $\tau_f(\sigma_{ik})$ by

$$q_0=\tau_f dq/d\tau, \quad (16)$$

where q_0 is either the initial distance between two points or the initial angle between two lines and τ stands for time. τ_f of course depends on the stresses and on the nature of the substance. Just what the factors are which determine τ_f is in itself an interesting problem, which as yet has not found any solution. For the present discussion it is of importance to notice that the ordinary theory of elasticity can only be applied if the external loads are applied for intervals $\tau \ll \tau_f$. Whether or not for crystals $\tau_f=\infty$ will be discussed later.

In Tables I and II we give the observed elastic constants in absolute units (dynes/cm^2) multiplied by 10^{-11}, for a number of single crystals at room temperature. Unfortunately no measurements of the elastic constants (except the compressibility) of typical *homopolar* crystals such as diamond are available. Such measurements are badly needed. In regard to the results given in Table II, it must be emphasized that these results were obtained by Voigt more than 20 years ago on one or two crystals of NaCl and KCl only and these measurements *have not been repeated* since. I hope that the realization of this *deplorable* state of affairs will induce some experimental physicists to undertake systematic investigations of the elastic constants of important ionic and homopolar crystals.

§5. Dependence on imperfections

From Table I it is seen that different observers differ as much as 10 percent, although the accuracy which they claim for their respective obser-

TABLE I. *Metals.*

Substance	System	c_{11}	c_{12}	c_{44}	c_{33}	c_{13}	c_{14}	c_{66}
Tungsten (Br)	cubic b.c.	51.27	20.58	15.27	$=c_{11}$	$=c_{12}$	0	$=c_{44}$
Aluminum (G)	" f.c.	10.54	5.84	2.80	"	"	"	"
Gold (G)	" f.c.	19.41	16.61	4.00	"	"	"	"
Brass (M.A.S.)	"	14.75	11.14	7.19	"	"	"	"
Iron (G.A.S.)	" b.c.	23.7	14.1	11.6	"	"	"	"
Magnesium (G.A.S.)	hexagonal	5.64	2.31	1.69	5.87	1.81	0	$=(c_{11}-c_{12})/2$
Zinc (Br.)	"	15.90	3.23	4.00	6.214	4.815	"	"
Zinc (Gr. A. G.)	"	16.08	4.31	4.00	5.424	4.375	"	"
Cadmium (Br.)	"	10.92	3.98	1.562	4.604	3.756	"	"
Cadmium (Gr.A.G.)	"	12.06	4.821	1.852	5.136	4.423	"	"
Antimony (Br.)	rhombohedral	7.52	2.875	2.44	4.28	2.62	0.91	"
Bismuth (Br.)	"	5.70	2.93	1.00	3.89	1.87	0.424	"
Tin (Br.)	tetragonal	8.39	4.63	1.77	9.66	2.81	0	0.74

b.c.=body centered. f.c.=face centered.
In parenthesis (Br.) etc. are given the initials of the observers. (See reference 2.)

TABLE II. *Ionic crystals.*

Crystal		System	c_{11}	c_{12}	c_{44}	c_{33}	c_{13}	c_{14}
NaCl	(Voigt)	cubic (NaCl type)	4.65	1.29	1.27	$=c_{11}$	$=c_{12}$	0
K Cl	"	" "	3.78	0.64	0.63	"	"	"
Ca F_2	"	"	16.5	4.50	3.40	"	"	"
Quartz	"	trigonal	8.66	0.71	5.81	10.73	1.44	1.72

TABLE Ia.

	Grüneisen and Goens	Bridgman	Goens	Hanson	
				Zinc I	Zinc II
s_{11}	8	8.23	8.4	8.08	7.70
s_{33}	28.2	26.38	28.7	26.28	27.66
s_{44}	25.0	25.0	26.4	25.15	24.40
s_{12}	−0.5	0.34	1.1	1.57	0.45
s_{13}	−6.05	−6.64	−7.75	−7.85	−6.39

vations should fix the elastic constants within a few percent. Three causes for this disagreement must be considered.

(a) Observational errors. If the accuracy claimed by the various authors is correct this cause for the discrepancies in Table I must be discarded.

(b) The crystals used by the different observers are not elastically identical. It would be necessary to investigate the effects of impurities, of growing conditions, etc., on the elastic constants. Evidence of the dependence of the elastic constants on the grade of the substance used has recently been obtained by A. W. Hanson[3] in the case of single crystals of Zn. It may be of interest to reproduce here in Table Ia all the values which so far were obtained for the elastic moduli (in $\text{cm}^2\ \text{dyne}^{-1}\times 10^{-13}$) of zinc single crystals.

Although Hanson's zinc I (Evanwall) and zinc II (Horsehead special) both are 99.99 percent pure the differences which he obtains for these two slightly different grades are considerable.

(c) Our scheme of interpretation of the observations in the elastic region is not correct. More about this will be said later.

It must be mentioned that one must clearly distinguish between *isothermal* methods of measuring the elastic constants (slow application of the load) and *adiabatic* methods (observations of elastic oscillations). In the latter case hysteresis effects may occur which are due to the change in temperature caused by the quickly alternating loads. The difference between the two types of measurement can be calculated from the fundamental laws of thermodynamics. The differences are usually small, amounting for instance to about 1/5 percent for steel at room temperature.[4] However in the neighborhood of crystallographic transformation points the apparent hysteresis effects related to adiabatic elastic changes may assume considerable proportions.

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[2] P. W. Bridgman, Proc. Nat. Acad. Sci. **10**, 411 (1924); Proc. Am. Acad. Arts and Sci. **60**, 306 (1925). E. Goens, Naturwiss. **17**, 180 (1929); Ann. d. Physik **17**, 234 (1933); **16**, 793 (1933). Mazima and Sachs, Zeits. f. Physik **50**, 161 (1928). E. Grüneisen and E. Goens, Zeits. f. Physik **26**, 235 (1924). E. Goens and E. Schmid, Naturwiss. **18**, 376 (1931); **19**, 520 (1931). W. Voigt, Lehrbuch d. Kristallphysik.

[3] A. W. Hanson, Phys. Rev. **45**, 324 (1934).

[4] A. Jaquerod and O. Zuber, Helv. Physica Acta **5**, 438 (1932).

§6. Dependence on pressure

Although the complete sets of the elastic constants are known for relatively few crystals only it must be mentioned that accurate values are available for the compressibilities of very many crystals. Of particular interest for the theory are the determinations of the change of compressibility with increasing pressure. Such observations have been carried out on alkali-halides[5] and their analysis has furnished us with important information concerning the interactions between the ions which constitute these crystals.[6] More about this will be said later.

The dependence of the other elastic constants on pressure seems not to be known.

§7. Dependence on temperature

Very few observations on the temperature dependence are available. Luckily a complete and very precise set of measurements exists on Young's modulus for quartz.[7] As these observations extend from 0°C up to 1100°C they give us valuable information concerning the behavior of Young's modulus in the neighborhood of the crystallographic transformation point at 576°C where quartz changes from the trigonal into the hexagonal system.

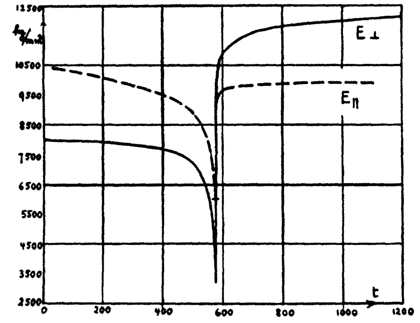

FIG. 1.

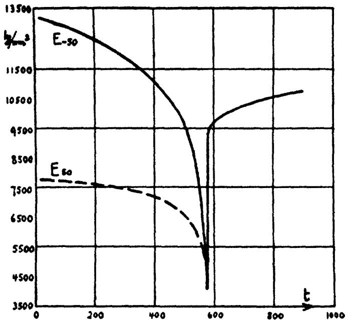

FIG. 2.

A. Perrier[7] has measured Young's modulus (E) for slabs cut parallel to the threefold axis ($E_{||}$), normal to this axis ($E_{\perp}$) and at ±50° to this axis ($E_{\pm 50°}$). In Figs. 1 and 2 his results are reproduced. The temperature t is in centigrade. The errors of the measurements amount to less than 0.5 percent except in the immediate neighborhood of the transformation point, where relatively great errors result because of the fact that the temperature could not be held constant better than within 1°C. Two curious facts are immediately apparent. In the first place the functions $E(t)$ at the transformation point have a derivative which is practically

$$dE/dt = \mp \infty. \tag{17}$$

In the second place $dE/dt<0$ below 576° and $dE/dt>0$ above 576°. This latter fact is particularly astonishing. For the purpose of the following discussion I insert here Fig. 3 somewhat out of place, giving the total thermal expansion $\lambda(t)$ per unit length of quartz as a function of the temperature t; where $t=0$ means 0°C and $\lambda(t=15°)=0$. The upper curve in Fig. 3 represents the expansion normal to the principal axis of the crystal; the lower curve is the expansion parallel to the principal axis.

The expansion was measured with the help of x-ray reflection from the crystal[8] and checks on the whole with the macroscopically measured expansion. However in the neighborhood of the transformation point the macroscopic measurements are not accurate enough for a comparison with the expansion of the crystal lattice as measured by x-rays. It is seen from Fig. 3 that

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

[6] H. M. Evjen, Phys. Rev. **44**, 491 (1933).

[7] A. Perrier and R. de Mandrot, Memoires de la Soc. Vaudoise d. Sc. Nat. (1923), p. 333.

[8] A. H. Jay, Proc. Roy. Soc. **A142**, 237 (1933).

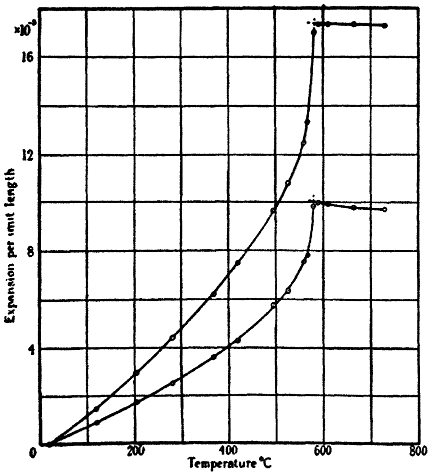

Fig. 3.

the thermal coefficient of expansion $(1/\lambda)(d\lambda/dt)$ is positive below 576° and *negative* above 576°.

The results shown in Fig. 2 are in accord with the expectations of crystallographic symmetry. For $t<576°$ it is $E_{50°}\neq E_{-50°}$ in accord with the trigonal symmetry of the α-quartz. For $t>576°$ it is $E_{50°}=E_{-50°}$ in accord with the hexagonal symmetry of the β-quartz.

It must furthermore be mentioned that Perrier found Hooke's law to be macroscopically valid up to loads which cause rupture. This fact, that up to rupture no deviations from Hooke's law are found, is theoretically of great importance. At the same time it was of course also established that the process of isothermal deformation takes place without any noticeable hysteresis effects.

There are many measurements of the compressibility and Young's modulus as functions of temperature which have been carried out on polycrystalline substances, for which data I refer the reader to the various tables of physical constants. On single crystals, besides Perrier's measurements on quartz, very few observations of the effect of temperature on the elastic constants are available.

Table III.

Metal	E_{20} in kg/mm²	$\beta\times10^4$	G_{20} in kg/mm²	$\gamma\times10^4$	$\alpha\times10^5$	T_m°K
Pb	1500	—	550	78.7	8.8	600
Al	6300	21.3	2300	24.7	7.3	932
Ag	5900	7.6	2500	8.2	5.9	1233
Cu	9900	3.6	4000	4.5	4.9	1356
Ni	23,500	2.5	9500	3.3	3.9	1783
Fe	18,300	2.2	7300	3.0	3.3	1803
Pt	16,000	0.7	6600	1.8	2.7	2028
Zn	4300	—	1600	48.4	9	692

In Table III we reproduce some of the data which have been obtained[9] for Young's modulus E and the torsional modulus G of various polycrystalline metals in the range $t=-180°C$ to $+20°C$. We write

$$E_t=E_{20}(1+\beta t) \qquad G_t=G_{20}(1+\gamma t). \tag{18}$$

All of these metals crystallize in the cubic face-centered system except $\alpha=$Fe which is cubic body-centered and Zn which is hexagonal. For purposes of later discussion I have added the thermal volume coefficients of expansion α between $t=0°C$ and $t=100°C$, and the absolute temperature T_m at the melting point. It is seen that β and γ run roughly parallel with the values of α and $1/T_m$ for all the various metals.

Furthermore for a number of metals $G(t)$ has been determined over quite a wide range of temperatures. As the various functions $G(t)$ are all more or less of the same type I reproduce as an example in Fig. 4 only $G(t)$ for platinum. These values were obtained[10] by a dynamic method and they are therefore adiabatic moduli.

For some of the other metals, which possess crystallographic or magnetic transition points *very flat* minima and maxima of $G(t)$ and $E(t)$ appear near these critical points. It might be expected that for single crystals these minima are very *sharp* (just as in the case of quartz), but unfortunately no accurate data seem to be available.

From the available data we conclude that the various elastic constants retain definite finite values up to temperatures near to the melting point T_m and that in a narrow interval $\Delta T(\Delta T/T_m\ll 1)$ just below T_m they drop abruptly to zero (E, G, etc.) except the compressibility κ which abruptly changes from κ_s (solid) to κ_m (melt).

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[9] G. Sachs, Handbuch d. Exp. Physik V, 251.

[10] K. R. Koch and C. Dannecker, Ann. d. Physik **47**, 196 (1915).

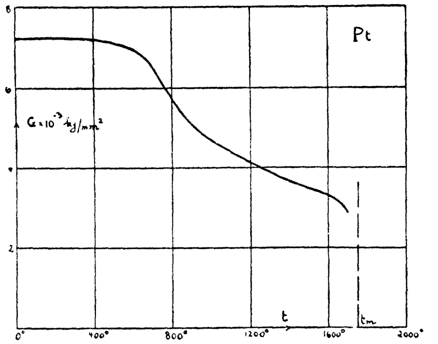

FIG. 4.

It seems further that $G(t)$ decreases somewhat more rapidly with t than $E(t)$. As the relative lateral contraction ν is given by

$$1+\nu=E/2G \tag{19}$$

it would follow that ν is somewhat increasing with t.

Some indirect information concerning the elastic behavior of metals in the neighborhood of the melting point T_m can be obtained from measurements of the velocity of sound v of *solid metals* (v_s) and their melts (v_m) near T_m. Table IV shows some of the experimental results.[11]

In the first place it is interesting to note that in most of the cases $v_s/v_m \leqq 2$. For longitudinal waves we have

$$v_s=(E_s{}^a/\rho_s)^{\frac{1}{2}}, \qquad v_m=(\kappa_m{}^a\rho_m)^{-\frac{1}{2}}, \tag{20}$$

so that in most of the above cases approximately

$$E_s{}^a\kappa_m{}^a=4, \tag{21}$$

where $E_s{}^a$ and $\kappa_m{}^a$ are the *adiabatic* values of Young's modulus (solid) and the compressibility (melt) both measured in absolute units.

TABLE IV.

Metal	$v_s\times 10^{-5}$ in cm/sec.	$v_m\times 10^{-5}$ in cm/sec.	v_s/v_m
Cd	2.665	1.313	2.03
Hg	2.673	1.289	2.07
Pb	1.350	0.699	1.93
Sn	2.643	1.294	2.04
Bi	1.809	2.179	0.83

For *lead* near the melting point $\rho_s=11.00$ and $\rho_m=10.65$ gm/cc so that at $t=327°\mathrm{C}$

$$\begin{aligned}\kappa_m{}^a&=1/\rho_m v_m{}^2=1.91\times 10^{-11}\ \mathrm{cm^2/dyne},\\ E_s{}^a&=\rho_s v_s{}^2=2.01\times 10^{+11}\ \mathrm{dyne/cm^2},\end{aligned} \tag{22}$$

whereas at room temperature the corresponding *isothermal* values are

$$\begin{aligned}\kappa_s{}^i&=24\times 10^{-11}\ \mathrm{cm^2/dyne},\\ E_s{}^i&=1.5\times 10^{11}\ \mathrm{dyne/cm^2}.\end{aligned} \tag{23}$$

The thermodynamic relations between the adiabatic and the isothermal constants are

$$\begin{aligned}\kappa^i/\kappa^a&=c_p/c_v=1+\alpha^2T/\rho\kappa^ic_v=1+k_1,\\ E^a/E^i&=1+\alpha^2TE^a/c_p\rho=1+k_2,\end{aligned} \tag{24}$$

where c_p and c_v are the specific heats per gram at constant pressure and constant volume, respectively. At room temperature the correction terms k for most metals are very small (less than 0.01). However, near the melting point, where the thermal coefficient of expansion may assume very great values, the correction terms k may become quite great. This is in some ways borne out by the values of Eqs. (22) and (23). For instance if for lead we assume a probable value of β between 5×10^{-4} and 10^{-3} (see Table III), we should have $E^i(t_m)$ considerably smaller than $E^i(20°)=1.5\times 10^{11}$ dyne/cm². On the other hand, $E_s{}^a(t_m)>E^i(20°)$, so that certainly $E_s{}^a(t_m)$ is several times as great as $E_s{}^i(t_m)$, and k_2 considerable greater than one, if the measurements of the velocity of sound are correct.

As we do not know either $G(t_m)$ or $\nu(t_m)$ it is not possible to compare the values of κ_s and κ_m at the melting point. It is known however in the case of mercury that along the curve of fusion approximately $\kappa_s=0.9\kappa_m$.

§8. Dependence on cross section

Theoretically a *dependence* of the elastic constants on the *cross section* of the samples must be expected, provided that this cross section is small enough. Little experimental material seems to be available on this important question. It may be of interest in this connection to mention the corresponding results which were obtained on

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[11] O. Stierstadt, Metallwirtschaft **11**, 18, 32 (1932).

drawn circular quartz fibers.[12] Young's modulus E and the torsional modulus G showed the following dependency on the diameter l:

$$E=a/l+E_\infty \qquad a=36{,}000 \qquad E_\infty=4500 \tag{25}$$

and

$$G=b/l+G_\infty \qquad b=17{,}000 \qquad G_\infty=2650 \tag{26}$$

where E and G are measured in kg/mm^2 and l is measured in units of $1\mu=10^{-4}$ cm. E and G do not change their values with aging of the fibers. This independence of E and G on aging is important in view of the fact that the rupture strength of thin quartz fibers decreases considerably with age.

We notice that dimensionally we may write

$$a=D_1E_\infty, \qquad D_1=8\mu \tag{25'}$$

and

$$b=D_2G_\infty, \qquad D_2=6.4\mu, \tag{26'}$$

which means that the observations on the elastic constants of thin fibers indicate the existence of lengths $D\gg d$, where d is of the order of the lattice constants (of $10^{-4}\mu$). D_1 and D_2 represent the critical values of l for which the contributions of the "surface" to E and G become equal to E_∞ and G_∞, respectively. It is of great importance to ascertain by further experiment whether or not these lengths D are structure-sensitive.

Similar lengths D of the order of 1μ come into appearance in adsorption phenomena on glass, which we shall discuss later. I shall try to show in the course of this review that lengths of this type are significant for the effects of so-called cooperative phenomena in the liquid, vitreous and crystalline state of matter.

Finally it must be stated that in general the elastic constants of single crystals must be grouped among the structure-insensitive properties. Considerable variations however may be expected if one measures for instance E or G of polycrystalline material depending on the size of the individual crystals as compared with the size of the whole sample. For a sample consisting of a few strongly anisotropic crystals naturally E and G may be quite different, depending on the orientation of the stresses.

§9. Elastic constants of mixed crystals

Young's modulus has been determined for binary alloys such as Au–Ag, Au–Cu, Al–Cu, etc. For the case of Au–Ag the values obtained[13] for the elastic constants $c_{ik}\times 10^{-10}$ in dynes/cm^2 are tabulated in Table V.

TABLE V.

	Ag	25 atom% Au	50% Au	75% Au	Au
c_{11}	120.0	138.2	148.9	166.0	187.0
c_{12}	89.7	104.5	113.5	132.2	157.0
c_{44}	43.6	48.7	50.8	48.5	43.6

Annealing, tempering and quenching of Cu–Au single crystals produce differences of Young's modulus of the order of 10 percent with changes of the density amounting to less than 1 percent. For more detailed information I refer to the literature.[13]

Technically the alloying of various metals for the purpose of obtaining suitable elastic properties is very important. It is for instance possible to produce substances (Elinvar) whose elastic constants vary very little with the temperature.

§10. Comparison with the ideal crystal theory

An ideal crystal is homogeneous throughout. There occur no local accumulations of stresses and the macroscopically measured elastic constants are therefore entirely determined by the forces between the atoms which constitute an elementary cell of the crystal. Considerable changes of the elastic constants can only be expected if one deals with samples of dimensions which are comparable with the dimensions of the elementary cells (10^{-8} cm). Such changes are therefore in most cases beyond the reach of experimental verification.

The principal forces, which are responsible for the formation of a crystal are of electrical origin. The theory of the ideal crystal therefore predicts that any elastic constant c_{ik} as we have defined it will in general be of the form[1]

$$c_{ik}=\gamma_{ik}e^2/d^4 \tag{27}$$

where e is the charge of an electron, d a length of the order of the dimensions of the elementary cell

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[12] O. Reinkober, Phys. Zeits. **33**, 32 (1932).

[13] H. Roehl, Ann. d. Physik **16**, 887 (1933); **69**, 309 (1931).

and γ_{ik} is a numerical constant of the order one, which varies of course from lattice to lattice. The elastic constants c_{ik} are therefore of the order of 10^{12} dynes/cm^2. The observed c_{ik}'s check this expectation. Concerning the accurate theoretical determination of the γ_{ik}'s much work has been done, especially in the case of heteropolar crystals, such as alkali-halides. The results obtained so far roughly check the experimental data, but much work is still needed to arrive at a really satisfactory agreement. There do not seem to be any difficulties involved in principle, except perhaps with regard to the so-called *Cauchy relations.* Cauchy derived these relations between the c_{ik}'s on the assumption that a crystal is built up of one type of atom only and that the mutual interaction between these atoms can entirely be described by central forces. Cauchy's relations for a triclinic crystal are

$$\begin{aligned} c_{44}&=c_{23}, & c_{55}&=c_{31}, & c_{66}&=c_{12}, \\ c_{56}&=c_{14}, & c_{64}&=c_{25}, & c_{45}&=c_{36}, \end{aligned} \tag{28}$$

hexagonal crystal:

$$c_{11}=3c_{12}, \qquad c_{13}=c_{44}, \tag{29}$$

cubic crystal:

$$c_{12}=c_{44}. \tag{30}$$

For a crystal which is built up of more than one type of atom, Cauchy's relations do not necessarily hold as M. Born[1] has shown. However in simple cases such as NaCl, KCl they should nevertheless be valid. The relation $c_{12}=c_{44}$ for these crystals is indeed experimentally verified, if the values given in Table II are correct. However as mentioned before it is of great importance to redetermine these constants. For cubic pure metals we also should expect $c_{12}=c_{44}$ as the interaction between the metal atoms is supposed to be central in character. Table I shows that in most cases definitely $c_{12}\neq c_{44}$. Our theoretical expectations concerning Cauchy's relations are not at all verified, and the question is whether the non-validity of Cauchy's relations is caused by the action of the so-called free electrons or whether the metals in question definitely do not form any ideal crystals. The Cauchy relations (27) are not satisfied for the hexagonal Zn and Cd either.

It might also be important to consider not only "binary" functions but also "ternary" functions and so on. For example, if we consider three particles i, k, l in a crystal their mutual potential energy may not be representable as a sum $U_1(r_{ik})+U_2(r_{kl})+U_3(r_{li})$ but must be written as $U(r_{ik}, r_{kl}, r_{li})$ which does not degenerate into three additive parts U_1, U_2 and U_3. The problem of the form of the function U is closely related to the problem of the "chemical" valencies, which determine the cohesion of the crystal. In any case the causes for the failure of Cauchy's relations seem to be of a fundamental nature.

In regard to the dependence of the elastic constants on temperature, the following may be said. If Hooke's law were rigorously satisfied for *all* values of the strain, dc_{ik}/dT would be equal to zero. The same is true for the thermal coefficients of expansion α_{lm} of a crystal. It can be shown that[9]

$$(dc_{ik}/dT)/c_{ik}=\Lambda_{ik}(\alpha_{lm}), \tag{31}$$

where Λ denotes a linear function of the α's with coefficients of the order 1–10. A numerical estimate is arrived at as follows. Suppose that the displacement of an atom from its equilibrium position in the crystal is a vector whose components are u, v, w. If a proper system of coordinates (principal axes) is chosen the components of the force can be written as

$$F_x=f_1[u/d+g_1(u/d)^2+\cdots] \quad \text{etc.}, \tag{32}$$

where d is the average lattice constant. The g_i's are constants which in practical cases assume values of the order 1–10. From the theory of ideal lattices one obtains for the thermal coefficients of expansion expressions of the type

$$\alpha_{lm}=\varphi_{lm}(g_i)kd/e^2, \tag{33}$$

where φ_{lm} is a linear homogeneous function of the g_i's, $k=1.36\times10^{-16}$ ergs/degree and e the charge of the electron. Therefore

$$\alpha_{lm}=6\times10^{-6}\Gamma_{lm}, \tag{34}$$

where the Γ's are numerical constants of the order 1 to 50. It is seen therefore that the theory of ideal crystals accounts in order of magnitude for the thermal coefficient of expansion $\alpha\sim10^{-5}$ and β, $\gamma\sim10^{-4}$. However the theory has not been worked out in any considerable detail, so that a precise theoretical determination of α, β and γ

based on our knowledge of the individual interactions between the atoms is still outstanding. I wish to emphasize in particular the desirability of a theoretical determination of α, β and γ in the neighborhood of transition points and especially just below the melting point. It will be argued later that the physical properties of crystals in the neighborhood of the melting point are perhaps one of the most direct expressions of those interactions between the atoms which are responsible for the existence of a crystalline state of matter.

In regard to the dependence on temperature of the elastic constants I add that the third law of thermodynamics requires[14]

$$dc_{ik}/dT=0, \quad \text{for} \quad T=0. \tag{35}$$

This relation is in agreement with the observations as far as such observations at sufficiently low temperatures are available.[15]

Attention should be called to the fact that the breakdown (fusion or sublimation) or transformation of the crystalline state by thermal agitation at constant pressure takes place essentially in and is completed within an extremely narrow interval ΔT around $T=T_m$. Indeed, Figs. 1, 2 and 3 show that to all appearances for $T=T_m$ the functions $\alpha(T)$, $\beta(T)$ and $\gamma(T)$ become very (infinitely) great. However breakdown or transformations announce themselves at temperatures $T=T_m-\Delta T$ which are appreciably smaller than T_m (for instance at approximately $\Delta T/T_m=0.05$). This is evident from the behavior of the derivatives $d\alpha/dT$, $d\beta/dT$ and $d\gamma/dT$ as functions of T. This means that *fusion* and *crystallographic transformation are processes which take place all throughout the volume of the crystal* as T_m is approached. *It seems therefore hopeless to construct theories of the fusion and the formation of crystals by considering only surface actions.* Considerations of how atoms are added to the surface of the crystal have especially been advanced by W. Kossel and T. N. Stranski[16] and have successfully been applied to the problem of the formation of definite crystallographic faces. However, in my opinion, one cannot hope on this basis to arrive at a deeper understanding of the crystalline phase of matter, as, according to the observations mentioned the fusion and formation of crystals are very definitely related to volume effects.

In passing I wish to mention that *the kinetic (statistical) theory of the existence of phases never has been worked out.* This is very surprising in view of the fact that the existence of various phases of a given substance is a phenomenon, which, needless to say, is of major importance. Just as is the case with so many familiar phenomena the existence of various phases has simply been taken for granted. During recent years I have several times pointed out the importance of a kinetic theory of phases.[17] A satisfactory preliminary solution of this problem was finally obtained by H. M. Evjen[18] and myself in the case of alkali-halides, and it is thought that the considerations given in our work will lead to a general solution of the problem of phases. Very recently K. F. Herzfeld[19] and P. Ehrenfest[20] also have remarked that there exists no general kinetic theory of formation of phases. More about this problem will be said later in the section dealing with the thermal and caloric properties of crystals.

On the theory of ideal crystals no dependence of the elastic constants on the cross section of the specimens should be expected except for thicknesses D of the specimens which are comparable with atomic dimensions (d). Effects of this order of magnitude are beyond the possibility of ordinary mechanical tests. It seems, therefore, that effects of the type expressed in Eqs. (25) and (26) cannot be understood if one considers only the short range interactions between neighboring atoms. The appearance of characteristic lengths $D \gg d$ points toward the necessity of considering what I have called[21] *cooperative phenomena.* In the following sections a considerable number of different physical properties of crystals will be discussed which support the observation just made, that, besides the lattice constants d, the introduction of intrinsic lengths $D \gg d$ will be

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[14] K. Bennewitz, Handbuch d. Physik **IX**, first edition.

[15] Tables annuelles internationales VIII (1927–28), p. 6.

[16] W. Kossel, Naturwiss. **18**, 901 (1930). T. N. Stranski, Zeits. f. physik. Chemie **A42**, 453 (1930).

[17] F. Zwicky, Proc. Nat. Acad. Sci. **17**, 524 (1931).

[18] H. M. Evjen, Phys. Rev. **44**, 501 (1933).

[19] K. F. Herzfeld and M. Goeppert-Mayer, J. Chem. Phys. **2**, 38 (1934).

[20] P. Ehrenfest, Comm. from the Kamerlingh Omnes Laboratory, Supplement No. 75 (1933).

[21] F. Zwicky, Phys. Rev. **43**, 270 (1933).

necessary in order to arrive at a coherent theory of the physics of crystals. The existence of characteristic lengths D supplies one of the strongest arguments for the view that real crystals cannot completely be described by the ordinary *ideal* crystallographic lattices.

§11. Comparison with the imperfection theory

As already mentioned, the effects of imperfections on various physical properties of crystals have been considered by many investigators. Some authors have even gone so far as to make imperfections responsible for all of those properties which on the theory of the ideal crystals are or seem incomprehensible. However, most of the literature on the subject of imperfections contains little quantitative discussion and I shall not review it in detail here.

Nevertheless the influence of imperfections is in many cases undoubtedly of great importance. I shall therefore attempt in the following to discuss the influence of those imperfections whose characteristics lend themselves to a quantitative description. Such imperfections are

(α) *Holes and fissures.* A hole shall be defined as an internal surface on which the normal and the tangential *stresses* are *always equal to zero*, regardless of whether or not an external *mechanical* load is applied to the crystal. This, to be sure is an idealized assumption, which is exactly true only for holes whose diameters are large compared with d. In a small hole the atoms of the various parts of its surface may interact with each other and produce surface forces. We shall not make any use of such more refined pictures and we shall therefore assume that the forces on the surface of a hole are vanishing. The effects of holes and fissures were systematically investigated first by A. A. Griffiths.[22]

(β) *Knots.* Knots are regions in the crystals in which there *always* exist inhomogeneous accumulations of stresses. These stresses exist whether or not a mechanical load is applied to the crystal. Knots may be caused by inclusion of foreign atoms into the crystal or they may be related to non-ideal arrangements of the atoms of the crystal.

(γ) *Twins.* Through twins we have local systematic *directional* changes of the elastic properties of the crystal. If the crystal is stressed *the components* of the resulting *strain tensor will abruptly change their values* when we cross the boundaries of the twin.

If in the following we speak about holes, knots and twins the meaning of these terms must always be taken as laid down in the above.

I also think that the combinations of holes, knots and twins in a schematic way cover a major part of all possible types of imperfection.

We have mentioned before that the elastic properties of crystals are structure-insensitive. This is understandable, as in general neither holes, knots nor twins greatly affect the elastic constants.

Holes act in the following way. Suppose for instance that holes of total volume v are imbedded in a cube of 1 cm^3 of an isotropic solid which is uniformly stretched parallel to an edge of the cube (x-direction). The principal stresses far away from the hole are $X_x=\sigma$, $Y_y=Z_z=0$. If the hole is of circularly cylindrical shape the stress distribution (σ') will be appreciably inhomogeneous ($|(\sigma-\sigma')/\sigma|>0.05$) in a volume v' which is of the order $v'=100\ v$. (For this and the considerations which immediately follow, see Appendix I of part II.)

It can be shown that in general Young's modulus E' of the imperfect crystal is

$$E'=E(1-hv)=E[1-h(\rho-\rho')/\rho], \quad (36)$$

where ρ' and ρ are the densities of imperfect and the perfect crystal. h is a pure number which is approximately equal to unity. A crude derivation of the relation (36) is obtained as follows. Suppose that a parallelepiped of an isotropic solid, with the edges L_1, L_2, L_3, is stretched in the L_3-direction by a load σ per cm^2. A hole (parallelepiped) with edges l_1, l_2, l_3 parallel to L_1, L_2, L_3 is the parallelepiped. The average stress $\bar{\sigma}$ in a cross section $\perp L_3$ is either $\bar{\sigma}=\sigma$ or $\bar{\sigma}=\sigma[1+l_1l_2/L_1L_2]$ depending on whether this cross section intersects the hole or not. Assuming strict validity of Hooke's law the average extension in the L_3 direction will be

$$\overline{\Delta L_3}=(\sigma/E)(L_3-l_3)+(\sigma/E)(1+l_1l_2/L_1L_2)l_3 \quad (37)$$

or

$$\overline{\Delta L_3}/L_3=(\sigma/E)(1+l_1l_2l_3/L_1L_2L_3)=\sigma/E'. \quad (38)$$

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[22] A. A. Griffiths, Proc. Int. Congr. Appl. Mechanics, Delft (1924), 55.

That is, the *apparent* Young's modulus is

$$E'=E(1-\Delta V/V) \tag{39}$$

if we put $l_1l_2l_3=\Delta V$ and $L_1L_2L_3=V$. A more exact calculation gives

$$E'=E(1-h\Delta V/V), \tag{40}$$

where h depends on the geometrical shape of the hole. However h is always of the order of unity. The above relation (36) is correct only if $hv \ll 1$. Also if many small holes are systematically lined up in one or several planes the effect on E may become greater than (36) indicates. In general, however, we may conclude that Young's modulus shows only a slight dependency on change of the internal structure of single crystals. Knots act very similarly to holes, whereas the presence of twins tends particularly to decrease the macroscopic anisotropy of crystals. No systematic experimental investigations seem available for testing the above considerations.

Imperfections hardly help to clear up the difficulties related to the failure of Cauchy's relations in cubic and hexagonal metal single crystals unless these imperfections are systematically arranged with respect to certain crystal planes. More about this possibility will be said in the later parts of this review. We may state however that the failure of Cauchy's relations must be related to some cause more fundamental than the existence of accidental and randomly distributed imperfections.

The theoretical determination of the elastic constants of polycrystalline aggregates from the knowledge of the elastic constants of single crystals has been worked out.[23] The agreement of these calculations with the observations may be regarded as fairly satisfactory.

One of the basic assumptions (δ) of the theory of elasticity is that an elastic region actually exists, so that no permanent deformations result if the applied stresses are sufficiently small. One might contest the correctness of this assumption as applied to all real crystals. Indeed it is known that very pure and perfect metal single crystals show indications of plastic flow even for the smallest loads applied. Actually no rigorously elastic region can be determined for such crystals, although we must theoretically expect of every dynamically stable configuration that it exhibit rigorously elastic effects for sufficiently small external forces. If the external forces are applied only for *very short* intervals of time the resulting deformations are sufficiently reversible to justify the basic assumptions of the theory of elasticity and the problem of flowing seems not very serious. For forces which act over a *long period* of time however it may become necessary to replace the ordinary theory by a more general one, as we have already discussed.

Finally it must be mentioned that the types of imperfection which we propose to consider are such as can be described in macroscopic terms. There is hardly any doubt that this macroscopic view point in many ways is very inadequate. The problem of deviations from ideal lattices, that is deviations which do not belong to the thermodynamically stable state of a crystal, can satisfactorily be solved only if imperfections are treated from a purely atomistic point of view. This has recently especially been emphasized by H. J. Gough[24] and also by myself.[25] About some preliminary attempts which have been made in this direction I shall report later. Here I wish to emphasize only that not much can be expected of the much professed way in which many of the difficulties in the physics of crystals have been blamed on imperfections without making any attempt whatever to describe the atomistic or macroscopic causes, the character and the behavior of these imperfections.

In keeping with a suggestion by Professor John T. Tate the whole review is held on an elementary plane, so as to address a general circle of readers. Some of the pictures of Chart I were kindly furnished me by Professor Dr. M. Straumanis in Riga, whereas the rest of the photographs were taken by Mr. D. S. Clark and myself. I am also indebted to Professor J. W. Buchta for advice in planning this review.

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[23] D. A. G. Bruggeman, Thesis Utrecht, 1930.

[24] H. J. Gough, E. Marburg Lecture, American Society for Testing Materials **33** (1933).

[25] F. Zwicky, Proc. Nat. Acad. Sci. **15**, 253 (1929).

[26] R. F. Mehl and C. S. Barrett, Technical Publication No. 353 (1930) of the American Institute of Mining and Metallurgical Engineers.

[27] Sir Rob. Robertson, J. J. Fox and A. E. Martin, Phil. Trans. Roy. Soc. **A232**, 463 (1934).

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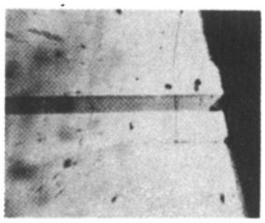

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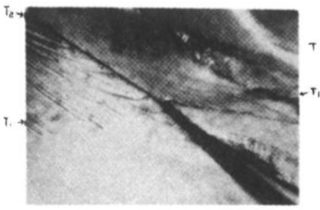

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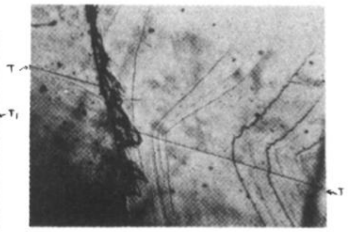

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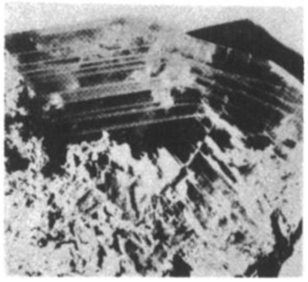

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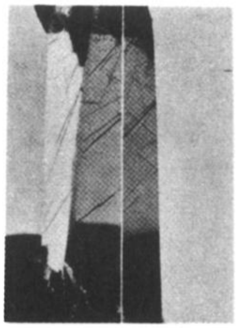

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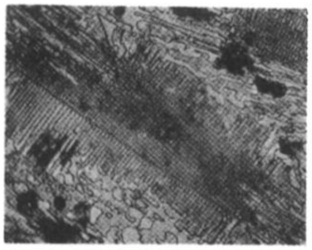

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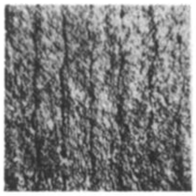

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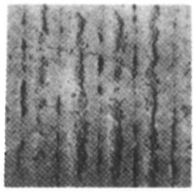

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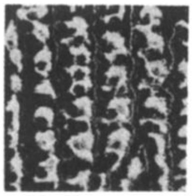

CHART I.

DESCRIPTION OF THE PHOTOGRAPHS OF CHART I

FIG. 1. Twin in calcite. At the edge one sees that the cleavage planes in the twin are of a different orientation from those of the whole crystal. Twins in calcite are very frequent and often show remarkable constancy of thickness over their entire length which may be several centimeters. (Magnification ×41.)

FIG. 2. Cleavage surface of calcite with the tracings of two crossing twins, T_1 and T_2. (Magnification ×41.)

FIG. 3. Stepped cleavage surfaces on calcite. The twin T appears displaced at every step, the displacements being proportional to the height of the steps. The existence of permanent stresses in the neighborhood of the twin is apparent from the cleavage contours. (Magnification ×41.)

FIG. 4. Cleavage face (010) of gypsum with precipitates arranged in two sets of planes (111) left and (001) right. Notice the curved surfaces which form the transition between these two sets of planes. (Specimen from the collection of Mr. H. Abraham in Pasadena.) (Magnification ×1.1.)

FIG. 5. Quartz crystal with needle shaped inclusions of Sillimanite $Al_2\,SiO_5$. The needles show no apparent relation to any low indices direction in the crystal. (Specimen from the collection of Dr. Sinclair Smith, Mt. Wilson Observatory.) (Magnification ×1.2.)

FIG. 6. Alloy of iron with 6.33% boron and 0.41% carbon. Notice the regularly spaced precipitations. (Magnification ×735.)

FIGS. 7, 8, 9, 10 are photographs by Professor M. Straumanis in Riga. They represent sections of a single crystal of Zn containing small amounts of Cd. The individual pictures are,

(7) Section parallel to (1120) through single crystal of Zn+0.25 percent Cd. (Magnification ×17.)

(8) Surface of the same crystal as in (7). (Magnification ×17.)

(9) Crystal of Zn+1 percent Cd. (Magnification ×17.)

(10) Single crystal of Zn+0.2 percent Cd+0.05 percent Ni. (Magnification ×14.)

For an account of the solubility of Cd in Zn see M. Straumanis, Metallwirtschaft XII, 1933 and Zeits. f. physik. Chemie **A148**, 112 (1930).

Here we wish to call attention only to the remarkable single and double periodicities of the precipitation of Cd in Zn. The problem of whether all such periodicities are caused by the growing conditions exclusively or whether some of them are intrinsically characteristic for the crystalline structure will occupy us later.

For excellent photographs of other types of imperfections, such as slip lines in metals, Wiedmannstätten figures and striations which are caused by permanent stresses (in diamond), see the publications (24), (26), (27), respectively.