

On the Physical Properties of Crystals.

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THE most characteristic feature of a crystal is its geometrical form. This is not a matter of mere coincidence but is specific with the nature of the internal bondage between the various units in the lattice. The crystal structure thus corresponds to minimum potential energy¹ and is thermodynamically the most stable one. The energetics of crystals have been studied by Born and others² and depend on the nature of crystals having (1) heteropolar or ionic lattice, metallic lattice being a special case with electrons as the negative ions; (2) dipole lattice, *e.g.*, the halogen acids; (3) molecular lattice of neutral atoms, *e.g.*, organic crystals. Of these those of class (1) have been studied in detail and the free energy and equation of state have been derived. Thus at absolute zero

$$E = -\frac{K}{\delta} + Ce^{-\alpha\delta} + \frac{C'}{\delta^6} + \epsilon$$

where δ is the lattice distance, K , C , C' are constants. The first term is the Coulomb energy, the second a repulsive energy term, the third van der Waal dipole-dipole-polarisation energy term and the last null-point energy. Besides these there may be other terms involving higher inverse powers of δ . The above equation may be used for the calculation of free energy, minimum distance of approach, pressure and cohesive force. Thanks to Sommerfeld, Bloch, Peierl and others,³ the theory of metals has been well established and it has been possible to account for conductivity and other properties on the concept of free electrons, the motion of which is somewhat restricted by 'interaction terms'. Wave-mechanical method has also been applied to complex crystals by Hund, Mulliken, Pauling and others.⁴

The properties of crystals as predicted by theory are not always borne out by experiment and several anomalies have been observed. In fact Smekal⁵ has classified these as structure-sensitive, semi-sensitive and insensitive. The last are in accord with theory and these include density, refractive index, elastic properties, specific heat, conductivity, etc. The first are selective and show wide departure from theory. To these belong plasticity, tensile strength

and some anomalous dielectric and magnetic properties. The second is intermediate between the first and the last, for instance, conductivity of non-metallic crystals, diffusion, X-ray extinction, etc. According to Darwin,⁶ intensity of X-ray scattering alone may serve to distinguish perfect crystals from imperfect ones. The ideally perfect crystals we have for integrated reflection

$$\rho = \frac{\delta}{3\pi} \frac{N\lambda^2}{\sin 2\theta_0} \cdot |F| \cdot \frac{e^2}{mc^2} \cdot \frac{1 + \cos |2\theta_0|}{2} \cdot \phi(\tau)$$

and for ideally imperfect ones

$$\rho = \frac{N^2\lambda^3}{2\mu \sin 2\theta} \left(|F| \frac{e^2}{mc^2} \right)^2 \cdot \frac{1 + \cos^2 2\theta}{2} \phi(\tau)$$

where

N = Number of crystal units per unit vol.; F = Scattering factor per unit cell; e , m , c have their usual significance; θ = Glancing angle; θ_0 = Bragg angle; λ = Wave-length; μ = Linear absorption coefficient.

Real crystals are usually intermediate between two extreme cases.

The classification due to Smekal is not also rigid. As a general rule structure-sensitive properties tend to become insensitive with rise of temperature, while cold-working has just the opposite effect. Again some apparently sensitive properties become insensitive, for instance, elastic after-effects and dielectric anomaly become structure insensitive in the case of single crystals.⁷

The most marked discrepancy has been observed in the case of plastic deformation, and cohesive strength even for single crystals. It was, however, noted by Joffé⁸ that deformation is attended with elongation of Laue spots (asterism) which is attributed to the breaking up of the single crystal into smaller single crystals. It reminds one of the fibrous structure. The destruction limit decreases rapidly with rise of temperature and reaches zero at melting point. The occurrence of lattice curvature may be explicable if we assume with Taylor and Yamaguchi that they have a local character and are due to slip over a limited region.

The discrepancy between the theoretical and observed value of cohesive strength is

still greater. Thus cohesion for rock-salt is only 4kg/mm.^2 as compared to the calculated value 300 kg/mm.^2 Joffé⁹ explains this as due to the surface cracks and showed that much better agreement can be obtained if the surface be dissolved out. His observations have been criticised by Polanyi and Ewald.

Structure sensitive properties find no explanation on the theory of ideal solid state. Since ideal crystals are dynamically most stable, real crystals which are imperfect should be pseudo-stable. Pseudo-stable imperfect crystals may occur at ordinary temperature and a sort of secondary structure due to temporary grouping (as in liquids) may also be possible. Low temperature favours the formation of these pseudo-stable configurations which tend to become transformed into the stable ones with rise of temperature. Application of pressure may cause a single crystal to take up a crystallite structure like that of glass. Bridgmann¹⁰ considers that at high pressure lattice itself may be destroyed and the crystal converted into a jelly (which again may be regarded to have a crystallite structure).

Bragg¹¹ has proposed another ingenious mechanism for the formation of real crystals. The repulsive forces within crystals may be directive and this may lead to asymmetry. With the lowering of temperature the crystal may be subject to strains which may lead to secondary grouping¹² and may also account for the cracks and flaws suggested by Smekal. Other instances of directive forces in molecular physics are not wanting and the above hypothesis may be of interest.

Causes of imperfection in real crystals may thus be reviewed as follows: (1) Mechanical distortion during growth of crystals (flaws, crevices, cracks). (2) Accumulation of stresses detected in metallic crystals. (3) Incorporation of impurities which may be hardly avoided.

The existing theories of real crystals are: (1) Mosaicity due to (i) primary and secondary flaws (Smekal), (ii) surface contraction and secondary structure, (iii) Darwin's theory, (iv) Apparent mosaicity due to lineage structure (Buerger¹³); (2) Griffith's theory of cracks extended by Orawan¹⁴; (3) Inner adsorption (Balarew¹⁵). Each of these has its merits and demerits adequately discussed lately. Brief mention of these will now be made.

Smekal considers the ideal lattice as

thermodynamically most stable and the flaws and cracks are due to defective growth and presence of impurities. These primary flaws may subsequently give rise to secondary flaws of microscopic dimension either by alteration of temperature or by mechanical effects. Properties of crystals depend on the condition of crystallisation and the anomalies may be readily explained. Structural flaws may actually be detected. The following criticism against Smekal's theory may however be advanced. Variation of density (Goetz), anomalous behaviour in connection with electrical conduction and low tensile strength cannot be quantitatively explained. Dimension and shape of blocks due to flaws are vague.

Zwicky assumes that real crystals are dynamically most stable and Goetz has advanced the following arguments in favour of the group structure: (i) Observation of lines and markings of etch figures, (ii) persistence of paracrystalline structure in liquids a few degrees above the melting point, (iii) difference in behaviour of crystals partly within and partly outside magnetic field, (iv) presence of a critical concentration of impurities, (v) difference in coefficient of expansion measured by optical and X-ray methods, (vi) size effect on certain properties and the existence of critical size. Buerger opines that the above evidences are fallacious and the secondary structure theory is based on misinterpretation of observed facts, all of which can be explained otherwise. The main objection is that theory is based on a erroneous calculation of energy (Orawan), and the ideal lattice is thermodynamically most stable. This is borne out by the fact that mosaicity is not a constitutional property and Ewald and Renniger¹⁶ have been able to prepare ideal crystals of rock-salt which is ordinarily mosaic. Crystallographic considerations are also against the secondary structure hypothesis.

Buerger's theory is based on observational evidences and its origin is not clearly understood. Darwin's theory is also not free from objection. Existence of crystals smaller than the critical size according to Darwin's model and certain difficulties as regards crystal formation may be cited as serious objection against Darwin's theory, which also presumes the crystallite structure for imperfect crystals.

It is interesting to study the effect of impurities on the physical properties. Foreign matters can hardly be avoided during

