BASIC PROPERTIES OF SOLIDS.

1. Classification of Solids

There is no unique way of classifying solids by their properties, but some divisions come naturally. One of the most useful is the segregation:

 a. Metals
 b. Ionic crystals
 c. Valence crystals
 d. Semiconductors
 e. Molecular crystals

The distinguishing factors on which this is based are:

a) Good electrical and thermal conductivity, all electropositive elements or combinations of electropositive elements.

b) Good ionic conductivity at high temperatures, strong infrared absorption, good cleavage. Formed by combinations of highly electropositive and highly electronegative elements.

c) Poor conductivity, great hardness. Combinations of light elements near centre of periodic table.

d) Poor electronic conductivity which increases with temperature. Conductivity improved by addition of impurity or when composition slightly different from stoichiometric.

e) Solids formed by inert gases and saturated molecules. Low MP and BP, generally evaporate as stable molecules.

Deal with types in outline in turn.

2. Metals.

2 classes - monatomic metals and alloys.

Monatomic metals.

Further subdivision according to whether or not d shells of constituent atoms are filled. If they are not, "transition" metals with distinctive properties.

Structures. Most are simple cubic or hexagonal (close-packed). Some are more like those of valence crystals, and are intermediate in type. Allotropy shown more by transition metals but can be demonstrated in simple metals by use of high pressures *. Describe atomic radii by volumes occupied by atoms in given compound. Nearest-neighbour distance seldom same for two allotropes, so rigid-sphere ideas cannot be accurate.

Conductivities. Scalar for cubic structures, two independent values for trigonal or hexagonal. Lowest resistivities in noble metals. Alkali metals only moderate conductors. Large decrease in resistivity on completing d shell (Ni --) Cu for example). Metals with highest resistivities have complex structures (intermediacy again).
    High temperature resistivity linear in T. Higher power at low temp., T^5 for those that are not superconducting. Many metals are superconducting, few regularities, except that no monovalent metals seem to be. Resistances of non-super metals and normal resistances of superconductors above transition temperatures are functions of past history. Part of resistance characteristic of material and part characteristic of imperfections. Residual resistance about same as "characteristic" resistance at and below 5°K.

Specific Heats. High temperature specific heats tend to Dulong-Petit but eventually exceed. T^3 law at low temperatures. Large anomalies in many, particularly if more than one atom in the unit cell.
    Specific heat of nickel below 10°K deviates from T^3 law and becomes linear. If linear function subtracted from observed specific heat, a T^3 residue found. Suggests that specific heat is Debye + electronic excitation into unfilled d shells.

Magnetism. Metals in short periods and preceding transition metals are paramag., those following transition metals are diamag. Susceptibilities so small that very small traces of ferromagnetic impurity can cause large variations in observed values. Susceptibility also depends on past treatment of material, e.g. susceptibility of Cu wire variable by 40 per cent by stretching ⌀. Also found that copper can be made to go from diamagnetic to paramagnetic by cold working, whereon annealing restored diamagnetism

* BRIDGMAN, Phys. Rev. 48, 893 (1935)   ⌀ BITTER, Phys. Rev. 36, 978 (1930) , also book "Introduction to Ferromagnetism" (McGraw-Hill).

Susceptibilities of non-ferromagnetic transition elements are all positive and generally greater than those of the paramagnetic simple metals.

Ferromagnetism. With ferromagnetics, the magnetic properties are so different from the linear paramagnetic relationship that they are best described by giving the magnetisation $\underline{M}$ as a function of $\underline{H}$. Domain concept, intrinsic moments along directions of crystallographic significance. Domains not identical with crystalline units, such as grains in polycrystal, may be larger or smaller. Variation with temperature shows that ferromagnetic property disappears at high enough temperature. Reciprocal of susceptibility goes as $T - \theta$ thereafter and suceptibility same magnitude as a paramagnetic. Specific heat has sharp peak at Curie temperature.

3. Alloys

Again two classes, subsitutional and interstitial. Phases need not be homogeneous, and many useful alloys are not. Most of discussion about homogeneous phases though. To form substitutional alloy radii of constituent atoms must be nearly equal. In interstitial alloys, the interstitial atom usually much smaller than atoms of host lattice, usually H, C, or N. Structures difficult to determine by X-ray analysis for this reason. Consider substitutional alloys now.

Atomic Sizes. Atoms must be within about 15 per cent of same size to form substitutional alloys over wide composition range. Rule restricted by condition that radii must be derived from monatomic phases with similar structures, and cannot be applied to systems showing valence characteristics, e.g. alloys involving As, Sb, Bi. Ag-Au perfect case of optimum conditions, both fcc, same valency, sizes same to 2 per cent, get single phase for entire composition range. Radius of copper less by 13 per cent than either, borderline cases. Cu-Au miscible except at low temperatures where complex phases appear. Cu-Ag do not mix. Pb-Cu immiscible in any proportion, differences 30 per cent. Rule of sizes not whole story.

Hume-Rothery Compounds. A-B type alloys in which size criteria satisfied. Characteristic electron:atom ratios.

Alloys of Strong Valence Metals. When one constituent only feebly electropositive, extensive solid solutions rare even when size factors favourable. Structures of phases when formed closer to ionic crystals, narrow composition ranges, metals tending to show their natural valency.

Superlattices. Appear at lower temperatures, ordering completely reversible if material maintained in equilibrium in case of β-brass. Specific heat anomaly exactly as in ferromagnetism.

Resistivity. Does not extrapolate to zero with decreasing temperature as well as that for pure metals - indicates large residual resistance. Ordering brings about much reduced resistance, kink in resistivity curve at temperature where ordering begins.

Transition Metal Alloys. Same general specific heat behaviour. If strongly paramagnetic or ferromagnetic, Dulong-Petit law fails at high temperatures. Close correleation between heights of specific heat peaks and saturation moment of ferromagnetic substance, for example addition of Cu to Ni quenches magnetic moment and lowers specific heat anomaly height.

Ionic Crystals.

Highly electropositive metals combined with halogens, oxygen or sulphur. Also metal carbonates, nitrates and ammonium halides, but consider mainly diatomic type. Obey closely classical rules of valency; valencies derived from investigation of combining ratios in these compounds.

Cohesion. Refer to standard states of monatomic constituent gases. Cohesive energy usually larger for compounds containing atoms of higher valency than for those with atoms of lower.

Structure. Usually one of a few simple structures (CsCl, NaCl, zincblende, wurtzite) Some have structures that tend to show a chemical molecule as an "island" in the lattice, can be described in terms of arrangement of molecules. Trend towards molecular behaviour, an example in TiO_2 (rutile).

The interatomic distances of alkali halides show regularity enabling definite values to be attached to ionic radii. Contact of rigid spheres works quite well as a model, and absolute determination of one radius suffices in principle to determine the rest.

Conductivity. Increases with temperature. Logarithmic dependence on $-1/T$. Fairly definitely ionic conduction, inferred by direct experiment, not from T-dependence, which also describes semi-conductors.

Specific Heats. Normal in that Dulong-Petit obeyed and decrease with decreasing temperature. Salts of transition metals do not conform, though, can show same sort of excess specific heat as that seen in metals, and can also be ferromagnetic.

Magnetism. Mostly diamagnetic, and susceptibilities additive for the two ions. This indicates that each ion preserves characteristic diamagnetic susceptibility in each compound, obeyed well for alkali halides. Cuprous ions appear to be diamagnetic, cupric paramagnetic, so that cuprous ion "simple", cupric "transition".

5. Valence Crystals.

Monatomic nonconducting materials of great hardness, prototype is diamond. Number of nearest neighbours equal to ordinary valence of atom. Many substances intermediate between this and other types, e.g. silicon and germanium have diamond structure but much higher conductivity (semiconductors). SiC has great hardness but absorbs I/R strongly. Properties of compounds of light elements tend to become those of valence crystals near centre of Periodic System.

6. Semiconductors.

Small electronic conductivity that increases with T. Category distinguished by electrical properties, and does not show same unity as other categories. Most have an ionic type of structure, but monatomic semiconductors are usually impure.

Conductivities. Two methods of measurement. Can place single crystal or pressed powder between metal electrodes and measure resistance by ordinary Wheatstone Bridge. This has advantages that can heat or cool sample easily. Miscellaneous stray resistances (electrode-sample, granule-granule) affect current-resistance curve, and it is difficult to be sure whether constants measured are properties of material or not. Can use semiconductor mixed with nonconducting dielectric in a condenser, and find the effective resistance of the condenser when it is part of a high-frequency circuit. This procedure eliminates contact resistance, but does not permit a very wide choice of experimental conditions. Conductivities tend to go as $A.\exp(-E/kT)$ where A and E are constant for given specimen.

Type of Conductivity. Three methods to find out whether it is electronic or not.
a) Transport Numbers, b) Hall constant, c) Thermoelectric coefficient.

a) Ionic conductivity is accompanied by electrolysis, and this should be completely absent if conductivity is electronic. If conductivity is mixed, there should be some electrolysis, but Faraday's transport law should break down in this case. Hence in principle can get the proportions of ionic and electronic conductivity by studying the deviations from Faraday's law. If it is suspected that a material MX conducts by the two processes together, a cell is constructed from pressed discs of material in the arrangement CATHODE/MY/MY/MY/MX/MX/MX/ANODE. MY is here a known fully M-ion conductor with the same metal M. The cathode, anode, and immediately adjacent discs are weighed previously. Current is passed in series with a coulometer, and if the conductivity is electrolytic, the discs near the electrodes become fastened to them. By weighing the electrodes + attached discs, the amount of material lost by the anode and gained by the cathode can be found, and hence the transport number of M is found. Use MY to check coulometer and to ensure that negative ions do not leave disc nearest cathode. Use three blocks of each in order that one in contact only with chemically similar substances, also to check that middle block's weight does not change. Found that some semi-conductors have a small but finite conductivity.

b) Hall effect is emf developed across strip of metal carrying current when placed in magnetic field. For cubic crystal $E = RJxH$, $R = -3\pi/8nec$, sign of charge carriers is that of R. Hall effect in ionic conductors very small. Semiconductors give a measurable effect, apparent sign of coefficient positive for as many as it is negative. For some specimens of cuprous oxide the Hall coefficient changes sign as temperature is raised, going through $R=0$ at $500^\circ C$. $R=0$ does not necessarily imply ionic conductivity.

c) Thermoelectric effect. Not observed in ~~semiconduct~~ ionic conductors, but is in semiconductors. Therefore a criterion of method of conductivity.

Influences. Conductivity of semiconductor affected by impurity content, past treatment and vapour pressures of gases of constituent atoms in surrounding atmosphere. Different specimens of most semiconductors do not in general have same conductivity at same temperature, hence impurities must be very important. Effect of vapour pressure typefied by cuprous iodide, conductivity increases with increasing pressure of iodine. Hall coefficient decreases at same time (it is positive), indicating that number of conducting elements increases with increasing iodine pressure. Due to deviations from stoichiometry influencing the conductivity.

7. Molecular Crystals.

Loosely bound aggregates of saturated atoms or molecules. Properties determined mainly by internal binding rather than inter-molecular forces. Prototypes are solid inert gases and saturated hydrocarbons. Nearly all diamagnetic because of pairing of electrons in saturated molecules. Oxygen is an exception - strongly paramagnetic. Large peaks in specific heat curves, due to changes in degree of molecular orientation.

BORN LATTICE THEORY.

Ionic materials, +vely charged metal ions and -vely charged halogen, oxygen, etc. Assume that ions spherically symmetric and interact thru simple central forces. Main interaction electrostatic, accounts for large cohesive energy of material. Balanced by repulsive forces of uncertain classical origin, varying much more rapidly with distance. Expression for total energy must satisfy

$$(dE/dV)_{V=V_o} = 0 \qquad (d^2E/dV^2)_{V=V_o} = 1/V\beta$$

so that crystal in equilibrium under all forces and compressibility matches observed value. These conditions serve to determine the two arbitrary parameters that are necessary to bring in the repulsive forces.

Theory correlates many of properties of ionic materials. Distinguishes also between those facts which can be understood on a simple classical model and those which cannot. Consider interactions in turn,

        a) Electrostatic
        b) Repulsive
        c) Multipole interaction.

a)   Assume ions have charges corresponding to their normal valencies. Sum Coulomb interaction over all pairs in crystal, considering each pair once. Must do this because of long range of Coulomb force. Find that sum can always be expressed in the form

$$E = - N.A^{(1)} e^+e^-/l$$

where N is number of ions considered, $A^{(1)}$ is a numerical constant, and l is a characteristic distance in the lattice, conventionally taken as the separation of the ionic centres, although this is only one of several possibilities. A is a numerical factor depending on the geometry of the lattice and the length taken as l. (Madelung constant). From this zero of energy is ions at infinite separation.

b)   Two forms assumed. Easier to manipulate is $E = B/r^n$, empirical. Fit to the equilibrium and compressibility relations, find n around 9. Can get different values for n by other methods, though. Pauling calculated the repulsion of closed-shell electronic configurations. Value of energy does not depend closely on n, though, change of unity (9-10) only casues change in cohesive energy of about 2 per cent. As all methods of estimating n agree to within this, this is reasonable. Observed and calculated cohesive energies come out well for ionic materials, but are doubtful for substances such as cupric oxide whose status on this theory is dubious.

Another form for repulsive interaction is exponential $C.exp(-r/R)$, in which A and R are constants to be determined. Can also add van der Waals interaction here. This form begins to have theoretical justification, and gives good agreement between observed and calculated results. The energy is written as before and fitted using the basic equations.

c)   Existence of solid inert gases shows that there is a residual interaction. London expression derived from quantum mechanics inserted,

$$E = - \frac{3h}{2r^6} \frac{F_1 F_2}{F_1 + F_2} p_1 p_2$$

where F_1 and F_2 are series limit frequencies of discrete spectra of two atoms or ions and $p_{1,2}$ are their polarisabilities. Interaction due to electron correlation.

Addition of this term amounts to about 1 per cent of the total energy. This does not therefore have much effect on the agreement between observed and experimental values. The additional term is however considerably important in determining relative stabilities of lattice types, for it is comparable with the energy differences between the various possible structures in most cases. Still not the whole story, when see that caesium chloride structure less stable than sodium chloride for case of caesium chloride. Can explain some of this but are getting away from the spirit of the Born model into the realms of fudgery. Dipole-quadrupole term calculated by Margenau gives 1/10 of the van der Waals energy (which is dipole-dipole). Zero-point energy also added, estimating maximum frequency from Debye model.

Relative Stabilities of Different Lattice Types.

Differences in free energies of various possible configurations are usually very small. Often less than the computational accuracy of the free energies. This is usually true in fact of the free energies of the four commenest types of ionic structure. Find that for most good ionic materials we get a fair answer, anomalies accountable for well within limits of a small change in the multipole interactions. For AgI however, change is the "wrong" way and far too large - suggests that AgI structure determined by covalent characteristics. May * suggested that some of the required corrections can be taken into account by deformation of ions. Distortion of an ion in a cubic crystal can be represented by fourth-order spherical harmonics and that the associated non-central potential goes as $1/r^9$.

Ionic Radii.

These are additive, but depend on co-ordination number. Definite nature of size well corroberated by the large power associated with repulsive forces. The Goldschmidt radii are in reasonable agreement with the electronic distributions found from quantum mechanics. Agreement among the Goldschmidt radii (self-consistency) is to about 5 per cent. These were found from optical properties, correlating those measured for fluorides and oxides with classical theory of dispersion. Can however approach by adjusting radii of alkali ions and halogen ions to give right lattice constant in the Born-Mayer equation; then get very great discrepancies with the Goldschmidt radii. Radius ratio considerations do not confirm the Goldschmidt values, and the rigid sphere model falls down badly if taken too far.

Cauchy-Poisson Relations

In most of the preceding, spherical ions with central forces are assumed. If this assumption were valid, the elastic constants of a cubic material should satisfy the relations given by Cauchy and Poisson ◊. This is not found to be the case in sodium chloride, discrepancies of 10 per cent between c_{12} and c_{44} being found. In magnesium oxide, the deviations amount to 50 per cent.

The terms in the Born theory may be divided into two classes, the short-range electrostatic interactions and the remainder. All the corrections to the electrostatic interactions that might arise from non-centrality of the forces have very high inverse powers (about 9) and can therefore be put in with the remainder terms. For the equilibrium values of the distances between ions actually found, the high-order terms only give about 10 per cent of the energy. As we pass from considerations of energy to considerations of forces, however, the importance of the high-order terms is made greater. The ratio of the derivatives of the electrostatic and remainder terms is n times as great as the ratio of the terms. By the time we have got as far as the elastic constants, which depend on the second derivatives, the remainder terms are dominating. As most of the theoretical uncertainty is centred on the corrections in the remainder terms, the disagreement in elastic constants is not surprising. This affects the energy relationships indirectly, for it can be ssen from the magnitude of the elastic discrepancy in magnesium oxide that the cohesive energy calculations cannot possibly be correct to better than about 10 per cent for the different possible structures. The problem of structure stability cannot therefore be settled without going further into the fine detail of the correction terms, as the differences between structures are only of this magnitude themselves.

Surface Energy.

One of factors determining whether or not a crytallographic plane is a cleavage plane is its surface energy. This is defined as the energy required per unit area to separate the crystal along this plane. Born and Stern calculated this for the sodium chloride lattice, and found that the surface energy of the lattice was such that a (100) cleavage was more favourable than a (110) cleavage, in agreement with experiment. Yamada repeated the calculation for all surfaces having normals lying in the (100) plane, and found that the (100) value was an absolute minimum for this set. If a polar diagram of surface energies against angle of normal to a reference direction is drawn, it can be proved that the most favourable crystal habit is obtained by taking the envelope of those planes that are orthogonal to lines passing through the origin at the points where these lines intersect the surface. In order to obtain the equilibrium form above the absolute zero, the free-energy polar diagram is used. If ionic crystals were perfect, their breaking strengths should be estimable from their surface energies. It is assumed that the interatomic forces are not important for distances of the parting planes greater than 10Å. The values obtained are vastly too high. Measurements of the surface tensions of molten salts are in fair agreement with theoretical values, though, and the conclusion is that the imperfections

---

* MAY, Phys. Rev. <u>52</u>, 339 (1937)   ◊ SEITZ, "Modern Theory of Solids", P.94 (1st Edn:)

of the structure are the dominating factor here. These have of course been omitted from the outset.

It may be concluded by remarking that the quantum-mechanical approach, based on the Heitler-London theory gives identifiable terms in the above treatment, and that the agreement between results for the fitted constants and the values calculated on this treatment are good to a first approximation. As the second approximation is very poor, however, it cannot be said that a very satisfactory fit has been obtained.