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CHEMICAL COMPOSITION AND PROPERTIES OF IONIC CRYSTALS

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I. INTRODUCTION

An understanding of the effect of composition on the properties of chemical compounds of different types is essential in the development of new materials having prescribed properties. The problem is usually tackled with compounds of simple, known composition and structure, and the results are then applied to the more complex materials used in industry.

The classical theory of ionic lattices provides a satisfactory explanation of many of the physical properties of ionic crystals, such as the compressibility, polarisability, dielectric constant, wave propagation, spectra of characteristic ionic vibrations, etc., and gives practical formulae which can be used to evaluate these parameters. However, there is as yet no unified theory dealing from a single standpoint with the effect of composition on the thermal, mechanical, optical, and dielectric properties of solids.

Satisfactory theoretical explanations are available for a number of crystal properties not involving disturbance of the continuity of the lattice, but we lack a comprehensive theory of the mechanical disintegration, melting, or electrical breakdown of crystals, allowing the strength of the material to be calculated exactly and without assumptions, and giving values consistent with experiment.

The earliest theories were developed to explain individual properties of the solid state, usually without reference to each other: for example, the theory of specific heat or the theory of electrical breakdown, and also the theory of the elastic properties of crystals, without reference to the chemical composition of the material. Phenomena such as electronic and ionic electrical conduction, losses, breakdown, diffusion, etc. were not among the topics proper to solid state theory.

An essential stage in the development of a unified theory of the solid state is to compare the properties of crystals, to correlate them, and to establish a relationship between properties and composition.

The correlations between various properties of ionic crystals have been discussed extensively.

Kurnakov[1] suggested that the dynamics of changes in properties of the material should be observed on at least two parameters, because one property may be insensitive to the interaction in question under the particular conditions of the experiment.

Simple correlations were found between the composition and structure on the one hand, and the physical properties on the other hand, of organic compounds and polymers.

According to Butlerov's theory of the structure of organic compounds, the physical properties of materials depend on their composition and structure. For example, in one homologous series of saturated hydrocarbons increase of molecular weight raises the boiling point; the melting point also increases with the number of atoms in the molecule, and so does the density of the hydrocarbons at the boiling point[2-4].

Special structural features of monomers leading to the preparation of polymers with prescribed properties have been pointed out. For example, the addition of fluorine is known to enhance the thermal and chemical stability of polymeric molecules, although the resistance to radiation is sometimes lowered. A high proportion of cyclic groupings consisting of benzene rings in the polymer molecule raises the thermal and the radiation-chemical stability of the polymer. Hence, methods of preparation of polymer molecules with the highest possible content of fluorine atoms or of groupings containing benzene rings are now being intensively studied in polymer chemistry.

A study of the properties of ionic crystals and of their dependence on composition and structure is of practical importance for the description of inorganic materials in general and ceramics and glasses in particular. Materials of different physical structure can be obtained by controlling the composition and the treatment of a ceramic body. Ceramic materials have different mechanical, thermal, and electrical properties according to their composition and structure. The rules which control the relationship between the composition, structure, and properties of ceramics have not been adequately investigated.

Ceramic materials are a multiphase system, including a crystalline phase, an amorphous phase, and a gas phase (the pores). The composition, structure, and relative amounts of the phases determine the properties of ceramic materials in a complicated way.

The crystalline phase largely determines the physical properties of ceramics. Hence, studies of the properties of ionic crystals have great practical importance. The crystalline phase consists of chemical compounds and of solid solutions of the components found in many ceramic materials.

The most advanced dielectric properties are found in ceramics based on gemstone spinels ($MgO.Al_2O_3$), forsterite ($2MgO.SiO_2$), periclase (MgO), perovskite ($CaO.TiO_2$), clinoenstatite ($MgO.SiO_2$), etc.

Ionic crystals have found the most varied practical applications, as in the production of optical systems, in crystal counters, amplifiers, etc. A study of the properties of ionic crystals should advance our understanding of the fundamental properties of corrosion resistant, structural, and other ceramic materials, and of the relationship between the composition and properties of these materials.

It should also provide a scientific basis for the rational specification of their composition and method of treatment.

A solid is a quantum-mechanical system of strongly interacting particles. The individual properties of the particles in a solid are largely lost and replaced by new, collective properties which characterise the solid as a whole. The basic properties of the solid are determined by its chemical composition, physical structure, and by external conditions. The energy of interaction between the component particles of the solid, which controls its physical properties, is determined by the position of the constituent elements in the Periodic Table.

It is interesting to examine the way in which the physical properties of the simplest ionic crystals depend on the position of the components in the Periodic Table (i.e. on their atomic weight and atomic number). The bonding between particles in crystals is most conveniently expressed by the energy needed to remove each ion to an infinitely large distance from all the other ions. This quantity is termed the crystal lattice energy.

The early work was done on compounds which had been chosen without regard for similarities or differences between the properties of anions and cations, or for periodicity in their parameters. This has caused difficulties in comparing the results obtained by different workers, particularly since even individual workers have reported measurements made under different conditions.

Comparison of the results of different workers (particularly on the kinetics of various processes in ionic crystals) is further complicated by the choice of a single measurement temperature for compounds of different composition having different Debye temperatures. In such a case the crystal lattices are in different relative states of breaking up and of approaching fusion. In all probability, the properties of ionic compounds of different composition should be compared at their respective Debye temperatures or at a common relative temperature T_m/T_f, where T_m and T_f are the measurement temperature and the melting point of the crystal respectively.

The observed trends have led to attempts to generalise and to relate the properties of ionic compounds to their composition in terms of the lattice energy, free volume, ionic radii, atomic numbers of the component atoms, etc.

The present article aims to establish a correlation between various properties of ionic compounds taking the lattice energy as the characteristic parameter controlling the properties of ionic crystals. This parameter is thermodynamic and, therefore, macroscopic. In solid state theory the parameter is expressed in terms of ionic radii and ionic charges, and is therefore associated with the microscopic structure and composition of the compound.

In practice, the structures and composition of single crystals are always different from the ideal. It has been assumed[5] that the defects of a real crystal and their concentration are directly related to the lattice energy.

Ionic structures are close packed, so that ionic motion in the crystal is possible only by jumps into neighbouring vacant lattice sites. Motion of an ion by jumps in a given direction is accompanied by the transfer of vacancies of that ion in the opposite direction. The activation energy attending the motion of ion vacancies is a very important quantity which determines the displacement of ions and their vacancies from one equilibrium position to the next. This quantity increases, as a rule, with the ionic radius, but the potassium ion in sylvite is exceptional in having a very small activation energy[5]. As the lattice energy decreases, the activation energy needed to transfer an ion or vacancy from one position to the next also decreases. Hence we may conclude that a correspondence exists between the macroscopic description of these processes in terms of the lattice energy and the microscopic description in terms of the activation energy for the motion of ions and vacancies in the solid.

The properties of bodies obey an internal relationship which can be expressed by the equation of state for a real, inhomogeneous solid. To set up the equation of state of a solid body we need information on all the internal parameters of the system.

The observed correlation between the properties of ionic crystals and the lattice energy[5] can be described thermodynamically in terms of the expression for the free energy of an inhomogeneous body. Ignoring the vibrations of the ionic nuclei, the free energy of an ideal crystal consists of the energy density of the statistical lattice plus the zero-point vibration energy[1]. The equation of state of an ideal crystal, describing the relationship between pressure, volume, temperature, thermal and mechanical properties, can be derived from the expression for the free energy. The free energy at low temperatures is determined by the internal energy, i.e. by the potential energy of the interacting ions at 0°K, which we call the crystal lattice energy.

Like many other properties of a crystal, the entropy also is related to the lattice energy. Hence the free energy in the linear approximation is expressed in terms of the lattice energy[7].

In the theory of crystal lattices the free energy is used to define the linear temperature expansion coefficient and the isothermal compressibility, which are related to other mechanical, thermal, optical, and electrical characteristics of the crystal. Hence, the relationship between various physical characteristics of a solid and changes in its free energy can be established thermodynamically[6].

It follows from what has been said that the relationship between the normal mechanical, thermal, optical, and electrical properties and the free energy can be replaced by a relationship between those properties and the lattice energy, the latter being simpler to determine. The lattice energy is proportional to the product of the valencies and inversely proportional to the sum of the ionic radii and depends only on the chemical composition and structure. Expressions for the properties of bodies in terms of the lattice energy reflect their dependence on chemical composition.

The free energy of a real solid differs significantly from the ideal value on account of the energy stored in defects. The defect structure is one of the properties of real crystals. Like other properties, the defect structure of crystals, characterised by the concentration of defects, is related to the lattice energy and under different measurement conditions this relationship can upset in various ways the dependence on lattice energy of a basic characteristic[8].

When defects form, energy is absorbed by the crystal and the internal energy increases. At the same time, point defects raise the configurational entropy of the system. Hence, the free energy of the system can decrease at high temperatures as a result of the increase in entropy[9] The excess of internal energy arising from the formation

of point defects in the ionic lattice increases with the concentration of defect pairs. The concentration of defects increases with deformation, irradiation, and increase of temperature. It decreases with radiational and thermal annealing.

The establishment of a correlation between various characteristics of ionic crystals in terms of the lattice energy alone is of practical importance, since it would enable a comparison of the changes in properties of ionic compounds resulting from changes in chemical composition. A satisfactory classification of the different ionic compounds according to their properties can be based on a single parameter: the lattice energy. When the relationship between the properties is known, the lattice energy can be used to determine many other properties of ionic crystals of practical importance.

II. CRYSTAL LATTICE ENERGY AND SURFACE ENERGY OF IONIC CRYSTALS

The stability and the strength of a crystal depend on the magnitude of the forces acting between the particles, and on the crystal lattice energy which is determined by these forces. For ionic crystal lattices of the same structural type, the energy of the bond between the particles is determined by the chemical composition. The energy of the crystal lattice is a valuable index of the energy level of the system.

In the classical Born–Madelung theory of ionic crystals [10,11] the interaction energy is determined by the electrostatic interaction between all the ion pairs. The interaction energy is calculated taking account of the electrostatic Coulombic attraction energy e^2/r (for charges of different sign) and of repulsive forces (for charges of the same sign). The energy of the repulsive forces due to the electron shells of the ions, B/r^n, is then computed.

In the calculation of the forces of attraction and repulsion acting between a cation and an anion the energy of the ionic lattice is given by the formula

$$U = -\frac{N}{2}\left[\frac{A\,\eta_1\,\eta_2\,e^2}{r_0} - \frac{B}{r_0^n}\right] \qquad (1)$$

where A is the Madelung constant, which depends on the crystal structure, η_1 and η_2 are the valencies of the ions of which the lattice is composed, r_0 is the shortest distance between the centres of oppositely charged lattice ions, n is the exponent in the expression for the potential of the repulsive forces, B depends on the crystal structure and on the structure of the ion, and N is the number of ions in the crystal. The magnitude of the repulsive force is determined by the distribution and by the number of electrons in the outer shells. The exponent n is greater for Na^+ ions, which have 8 electrons in the outermost shell, than for Li^+ ions, which have only 2 electrons.

The complete expression for the crystal lattice energy, including quantum-mechanical corrections, is an additive function of the energy of the electrostatic attraction forces, the energy of the repulsive forces, the energy of the van der Waals cohesive forces between ions, and the zero temperature vibrational energy. The vibrational energy of a lattice consisting of N atoms at absolute zero is $9h\nu N/4$, where ν is the residual radiation frequency and h is Planck's constant.

Thus, the full expression for the lattice energy at 0°K of an alkali metal halide crystal per mole can be written [2]

$$U = N\left[\frac{\eta^2 e^2 A}{r_0} + \frac{C}{r_0^6} - B(r_0) - {}^9/_4 h\nu\right] \qquad (2)$$

where U is the lattice energy, η^2e^2A/r_0 the part of the energy arising from electrostatic attraction, η the lowest valency found in the lattice, C/r_0^6 the van der Waals energy, and $B(r_0)$ the potential energy due to the repulsive forces in the lattice.

Calculations of the lattice energy by formulae (1) and (2) involve serious difficulties in the determination of the value of r_0 by X-ray diffraction and in the computation of the quantities A and n.

Kapustinskii [12], using Born and Mayer's quantum-mechanical expression for the lattice energy, derived an equation for the energy of a crystal lattice not involving A or n:

$$U = 287.2\,\frac{\Sigma m \eta_C \eta_A}{R_A + R_C}\left(1 - \frac{0.345}{R_A + R_C}\right), \qquad (3)$$

where Σm is the number of ions in the molecule and η_A, η_C, R_A, and R_C are the valencies and the radii of the anion and the cation respectively.

The majority of inorganic compounds are not usually ionic. In ionic crystals we observe a continuous transition from ionic to covalent bonds, but there is no satisfactory criterion for determining the degree of polarity.

Sarkisov [13] proposed that the lattice energy of ionic compounds should be calculated on the basis of the electron gas concept, in which the ionic bond is, effectively, replaced by a covalent bond. Any crystalline inorganic compound is envisaged as an assembly of cores of interacting atoms: the chemical bond between the atoms is created by an electron cloud formed by the delocalisation of the valency electrons of the metal atoms and of an equivalent number of peripheral electrons from the non-metal atoms. The chemical bond in a lattice of the NaCl type is described as a strongly polar covalent bond. The electron cloud of the bond between the sodium and chlorine atomic cores consists of two electrons, made up of one valency electron from the sodium and one peripheral electron from the chlorine. In homopolar crystals the maximum density of the electron cloud of the bond is located exactly half-way between the neighbouring nuclei, and in typically ionic crystals it suffers a maximum displacement towards the non-metal. When this shift occurs, the electron cloud cannot be considered to belong exclusively to the non-metal, but the motion of the electrons must be treated in the field of the two positively charged cores of the interacting atoms.

Thermochemically, the lattice energy is defined by the Born–Haber cycle.

The lattice energy of chemical compounds varies in accordance with the periodicity of the properties of their constituent elements in the Periodic Table. Fig. 1 shows the change in lattice energy with composition for the alkali metal halides. An increase in the size of the ions (and therefore in the size of the unit cell) is accompanied by a decrease in lattice energy. Replacing the anion whilst keeping the cation constant, or replacing the cation whilst keeping the anion constant, produces a monotonic change in lattice energy. This substitution causes the lattice energy to decrease as the sum of the atomic numbers of anion and cation ($Z = Z_C + Z_A$) increases, and to approach a constant value for large Z. However, if we go to the halides of

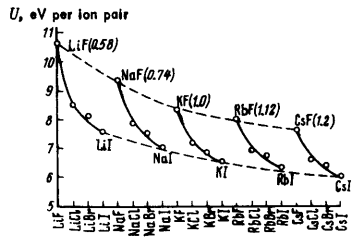


Fig. 1. Variation of lattice energy with composition for the alkali metal halides. (The numbers in brackets denote the cation to anion radius ratio.)

another metal or to the compounds of metals with other halogens we land on a different curve.

There are several rules which describe the change in lattice energy of a chemical compound with composition. Increase of ionic charge raises the lattice energy. The lattice energy of alkali halide crystals, consisting of singly charged ions, is 100–200 kcal mole^{-1}. The lattice energy of metal oxides such as MnO, FeO, NiO, and others, composed of doubly charged ions, is ~ 900 kcal mole^{-1}.

Compounds of the cations of secondary subgroups, with 18 electrons in the outer shell, have a greater lattice energy than compounds with ions of the same period but having the inert gas structure, thus [5]:

$$U_{CuCl} > U_{KCl};\ U_{ZnBr_2} > U_{CaCl_2}.$$

This rule probably follows from the smaller size of the ions in the secondary subgroups, and particularly from the influence of the polarisation energy, which is evident also from the following rule. The lattice energy of the halides of secondary subgroup elements is much less sensitive to anion radius than that of the main subgroup elements. If the radius of the anion increases, the lattice energy should decrease. However, the polarisation energy also increases, and in the secondary subgroup elements this has a much more profound effect than in the main subgroup elements.

Quantum-mechanical corrections to Born's theory have enabled us to calculate the vibrational energy of the crystals at 0°K and the contribution to the attractive energy from van der Waals dipole–dipole or dipole–quadrupole interaction, amounting to several per cent of the total lattice energy. In silver halides this additional term in the interaction energy is very much greater because of their large polarisability, and reaches 14% in AgBr. The correction for the van der Waals interaction forces in these compounds is greater for the heavier elements, which experience a greater polarisation. The correction for zero-point energy is greater for compounds composed of light elements, which have a higher Debye characteristic frequency. Therefore, a change in composition in the alkali and alkaline-earth metal halide series is accompanied by a change in the role of a given type of chemical bond in the compound, which in turn induces a change in the properties of the compound.

The lattice energy is linearly related to the heat of formation [10]. Oxides having a low heat of formation (and therefore a low lattice energy) are likely to be semiconductors. These include Ag_2O, CuO, NiO, CoO, FeO, CdO, HgO. Oxides with a high lattice energy and heat of formation (CaO, MgO, ZnO, BeO, BaO, SrO) are dielectrics of high electrical and mechanical strength.

The rates of processes depending on the thermal mobility of atoms in diatomic and polyatomic systems are related to interatomic interactions. The rates of processes depending on the thermal motion of atoms are functions of lattice energy.

The most stable structures are obtained by forming compounds of tetravalent elements. The oxides of Group II elements of the Periodic Table, BeO, MgO, CaO, SrO, BaO, have high lattice energies, heats of formation, melting points, and also good electrical and mechanical properties.

The lattice energy determines: (a) the tendency to form stable heteropolar lattices; (b) the mechanical strength of the compounds; (c) the stability of the compounds towards melting, but not necessarily towards dissociation, and (d) the solubility in aqueous solutions. However, the lattice energy cannot completely define the stability of the system. Polarisation and depolarisation phenomena must also be taken into account: these can have a considerable influence on the ionic radius and therefore on the course of various processes. Lattice energy depends on the crystal structure [14].

The lattice energy is lowest for lattices of the caesium chloride type, and highest for wurtzite. This increase in lattice energy corresponds to a decrease in the ionic radius from 1–0.7 (for a caesium chloride type lattice) to a value below 0.4 (wurtzite). The modern theory of the crystal lattice and well-known experimental results provide the data needed to compare the properties of ionic lattices with their energetic and structural characteristics [15].

The surface particles of a solid experience considerable forces of attraction from particles in the interior. This attraction is not compensated by attractive forces from particles in the surrounding medium. Hence, the particles on the surface have a greater potential energy than the particles in the interior of the body. The excess energy of the surface particles can be determined by transferring particles from the interior to the surface. When a crystal is broken into pieces the work required to transfer particles to the surface has to be expended [15].

The specific surface free energy is measured by the work done in creating 1 cm^2 of surface layer by an isothermal process and is different for different crystal faces. For crystals of the rock salt type, the specific surface energy of the cubic face, $\sigma_{(100)}$, is lower than that of the rhombic dodecahedral face, $\sigma_{(110)}$, or of the octahedral face, $\sigma_{(111)}$. If molecules of active substances are adsorbed on the surface of a solid the specific surface energy of the face decreases. The surface energy of crystals decreases after irradiation.

The surface energy has a considerable effect on the course of many processes taking place at the interface between two solids, especially on phenomena involving the formation or disappearance of a surface, diffusion, adsorption, etc. By its physicochemical nature, the surface energy is a manifestation of interaction forces and of chemical bonding between particles, and can be calculated by applying the formulae for the lattice energy.

The surface energy is small compared with the lattice energy. To divide one mole of rock salt into small cubes

of linear dimensions of the order of one micron, thus imparting to it a surface area of 1.62×10^6 cm^2, requires the expenditure of only 0.0057 cal, whereas the lattice energy is [16] 183 kcal mole^{-1}.

The surface energy is relatively unaffected by changes in composition. Hence, pronounced changes in properties with chemical composition must be associated with lattice energy rather than with surface energy, the latter being relatively insensitive to the composition of the material [15].

III. CORRELATION BETWEEN PROPERTIES OF IONIC CRYSTALS AND LATTICE ENERGY

The properties of ionic structures are interrelated, but the rules which govern these relationships have as yet been theoretically established in only a few cases. Hence, until quite recently, the various properties were investigated in most cases separately. During the last decade complex studies of different properties and of their interplay have become more frequent [15,16].

On heating, applying mechanical or electrical stress, or on dissolution, the bonds between the particles in an ionic crystal are overcome, which leads to the collapse of the lattice. The energy needed to break down the lattice depends on the forces between the particles which form the lattice. An increase in lattice energy leads to enhanced mechanical, electrical, and thermal stability in ionic compounds. These results were obtained from measurements on single crystals and compacts pressed from powdered oxides, sulphides, and halides of metals of Groups I and II.

The lattice energy determines the physicochemical properties of a crystal involving separation of the ions, their motion in the lattice, and changes in interaction forces between the ions.

The plastic properties of solids are described by the dislocation theory. The mechanical properties of real crystals vary in a regular manner with lattice energy, which characterises the ideal lattice. This correlation exists because structural defects, their concentration and mobility, and dislocations are all determined by the same structure and are related to its energetics [17].

The polarisability and the chemical bonding between ions depend on the nature of the ions. In a series of metal halides of a single type the polarisability decreases on going from rubidium to lithium compounds and increases as the anionic radius increases from fluorine to iodine [18].

Changing the structural type of the rubidium fluoride lattice, which has the caesium chloride structure at normal temperature and pressure, does not disturb the overall regularity. Associated with changes in the polarisability and concentration of the ions, the dielectric constant and its electronic and ionic components are found to increase or decrease as the lattice energy increases.

The electrical conductivity of ionic compounds in the solid state is determined by the motion of cation vacancies both in the intrinsic and in the impurity region. The heat of activation for electrical conduction, measured from the temperature coefficient of conductivity, increases as the lattice energy increases, whilst the magnitude of the conductivity decreases. The temperature of onset of intrinsic conduction in ionic compounds is shifted upwards as the lattice energy increases.

Dielectric loss arising from conduction at low or at high frequencies behaves similarly. An explanation has been given [19] of observed discrepancies from the general pattern, due to impurities, including the formation of vacancy aggregates, the distribution of impurities throughout the crystal, etc.

The specific heat and the heats of fusion, sublimation, evaporation, and dissociation increase as the lattice energy of ionic compounds increases, whilst the linear thermal expansion coefficient decreases [5].

The electronic component of the dielectric constant of alkali metal halide crystals increases as the polarisability of the halogen is increased (keeping the metal constant) and the lattice energy is decreased.

The replacement of magnesium by calcium, strontium, etc. in titanates produces an increase of dielectric constant, accompanied by a decrease of the binding energy of the particles in the lattice [19].

In crystals, the physical phenomena determined by the elastic vibrations of ions are related to the lattice energy. The specific heat per g-atom of compounds of metals of Groups I and II decreases as the lattice energy increases. The melting points of alkali metal halide crystals increase with the lattice energy. The fundamental vibration frequency of the lattice ions of the compounds of metals from Groups I and II also increases with the lattice energy.

The surface energy has a substantial effect on many processes occurring at the contact between two solids. The surface energy can be considered, physicochemically, as the manifestation of the interaction forces between particles and of the chemical bond between them. Hence, the crystal lattice energy and the surface energy of a solid in a vacuum are interrelated. Any increase in specific surface energy is accompanied by an increase in lattice energy. A successful attempt has been made [20] to relate the surface resistance of solid dielectrics to the value of the surface energy.

High values of the lattice energy and surface energy in ionic compounds cause hydrophilicity and increase the surface conductivity. They also degrade, in general, the favourable electrical properties of ionic dielectrics. The highest surface resistivity is found in materials having a structure intermediate between those of materials with ionic and with atomic bonds (for example, in fused quartz).

When the binding energy of ions in the lattice increases, the electrical conductivity and dielectric losses of ionic crystals decrease.

Some crystal properties, e.g. thermal conductivity, specific heat, elastic moduli, etc., are determined not so much by the lattice energy as by its derivatives with respect to various parameters. Due to the simple relationship between the properties of ionic crystals and the lattice energy, the various properties are also simply interrelated. A knowledge of the lattice energy allows a complicated evaluation of the properties of ionic compounds of a given series. Compounds with a high lattice energy have more desirable properties in practice. For example, beryllium and magnesium compounds are more refractory and have a higher mechanical and dielectric strength than barium or zinc compounds [19,21-29].

However, not all the properties and characteristics of ionic crystals can be simply correlated with lattice energy. Processes in which ionic compounds are broken down to

atoms or radicals rather than ions do not show a simple correlation. For example, the stability of azides towards thermal decomposition increases from lithium to caesium azide, i.e. on going from compounds with higher towards compounds with lower lattice energy [30]. The heat of formation increases from lithium towards caesium [31]. In this case the failure of the rule according to which the stability of ionic compounds should increase with the lattice energy can be explained as follows. Azides decompose into atoms as a result of electron transfer from the anion to the cation. Hence the elementary act is ionisation of the anion, followed by the collapse of the lattice. The sign of the ionisation potential is opposite to that of the lattice energy, and its magnitude varies more markedly than the lattice energy from cation to cation. When the azides are decomposed into ions (e.g. in aqueous solutions) their stability is found to increase in the same sense as the lattice energy [32].

Departures from the simple correlation between lattice energy and various physicochemical characteristics are observed also when the compound includes chemical bonds of different types and strengths. Among such compounds we find, for example, the crystal hydrates, in which coordinate bonds are present as well as ionic bonds. The stability of these compounds towards mechanical, thermal, chemical, and electrical breakdown increases with the number of water molecules present in the lattice, because this increases the strength of the bond between the particles of the lattice.

The weak van der Waals bond between the layers of layered structures explains the low strength of these materials towards cleavage along the layers. When such a body is fractured across the layers, against the large coulombic interaction forces, the strength is found to be high [17,18,20,33].

The exceptions which we have considered allow us to formulate more precisely the rule for the stability in a series of chemical compounds of a single type: when the compounds are broken down into their structural units (for example, ions in the case of an ionic lattice), the stability is found to vary in the same order as the strength of the bond between the structural units.

Homopolar lattices can form a strong framework made up of covalent bonds (diamond lattice). Unlike compounds having an ionic lattice, homopolar compounds retain their dielectric properties in the melt. The main physicochemical and electrical properties of solids with a homopolar lattice depend on the parameters of their constituent atoms (radius, deformability of electronic shells, etc.). Thus, for example, in Group IV carbon (diamond) is a good insulator, silicon (which crystallises in the diamond lattice) is a semiconductor, and tin has the electrical properties of a metal. The quantity equivalent to the lattice energy of ionic crystals is, in homopolar materials, the energy of atomisation, i.e. the energy needed to dissociate the atoms forming the homopolar lattice (or the energy needed to convert these materials into a monatomic vapour).

The physicochemical properties of homopolar structures are determined by the heat of atomisation and depend on the parameters of the constituent atoms [34-39].

In a molecular lattice, as well as in crystals with mixed ionic and covalent bonds in comparable proportion, no simple correlation is found between the overall binding energy and the physicochemical characteristics of the material. Most practically useful materials are compounds of this type.

The lack of simple, unique correlations between the physicochemical properties and the energy of the bond between the particles of compounds having chemical bonds of different types probably follows from the fact that the role of the various bonds is different under different external interactions. Some processes reflect one type of chemical bond, other processes reflect the other.

The physicochemical properties of liquid and of gaseous organic compounds have been compared with their dielectric strength. In the alkane series the dielectric strength increases with the strength of the bonds between molecules, and is practically independent of the strength of the intramolecular bonds. From these results, the electrical breakdown of organic dielectrics has been visualised as a process which begins with the breaking of intermolecular bonds. As the energy becomes concentrated in a discharge channel, breakdown may involve the breaking of intramolecular bonds [39].

The fact that the properties of real crystals depend on defects as well as on the lattice energy stems from the influence of the energetics of the crystal lattice on the behaviour of defects (in particular, of dislocations). Dislocation theory shows that the size and mobility of a dislocation are determined by the forces between the constituent particles of the crystal. The density of dislocations in crystals grown from the melt decreases as the crystal lattice energy increases.

The influence of defects and of the lattice energy on the electrical properties of ionic crystals has been established in the case of electrical conductivity. In ionic crystals, current is carried almost exclusively by cation vacancies [40]. Under these conditions, the conductivity is determined by the number of cation jumps per unit time. This number is proportional to the probability of a cation adjacent to the vacancy having sufficient energy for the jump. The concentration of vacancies in the crystal is proportional to

$$\exp\left(-\frac{W}{2kT}\right),$$

where W is the work of formation of a vacancy pair.

This quantity is related to the energy of the crystal lattice, and this accounts for the dependence of the electrical conductivity of alkali metal halide crystals on lattice energy.

As the lattice energy increases, both the electrical conductivity and the conductance losses in alkali metal halide crystals decrease.

The relation which exists between the defect structure and the energy of a crystal lattice leads us to expect that the laws derived for single crystals will be found to be equally applicable to the polycrystalline substances used in technology. In polycrystalline samples of oxides and halides of Group II elements, prepared by pressing followed by heat treatment, the electrical conductivity and the dielectric losses decrease as the lattice energy increases, and at the same time the activation energy increases.

Ceramic materials and minerals in which the binding energy between ions is large have a high thermal and chemical stability and high mechanical and dielectric strength.

The stability towards neutron bombardment of the properties of beryl, quartz, phenacite, chrysoberyl, barium titanate, and other minerals decreases in the following

order: beryllium–oxygen, silicon–oxygen, aluminium–oxygen, titanium–oxygen, zirconium–oxygen, and barium–oxygen. The decrease in radiation stability of the oxides is accompanied by a corresponding increase in cation radius: Be (0.34 Å), Si (0.39 Å), Al (0.57 Å), Ti (0.64 Å), Zr (0.87 Å), Ba (1.43 Å).

Replacement of the cation in this sequence also lowers the ionic bond character and the lattice energy per ion [41-43].

IV. STORED ENERGY IN IONIC CRYSTALS

The energy absorbed by crystals during mechanical or heat treatment, or irradiation, causes heating or the formation of various types of damage to the lattice: this increases the internal energy of the crystal and the elastic deformation energy. In particular, after irradiation a crystal has an excess of free energy (over the equilibrium value) which is termed latent or stored energy. The amount of stored energy is related to the radiation-induced defects: it can be used as a measure of the number of these defects, and it controls the change in physical and chemical properties of the material.

Compounds having a relatively large effective atomic number form crystals of relatively low lattice energy. When subjected to a given dose of radiation, these crystals absorb more energy than crystals with a high lattice energy.

Because defects are annealed more rapidly in crystals of low lattice energy, the stored charge at room temperature is smaller than in crystals with a higher lattice energy.

If the energy of formation of a defect is known, the number of defects can be determined by measuring the total stored energy. If the number of defects is known, the energy of formation of a single defect can be calculated. Provided the irradiation is carried out at low temperature, when the annealing of defects is suppressed, the stored energy is a measure of the energy of formation of the given number of defects. Radiation damage to solids is in some respects analogous to the influence of plastic deformation, and is attended by similar changes in properties. In contrast to cold working, radiation damage has the following characteristics: (1) it causes a different type of microscopic damage to the lattice; (2) radiation damage is more extensive than the damage caused by plastic deformation; and (3) radiation damage appears in a microscopic volume, and is not crystallographically oriented [41].

After a high integral dose of neutron irradiation, spallation of the crystals was observed. The minimum dose of radiation needed for significant breakdown of the crystals into blocks increases with the stability of the crystals (i.e. with the lattice energy). For quartz and for lithium fluoride the dose was, respectively, 1×10^{19} and 8×10^{17} neutrons cm^{-2}. [42]

The energy stored in rock salt after 6.64% relative plastic deformation at room temperature and a maximum stress of 1.02 kg mm^{-2} was 0.4 J g^{-1}. Less than 10% of this energy is stored in point defects [43].

The stored energy increases the free energy and weakens the cohesion of the lattice. Hence, the Debye temperatures (calculated from X-ray diffraction data) of undeformed and deformed crystals of rock salt are 260–290° and 150–170° respectively [44,45].

When the concentration of F-centres was increased from 2.5×10^{17} to 6.5×10^{17} cm^{-3} by irradiation with X-rays the stored energy was found to increase linearly [46], with a tendency towards saturation at higher doses.

On annealing NaCl crystals containing stable vacancy complexes, maxima were observed on the curve of heat evolution versus temperature. These corresponded to the annihilation of mobile defects at the lower temperatures and to dissociation of the vacancy complexes at the higher temperatures [47,48]. The stored energy was measured in crystals which had been irradiated with 4.3 MeV protons in a flux of 1.5×10^{14} protons cm^{-2} s^{-1}, with X-rays, and with γ rays from ^{60}Co. Single crystals of CaF, SrF_2, BaF_2, LiF, NaCl, KCl, KBr, and KI, and of solid solutions in the KCl–KBr system, were investigated. The measurements were made by annealing and also, in the case of the alkali metal halides (with the exception of LiF), by dissolution in water as well as by annealing.

Fig. 2 shows the temperature variation of the rate of evolution of heat from NaCl crystals, heated after the stated dose of ^{60}Co γ radiation. As the dose was increased, the amount of energy stored in the crystal increased, and the first (low-temperature) peak grew. The stored energy was greater in the crystals with the higher lattice energy. The amount of energy stored increases with dose of radiation. In crystals with a large lattice energy the stored energy accumulates faster than in crystals with a smaller lattice energy.

Several times more energy is stored in alkali metal halide crystals than in copper crystals, probably because of energy scattering by the free electrons in copper. The difference may be associated with the nature of radiation damage in alkali metal halides under X-ray irradiation. The defects are formed in these crystals by ionisation processes, which consume 99% of the absorbed energy. In copper the radiation damage occurs mainly by elastic interactions between the particles and the atoms of the material.

The energy stored upon irradiation can be as much as 7% of the lattice energy in NaCl. The energy stored in NaCl after irradiation at room temperature can be 200 times higher than the energy stored under maximum plastic deformation. As the temperature is lowered the amount of stored energy increases. Irradiation is a much more powerful agency than plastic deformation [49-52].

In NaCl + Ca crystals irradiated with X-rays the stored energy increases with increase of the calcium content. The position of the peak rate of heat evolution of the temperature axis shifts towards lower temperatures when the concentration of impurity is increased. This result is in keeping with the hypothesis that the activation energy for

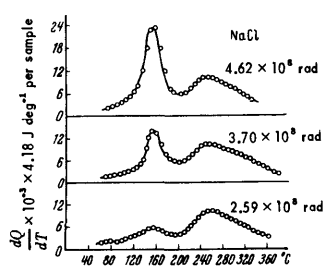


Fig. 2. Variation of the rate of evolution of heat with temperature on heating NaCl crystals irradiated with γ rays [46].

annealing radiation damage is smaller in the presence of impurities [52].

The stored energy after irradiation in solid solutions is less than in the original, pure crystals. Hence, crystals of solid solutions are more stable to radiation than pure crystals.

The amount of free energy which can be stored in the structure is determined by the experimental conditions and by the composition of the compound. As the bond energy increases, the energy storage capacity (i.e. the free energy) of the crystal increases. Substances having a high lattice energy and able to store the energy dissipated by mechanical or thermal treatment, or by irradiation, can be used as memory elements for external interactions giving rise to excess free energy.

The radiation-induced changes in the properties of materials with ionic bonds vary in the same sense as the stored energy. The amount of energy stored after relatively low doses of radiation or by quenching is of the same order of magnitude as in systems containing impurities or in solid solutions. Thus, solid-state reactions, whose characteristics show a correlation with the free energy in ionic compounds, are influenced by irradiation in the same way as by heat treatment.

The postulated strong influence of the after-effects of irradiation on the rate of processes determined by free-energy changes, and the expectation of a significant change in the properties of substances with bonds of the ionic type, were not confirmed by experimental measurements. The changes taking place in the material during irradiation are determined by the amount of energy absorbed: this increases as the lattice energy of the crystal is decreased. A compound with a low bond energy absorbs more energy in the radiation field and is weakened to a greater extent than a compound with a higher lattice energy. The energy absorbed exceeds the stored energy by two or more orders of magnitude. Hence, radiation technology should be based on the effects occurring during irradiation rather than after irradiation [41].

V. DISSOLUTION AND EVAPORATION OF ALKALI METAL HALIDES

When alkali metal halides come into contact with water or unsaturated aqueous solutions the following processes can occur: diffusional or diffusion-kinetic dissolution, hydrate formation, dissociation, and crystallisation from solution. The probability and rate of each of these processes depend on the bond energy of the chemical compound being dissolved, on the nature of the solvent, and on the dissolution conditions.

When a crystal dissolves and the system passes from an ordered to a disordered state the energy of the system increases. The ordered state of the particles in the crystal corresponds to a minimum in potential energy.

The heat of solution Q_{sol} is made up of the heat needed to break down the crystal structure, including the lattice energy U (taken with the negative sign) and the heat of interaction of the solute with the solvent ($H > 0$), which is evolved on dissolution. Thus, we have approximately

$$Q_{sol} = H - U. \qquad (4)$$

On dissolution in water with formation of hydrates the quantity Q_{sol} [*H*? (Ed. of Translation)] is termed the heat of hydration.

Fig. 3 shows the variation of the heat of hydration of the alkali metal halides, taken as the sum of the heats of hydration of the ions, with the lattice energy. The expected linear relationship (4) is satisfactorily supported by the experimental data (see Fig. 3).

The chemical stability of ionic compounds increases with increase of lattice energy [5]. The monotonic relationship between solubility and thermal effect is infringed if compound formation with water takes place [5]. If the salts dissolve without forming hydrates, and dissolution occurs with absorption of heat, i.e. $\Delta H > 0$, the solubility decreases with increase of lattice energy as shown in Fig. 4. For compounds which form crystal hydrates the thermal effect on dissolution increases with increase of lattice energy.

For aqueous salt solutions, if $\Delta H > 0$, we also have $T\Delta S > 0$, where ΔS is the increase in entropy of the system resulting from dissolution [53]. The thermal effect on dissolution of these systems, coupled with the condition $T\Delta S > \Delta H$, automatically controls the dissolution. The large increase in entropy of the system during dissolution of a crystal lowers the free energy of the system and therefore favours the dissolution process. The entropy increase ΔS attending dissolution in water of the alkali metal halides which do not form hydrates is smaller, the higher the lattice energy. This accounts for the decrease in solubility illustrated in Fig. 4.

Crystals of alkali metal halides can dissolve in water and in aqueous solutions in the diffusional regime when the rate of dissolution is determined exclusively by diffusion, and in the diffusion-kinetic regime, which depends on the structure of the crystal [54].

The difference in the dissolution mechanism of crystals along different crystallographic directions gives rise to

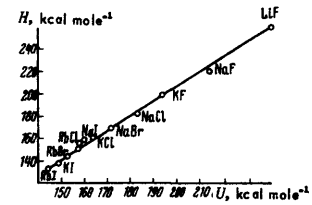


Fig. 3. Variation of the heat of hydration of alkali metal halides, taken as the sum of the heats of hydration of the ions, with lattice energy.

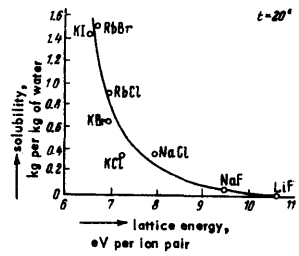


Fig. 4. Solubility of the alkali metal halides in water at 20° against lattice energy.

anisotropy in the rate of dissolution. The rate of dissolution of a crystal in the mild solvents recommended for etching is probably more under the control of the reaction by which particles are transferred from the crystal into the solution than under the control of diffusion into the bulk of the solution [31,55].

In the diffusion-kinetic regime the rate of dissolution of a crystal becomes anisotropic. At room temperature the highest rate of dissolution is observed on the (110) face, and the lowest on the (100) face. The ratio of the rates $v_{(110)}$ and $v_{(100)}$ increases [with lattice energy? (Ed. of Translation)] [31]. The rate of dissolution is highest when the reticular density of the ions on the crystal face is highest and the energy of the bonds between the ions is lowest. The rate of dissolution is lowest on the (110) face, which has the highest density of ions, but on the other hand the bonds between the ions on the (100) face are the strongest [sic]†. Thus, the rate of dissolution in this case correlates satisfactorily with the bond energy of the ions, but not with their density. In the (110) plane the rate of dissolution is greatest, the ionic density is less than on the (100) face, and the bonds between neighbouring ions are less strong than on the (100) face. Therefore, we again note a satisfactory correlation between the rate of dissolution and the energy of the bond between the particles [31].

The dissolution anisotropy of crystals increases with increase of surface energy and of lattice energy. The rates of contact melting of the various faces of crystals display a similar relationship to that of the rates of dissolution of the faces: the rate of contact melting of the crystals is a maximum on the (110) face and a minimum on the (100) face [7-9]. The ratio of the dissolution rates, $v_{(110)}/v_{(100)}$, for a given undersaturation increases with the crystal lattice energy. Therefore, the transition to the diffusion-kinetic dissolution mechanism takes place at lower concentrations in the aqueous solutions used as solvents [31] when the lattice energy of the crystals is greatest. When the crystals are dissolved in doubly distilled water the anisotropy $v_{(110)}/v_{(100)}$ of the rate of dissolution increases with the lattice energy and with stirring rate of the solution.

In radiation chemistry and technology it is important to know the dissolution mechanisms of materials during and after irradiation. The damage to the structure of an irradiated crystal leads to an increased density of dissolution centres and to a higher rate of dissolution under certain conditions. The (100) and (110) faces, which contain ions of both kinds, were chosen for comparison: the (111) plane contains only ions of a single kind.

The interionic distance on the (110) face is greater than on the (100) face by a factor of $\sqrt{2}$, and the bond energy is accordingly lower. The density of defects is greater on faces with a lower bond energy. Because of its lower bond energy and higher defect concentration, the (110) face dissolves faster than the (100) face [56].

Because of the bond energy differences in the various crystal planes, in practice a crystal always breaks along a (100) cleavage plane, whose bond energy is lower than that of alternative planes. This is because the bond energy between ions in neighbouring (100) planes is decreased by the relatively large interplanar spacing. Irradiation of a crystal with soft X-rays, which are absorbed in a thin layer, increases the linear rate of dissolution of the (100) face without affecting the rate of dissolution of the more defective (110) face. For any given rate of arrival of the solvent flow at the surface undergoing dissolution, and for each crystal composition, we can define a limiting undersaturation σ_0 of the solvent. The linear rate of dissolution of a (100) crystal face is affected by irradiation only if the relative undersaturation is less than σ_0.

The value of σ_0 increases with lattice energy. To remain in the region of low dissolution rate, in which the rate is a function of the previous dose of radiation, the degree of undersaturation of the solvent must be lowered in proportion to the energy of the chemical bond [55].

These results justify the general conclusion that the linear rate of dissolution should be structure-sensitive at low dissolution rates and low undersaturations of the solvent [31].

Fig. 5 shows curves for the relative linear rate of dissolution of an irradiated (100) face (v_0/v_n, where v_n is the rate before irradiation) for various values of the relative undersaturation σ and for crystals of different chemical composition after irradiation with a dose of 10^5 rad of 8 keV X-rays. Irradiation and dissolution were both carried out at room temperature.

The largest increase in rate of dissolution is found in crystals with high lattice energy. This result agrees with the hypothesis that radiation-induced defects, which increase the rate of dissolution, are more permanently retained in the lattice of compounds with more stable chemical bonds [55].

The deviation from the general rule (of the ratio v_0/v_n increasing with lattice energy) shown by KI and KBr crystals at $\sigma \geq 0.006$ is ascribed to transition from the diffusion-kinetic dissolution regime to the diffusion-limited regime.

For each ion of a compound it is possible to select dissolution conditions and a solvent such that the parameters of the dissolution process (e.g. the rate of dissolution) are

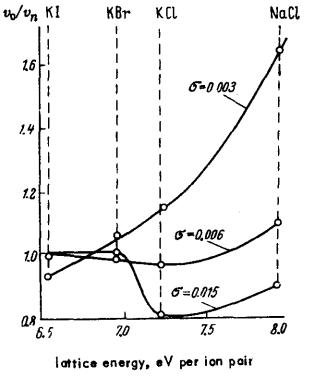


Fig. 5. Ratio of the linear dissolution rate v_0 of an irradiated (100) face to the rate of dissolution of a non-irradiated (100) face at different values of the relative undersaturation, σ, for crystals of different chemical composition after irradiation with 10^5 rad of 8 keV X-rays.

† Presumably the author means: The rate of dissolution *should be* lowest on the (110) face which has the *lower* density of ions compared with (100) but on the other hand the bonds between the ions on the (100) face are the strongest (Ed. of Translation).

sensitive to external interactions (e.g. to irradiation [55]). Thus, the linear rate of dissolution under specific conditions is a measure of the radiation stability of an ionic compound. Irradiation increases the density of defects in the material, loosens its structure, and increases the rate of dissolution. These effects are more marked in compounds of relatively high bond energy, since these can store radiation effects more successfully. High-energy compounds undergo changes in properties after irradiation because of the rapid annealing of radiation-induced defects. It can be assumed that the density of radiation defects will be greater in compounds with a lower bond energy, and that their properties will show relatively greater changes than those of compounds with a higher lattice energy.

Hence, it is important to investigate the dissolution mechanism and the characteristics of the process during irradiation of the solid to be dissolved.

The dependence of the time [sic], rate of melting, and rate of evaporation of a solid upon temperature is of scientific interest in the description of radiation damage (thermal spike), of the thermodynamics and theory of the solid state, and of the thermal decomposition of solids, etc.

The rate of thermal disintegration of a solid varies with experimental conditions, pressure, dose of radiation, and also with the structure of the solid (including structural defects).

The temperature dependence of the rate of evaporation v_{ev} of a solid in a vacuum is given by the expression

$$\log v_{ev} = A_1 - B_1/T, \quad (5)$$

where A_1 and B_1 are constants, and T (°K) is the evaporation temperature, or

$$v_{ev} = v_0 \exp(-E/RT)$$

where E is the heat of evaporation and R is the gas constant.

The temperature dependence of the vapour pressure P of metal oxides and of alkali metal halides is described by the approximate formula

$$\log P = A - \frac{B}{T} \quad (6)$$

where A and B are constants [57,58].

At higher temperatures the rate of evaporation increases, and the evaporation time τ decreases exponentially; the effect is analogous to an increase of stress during mechanical fracture.

The temperature dependence of the vapour pressure and the heats of evaporation of NaCl, KCl, KBr, and KI have been measured in the pressure range 10^{-1}–10^{-7} mmHg by the surface ionisation method. The heat of evaporation and the entropy were calculated from the results. The heat of evaporation and entropy for a temperature of 298° were also evaluated [58].

Fig. 6 shows graphs of $\log P = f(1/T)$. In the temperature range 1000–600°K the vapour pressure P (and therefore also the rate of evaporation) increase exponentially with specimen temperature.

The heat of evaporation of a substance and the entropy of solid compounds increase when the temperature is raised [59]. An increase of lattice energy also raises the heat of evaporation, lowers the entropy of the solid, and raises the entropy of the vapour. The vapour pressure and the rate

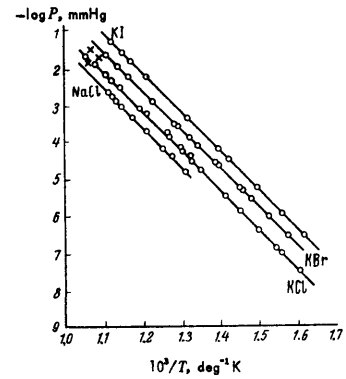


Fig. 6. Variation of $\log P$ with $1/T$. [57]

of evaporation of single crystals in a vacuum increase exponentially with temperature [59]. The evaporation coefficient, defined as the rate of evaporation from 1 cm² in 1 s divided by the rate of molecular collisions from the saturated vapour on 1 cm² in 1 s at the same temperature, is independent of temperature over a certain interval.

The higher the evaporation coefficient, the greater is the number of molecules evaporating from the surface and the weaker is the bond between particles.

At elevated temperatures the heat of evaporation decreases somewhat. Because of the different in the rates of evaporation from different crystal faces, stepped and mosaic structures are found after evaporation.

A similar behaviour is observed in tension: as the stress σ is increased, the heat of activation of the rupture process decreases according to the equation $U = U_0 - \gamma\sigma$, and the rate of tensile deformation increases exponentially [59].

The rate of evaporation of molybdenum and tungsten in a vacuum is increased by 80% or more on applying a field of 10^6 V cm^{-1}. The effect of strong electric fields (10^6 V cm^{-1}) on the rate of evaporation of the alkali metals is not yet known.

The evaporation of metals, oxides, and alkali metal halides in a vacuum and the mechanical failure of these materials show the same type of behaviour. As the driving force (temperature or tensile stress) increases, the rate of breakdown increases exponentially and the time of breakdown correspondingly decreases. Temperature increase lowers the heat of activation for evaporation and also the heat of activation of the process of failure in tension; the formation energy of the breakdown process decreases with increase of excess stress [59].

VI. SEMICONDUCTOR (ELECTRON–HOLE) PROPERTIES OF IONIC CRYSTALS AND THEIR CHEMICAL COMPOSITION

The electronic properties and other characteristics of crystals show a regular dependence on the lattice energy. The electronic properties can be discussed by treating the crystal as a system of interacting ions. We shall define the electronic levels in the isolated atoms by taking the energy of a free electron at rest in a vacuum as zero. The lowest unoccupied level of a free Na ion, corresponding to

the 3*s* state, is located below the zero level by an amount equal to the ionisation energy of 5.12 eV. The highest occupied level for the Cl^- ion is a 3*p* level, located below the vacuum level by an amount equal to the electron affinity of the Cl atom (4 eV).

Thus, the free 3*s* level lies below the occupied 3*p* level by 1.12 eV. As the free Na^+ and Cl^- ions are brought closer together, and the fraction of the chemical bond energy due to Coulombic interaction increases, the relative positions of the energy levels begin to change at a certain interionic distance, beyond which they become inverted. With further decrease of the interionic distance, the highest occupied 3*p* levels of the Cl^- ions are found to lie below the free 3*s* levels of Na^+.

When the distance between neighbouring ions reaches a value equal to the lattice parameter, by which time the wave functions of nearest ions of the same sign have begun to overlap, the discrete electronic levels of the atoms spread out into bands. The lattice parameter determines the band gap and the width of the bands. The levels corresponding to pairs of ions of the same kind overlap to form an energy band. The energy level diagram for electrons in crystals depends on the lattice parameter and on the energy spectrum of the lattice on the one hand, and on the electronic structure and levels of the atom on the other hand. For example, the lower (filled, or valence) band of an NaCl crystal is associated with the highest filled 3*p* levels of Cl^-, whilst the empty upper band of energy levels of the crystal corresponds to lowest unoccupied 3*s* levels of the Na^+ ions (Fig. 7).

The interaction between the atoms of a solid is reflected most strikingly by the energy conditions of the outer electrons of the atoms having the highest energy and exposed to the fields of neighbouring atoms situated at a distance a_0 apart.

The energy levels of the inner electrons for $r \leqslant a_0$ either do not split at all (1*s*) or split very slightly (2*s*). In this sense the crystal can be treated as a giant molecule, consisting of a large number of atoms and having the system of energy levels described above. The inner electrons of these atoms behave almost as though the atoms were isolated, whilst the outer electrons belong to the whole molecule-crystal. The energy of the electrons can lie within the regions shown hatched in Fig. 7 (the energy bands).

The valence electrons in atoms have several allowed levels, and therefore several bands of allowed electron energies are usually formed in crystals. The width of the forbidden energy gap is comparable to that of the allowed d bands. As the lattice energy decreases in Fig. 7, the width of the allowed energy bands increases and that of the forbidden gap decreases.

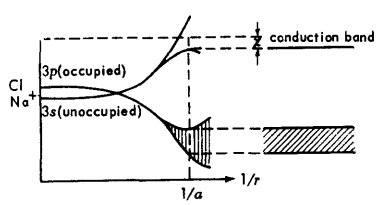


Fig. 7. Splitting of the different atomic levels under the influence of the field of neighbouring atoms.

The filling of the energy bands by electrons must satisfy Pauli's exclusion principle and at the same time minimise the energy of the system: hence, the lowest levels of the valence band are filled by electron pairs.

In real crystals the number of atoms, n, in 1 cm^3 is of the order of 10^{22}–10^{23}. The number of levels in each band must also be of the same order. The total width of the band is a few eV, and therefore the distance between adjacent levels is as low as $\sim 10^{-22}$ eV.

These effects give rise to some experimental observations interrelating the electron–hole transitions and properties in alkali metal halide crystals with the energetics of the ionic lattice in general, and with the chemical composition of a compound.

When the crystal lattice energy decreases, the width ΔE of the forbidden gap of electron energies also decreases, and the dielectric constant ϵ of the crystal increases. In alkali metal halides with *F*-centres the Mott relationship $\epsilon^{-2} \simeq \Delta E$, which was proposed for extrinsic semiconductors, is approximately obeyed.

The systematic increase of ϵ with decrease of lattice energy follows from the increasing polarisability of the anions on going from fluorides to iodides and of the cations on going from lithium to caesium, and also from the weakening of the Coulombic binding in the structure and from the increasing contribution of van der Waals interactions to the chemical bonding in these compounds. The dielectric properties and the stability deteriorate on going from lithium fluoride towards caesium iodide, as the ionic character of the chemical bond decreases.

The optical refractive index and the absorption coefficient over a wide range of radiation energies decrease as the lattice energy increases. The short-wave edge of the fundamental absorption and the maxima of the fundamental and additional absorptions in the infrared, visible, and ultraviolet regions of the spectrum for crystals activated by impurities are shifted towards shorter waves in this series of compounds by moving towards greater lattice energies whilst keeping the cation constant.

Some physical processes in crystals are not directly related to the lattice energy. For example, the scattering of phonons, photons, and high-energy particles at the atoms of which the crystal is composed. These processes are determined by the cross-section of the scattering centres, by the ionic radius, by the number of electrons, etc. As the radius of the ions in the compound increases the lattice energy decreases whilst photon, phonon, and particle scattering increases. Thus, a decrease in lattice energy is accompanied by enhanced absorption of radiation and of phonons, and by a decrease in the thermal conductivity and velocity of sound in the crystals.

This correlation allows us to extend to these properties the classification of the properties of ionic structures by means of a single parameter: the crystal lattice energy.

The properties of structures including other chemical bond types can likewise be classified in terms of a characteristic energy. Thus, in covalently bound semiconductors we note a correlation between various properties and the energy of atomisation or the heat of formation of the compound.

A classification of the properties of various glassy polymers can be based, as in the case of crystals, on the force binding together the structural units which give rise to the

polymer and into which the polymer breaks down when it decomposes. Increase of binding energy between the structural units of the glasses is accompanied by an increase in the temperature and heat of the glass transition, and of the thermal, mechanical, and chemical stability of the glass, as well as by a decrease in the loss angle and the electrical conductivity, and by a shift of the region of anomalous dispersion of the dielectric constant and of the losses towards higher temperatures.

The stability of solids towards radiation varies with chemical bond type. Chemical bonds can be placed in the following order of decreasing stability towards the action of ionising radiation: metallic, ionic, covalent, and (the least stable) molecular.

The available fund of experimental data allows us correctly to evaluate changes in the properties of compounds due to changes in chemical composition, and to arrive at a general picture of the rules which determine the influence of the chemical bond in a solid on the properties of the solid.

The classification of compounds on the basis of the chemical bond can give guidance in the search for new dielectrics and semiconductors, and in the determination of their properties. It may be less complicated to treat the properties of materials in terms of the chemical bond than to calculate them on the basis of band theory.

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