

Principle Types of Crystalline Binding

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Abstract: The property which holds a crystal together is crystal binding. In this paper inert gas, ionic crystal, covalent crystal and the factors influenced on this binding are studied. Moreover, characteristics feature of metallic binding, hydrogen bonds for H₂O molecules are investigated.

Key Words: Crystal, Cohesive Energy, Vander Waals Forces.

1. INTRODUCTION:

The attractive electrostatic interaction between the negative charges of the electron and the positive charges of the nuclei is entirely responsible for the cohesion of solids. Magnetic forces are negligible. Specialized terms categorize distinctive situation: exchange energy, Vander Waals forces, and covalent bonds.

Zero- point motion of the atoms is kinetic energy at absolute zero. It is a quantum effect that plays a dominant role in He³ and He⁴. They do not solidify at zero pressure even at absolute zero. The average fluctuation at 0°K of a He atom from its equilibrium positions of the order of 30 to 40 percent of the nearest- neighbor distance. The heavier the atom, the less important are zero- point effects. In the ground state of helium the zero- point motion of the atoms must be taken account.

2. CRYSTAL

Crystal is a particularly important form of solid. Many elements and compounds are crystalline, including the common semiconductors. In structure, a crystal is a highly ordered, three-dimensional grid which contains atoms at the intersections. The lines forms by the grid are lattice. The atoms lie in flat planes, and the plane are stacked to form the crystal. The crystal structure of the common semiconductors is based on one type of lattice: the cubic lattice.

The simplest form of cubic lattice is known as the simple- cubic (SC) crystal structure. The smallest group of atoms which represent the crystal is called a unit cell: when repeated throughout space (i.e. along all three dimensions) the unit cell replicates the whole of the crystal. There is one atom at each of the eight corners of the SC unit cell and each atom is shared between eight cells, so within the unit cell itself there is one-eighth of an atom at each of the eight corners. The simple- cubic unit cell therefore contains one atom.

There are two other types of cubic crystal: the body-centered cubic (BCC) crystal and the face-centered cubic (FCC) crystal. In the BCC structure, there is one atom at each of the eight corners and one atom in the center of the cube. In the FCC structure, there is one atom at each corner of the cell, plus one atom in the center of each of the six faces.

3. THE PRINCIPLE TYPES OF CRYSTALLINE BINDING

The observed differences between the forms of condensed matter are caused in the final analysis by differences in the distribution of the outermost electrons and the ion cores.

Neutral atoms with closed electron shells are bound together weakly by the Van der Waals forces associated with fluctuations in the charge distributions. Electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions are held together by attractive electrostatic forces between the positive and negative ions. The valence electrons are taken away from each alkali atom to form a communal electron sea in which the positive ions are dispersed. The neutral atoms appear to be bound together by the overlapping parts of their electrons distributions.

The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest at infinite separation, with the same electronic configuration. The term lattice energy is used in the discussion of ionic crystals and is defined as the energy that must be added to the crystal to separate its component ions into free ions at rest at infinite separation.

The inert gas crystals are weakly bound, with cohesive energies less than a few percent of the cohesive energies of the elements C, Si, Ge. The alkali metal crystals have intermediate values of the cohesive energy. The transition elements metals are quite strongly bound. The melting temperatures and bulk moduli vary roughly as the cohesive energies.

4. COHESIVE ENERGY

The cohesive energy of inert gas crystals at absolute zero and at zero pressure is

$$U_{\text{total}}(R) = 2 N \epsilon \left[(12.13) \left(\frac{\sigma}{R}\right)^2 - (14.45) \left(\frac{\sigma}{R}\right)^6 \right]$$

And at $R = R_0$

$$U_{\text{total}}(R) = -(2.15) (4 N \epsilon),$$

The same for all inert gases. This is the calculated cohesive energy when the atoms are at rest. Quantum-mechanical corrections act to reduce the binding by 28, 10, 6 and 4 percent of above equation for Ne, Ar, Kr and Xe respectively.

The heavier the atom, the smaller the quantum correction. We can understand, the origin of the quantum correction by consideration of a simple model in which an atom is confined by fixed boundaries. If the particle has the quantum wavelength λ , where λ is determined by the boundaries, then the particle has kinetic energy $\frac{p^2}{2M} = \left(\frac{h}{\lambda}\right)^2 / 2M$ with the de Broglie relation $p = \frac{h}{\lambda}$ for the connection between the momentum and the wavelength of a particle. On this model the quantum zero-point correction to the energy is inversely proportional to the mass.

One consequence of the quantum kinetic energy is that a crystal of the isotope Ne²⁰ is observed to have a larger lattice constant than a crystal of Ne²². The higher quantum kinetic energy of the lighter isotope expands the lattice, because the kinetic energy is reduced by expansion.

5. INERT GAS:

The inert gas from the simplest crystals. The electron distribution is very close to that of the free atoms. The crystals are transparent insulators, weakly bound, with low melting temperatures. The atoms have very high ionization energies. The outermost electron shells of the atoms are completely filled, and the distribution of electron charge in the free atom is spherically symmetric. In the crystal the inert gas atom pack together as closely as possible.

The electron distribution in the crystal cannot be significantly distorted from the electron distribution around the free electrons atoms, because the cohesive energy of an atom in the crystal is only 1 percent or less of the ionization energy of an atomic electron. Thus not much energy is available to distort the free atom charge distributions. Part of this distortion gives the Van der Waals interaction.

6. VAN DER WAALS INTERACTIONS:

Two identical inert gas atoms at a separation R large in comparison with the radii of the atoms will be considered. If the charge distributions on the atoms are rigid, the interaction between atoms would be zero, because the electrostatic potential of a spherical distribution of electronic charge is canceled outside a neutral atom by the electrostatic potential of the charge on the nucleus. Then the inert gas atoms could show no cohesion and could not condense. But the atoms induce moments in each other, and the induced moment causes an attractive interaction between the atoms.

As a model, we consider two identical linear harmonic oscillators 1 and 2 separated by R. Each oscillator bears charges $\pm e$ with separation x_1 and x_2 . The particles oscillate along the x- axis. Let P1 and P2 denote the momenta. The force constant is k. Then the Hamiltonian of the unperturbed system is

$$H_0 = \frac{1}{2m} P_1^2 + \frac{1}{2} K x_1^2 + \frac{1}{2m} P_2^2 + \frac{1}{2} K x_2^2 \text{-----(1)}$$

Let H_1 be the coulomb interaction energy of the two oscillators.

The internuclear coordinate is R.

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R_1+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2} \text{-----(2)}$$

In the approximation $|x_1|, |x_2| \ll R$ we expand equation (2) to obtain in lowest order.

$$H_1 \cong - \frac{2e^2 x_1 x_2}{R^3} \text{-----(3)}$$

$$x_s = \frac{1}{\sqrt{2}} (x_1 + x_2); x_a = \frac{1}{\sqrt{2}} (x_1 - x_2) \text{-----(4)}$$

Or on solving for x_1 and x_2 ,

$$x_1 = \frac{1}{\sqrt{2}} (x_s + x_a); x_2 = \frac{1}{\sqrt{2}} (x_s - x_a) \text{-----(5)}$$

The subscript 's' and 'a' denote symmetric and antisymmetric modes of motion.

Further, we have the momenta P_s, P_a associated with the two modes.

$$P_1 = \frac{1}{\sqrt{2}} (p_s + p_a); p_2 = \frac{1}{\sqrt{2}} (p_s - p_a) \text{-----(6)}$$

The total Hamiltonian $H_0 + H_1$ after the transformations (5) and (6) is

$$H = \left[\frac{1}{2m} p_s^2 + \frac{1}{2} \left(k - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{1}{2m} p_a^2 + \frac{1}{2} \left(k - \frac{2e^2}{R^3} \right) x_a^2 \right] \text{-----}(7)$$

to be

$$w = \left[\left(k \pm \frac{2e^2}{R^3} \right) / m \right]^{1/2} \cong w_0 \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{kR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{kR^3} \right)^2 + \dots \right] \text{--}(8)$$

with w_0 given by $(k/m)^{1/2}$

The zero point energy of the system is $\frac{1}{2} \hbar (w_s + w_a)$; because of the interaction the sum is lowered from the uncoupled value $2 \cdot \frac{1}{2} \hbar w_0$ by

$$\Delta U = \frac{1}{2} \hbar (w_s + w_a) = - \hbar w_0 \frac{1}{8} \left(\frac{2e^2}{kR^3} \right)^2 = - \frac{A}{R^6}$$

This attractive interaction varies as the minus sixth power of the separation of the two oscillators. This is called the Van der Waals interaction, also known as London interaction or induced dipole – dipole interaction.

It is the principle attractive interaction in crystals of inert gases and also in crystals of many organic molecules. The interaction is a quantum effect, in the sense that $\Delta U \rightarrow 0$

as $\hbar \rightarrow 0$. Thus the zero point energy of the system is lowered by the dipole=dipole coupling of equation (3). The van der Waals interaction does not depend for the existence on any overlap of the charge densities of the two atoms.

The approximate value of A for identical atom is given by $\hbar w_0 \alpha^2$, where $\hbar w_0$ is the energy of the strongest optical absorption line and α is the electronic polarizability.

7. THE EFFECT OF PAULI PRINCIPLE ON THE REPULSIVE ENERGY:

As the two atoms are brought together their charge distributions gradually overlap, thereby changing the electrostatic energy of the system. At sufficiently close separations the overlap energy is repulsive in large part because of the Pauli exclusion principle. The elementary statement of the principle is that two electrons cannot have all their quantum numbers equal. When the charge distributions of two atoms overlap, there is a tendency for electron from atom B to occupy in part states of a atom A already occupied by electrons of atom A and vice-versa. The Pauli principle prevents multiple occupancy, and electron distribution of atoms with close shells can overlap only if accompanied by the partial promotion of electron to unoccupied high energy states of atoms. Thus the electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction.

The inter particle interaction has the same qualitative form for a vast number of different atoms and molecules. There is an attractive interaction, which at large distances approaches the Van der Waals behavior, $1/R^2$. There is a minimum energy on the atomic scale followed by an abrupt increase in repulsion.

In an extreme example, two hydrogen atoms are pushed together until the protons are almost in contact. The energy of the electron system alone can be taken from observations on atomic He, which has two electrons. When the electrons have antiparallel spins, the Pauli principle has no effect and the electron are bound by -78.98 eV. When the spin are parallel, the Pauli principle forces the promotion of an electron from a $1s\uparrow$ orbital of He. The electrons now are bound by -59.38eV, less than antiparallel spin by 19.60eV. This is amount by which the Pauli principle has increased the repulsion.

8. IONIC CRYSTAL:

Ionic Crystal are made up of positive and negative ions. The ionic bond results from the electrostatic interaction of oppositely charged ions.

The electronic configurations of all ions of a simple ionic crystal correspond to closed electronic shells, as in the inert gas atoms. In lithium fluoride the configuration of the neutral atoms are Li: $1s^2 2s^1$, F: $1s^2 2s^2 2p^5$. the singly charged ions have the configurations Li^+ : $1s^2$, F^- : $1s^2 2s^2 2p^6$, as for helium and neon, respectively. Inert gas atoms have closed shells, and the charge distributions are spherically symmetric. The charge distributions on each ion in an ionic crystal will have approximately spherical symmetry, with some distortion near the region of contact with neighbouring atoms.

A quick estimate suggest that we are not misguided in looking to electrostatic interactions for a large part of the binding energy of an ionic crystal. The distance between a positive ion and the nearest negative ion in crystalline sodium chloride is 2.81×10^{-8} cm, and the attractive coulomb part of the potential energy of the two ions by themselves is 5.1eV.

9. COVALENT BOND:

The covalent bond is the classical electron pair. It is a strong bond. It is a strong bond: the bond between two carbon atoms in diamond with respect to separated neutral atoms is comparable with the bond strength in ionic crystals. The covalent bond has strong directional properties. Thus, carbon, silicon, and germanium have the diamond structure, with atoms joined to four nearest neighbours at tetrahedral angles, even through the arrangement gives a low filling of space, 0.34 of the available space, compared with 0.74 for a close-packed structure, The tetrahedral bond allows only

four nearest neighbours, whereas a close-packed structure has 12. Carbon gives biology, but silicon gives geology and semiconductor technology.

The covalent bond is usually formed two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. The spins of the two electrons in the bond are antiparallel.

10. CHARACTERISTICS FEATURE OF METALIC BINDING:

Metals are characterized by high electrical conductivity, and a large number of electrons in a metal are free to move about, usually one or two per atom. The electron available to move about are called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal.

In some metals the interaction of the ion cores with the conduction electrons always makes a large contribution to the binding energy but the characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.

The binding energy of an alkali metal crystal is considerably less than that of an alkali halide crystal; the bond formed by a conduction electron is not very strong. The interatomic distances are relatively large in the alkali metals because the kinetic energy of the conduction electrons is lower at large interatomic distances. This leads to weak binding. Metals tend to crystallize in relatively close packed structure: hcp, fcc, bcc, and some other closely related structures, and not in loosely-packed structures such as diamond.

In the transition metals there is additional binding from inner electron shells. Transition metal and the metals immediately following them have large d-electron shells and are characterized by high binding energy.

11. HYDROGEN BOND:

It should form a covalent bond with only one other atom because neutral hydrogen has only one electron. It is known, however that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, thus forming a hydrogen bond between them, with a bond energy of the order of 0.1 eV. It is believed that the hydrogen bond is largely ionic in character, being formed only between the most electronegative atoms, particularly F, O and N. In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond. The atoms adjacent to the proton are so close more than two of them would get in each other's way; thus the hydrogen bond connects only two atoms. The hydrogen bond is an important part of the interaction between H₂O molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. It is important in certain ferroelectric crystals.

12. CONCLUSION:

Crystal of inert gas atoms are bound by the Van der Waals interaction (induced dipole- dipole interaction), and this varies with distance as $1/R^2$.

The repulsive interaction between atoms arises generally from the electrostatic repulsion of overlapping charge distributions and the Pauli principle which compels overlapping electrons of parallel spin to enter orbitals of higher energy. Ionic crystals are bound by the electrostatic attraction of charged ions of opposite sign. The electrostatic energy of a structure of $2N$ ions of charge $\pm q$ is

$$(CGS) \quad U = -N_{\alpha} \frac{q^2}{R} = -N \sum \frac{\pm q^2}{r_q}$$

where, α is the Madelung constant and R is the distance between nearest neighbours.

Metal are bound by the reduction in the kinetic energy of the valence electrons in the metal as compared with the free atom.

A covalent bond is characterized by the overlap of charge distributions of antiparallel electron spin. The Pauli contribution to the repulsion is reduced for antiparallel spins, and this makes possible a greater degree of overlap. The overlapping electrons bind their associated ion cores by electrostatic attraction

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