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Crystal structure of ionic compounds

Ions in ionic crystals are bound together by electrostatic attraction. Describe how ions form ionic crystals. Key Takeaways Key Points Ions bound together by electrostatic attraction form ionic crystals. Their arrangement varies depending on the ions’ sizes or the radius ratio (the ratio of the radii of the positive to the negative ion). A simple cubic crystal lattice has ions equally spaced in 3D at 90° angles. Stability of ionic solids depends on lattice energy, which is released in the form of heat when two ions are brought together to form a solid. Lattice energy is the sum of all the interactions within the crystal. The properties of ionic crystals reflect the strong interactions that exist between the ions. They are very poor conductors of electricity, have strong absorption of infrared radiation, and are easily cleaved. These solids tend to be quite hard and have high melting points. Key Terms lattice energy: The energy required to separate the ions of an ionic solid (especially a crystal) to an infinite distance apart. crystal lattice: A regular three-dimensional geometric arrangement of atoms, molecules, or ions in a crystal. ionic crystal: A class of crystal consisting of a lattice of ions held together by electrostatic interactions; they exhibit strong absorption of infrared radiation and have planes along which they cleave easily. An ionic crystal consists of ions bound together by electrostatic attraction. The arrangement of ions in a regular, geometric structure is called a crystal lattice. Examples of such crystals are the alkali halides, which include: potassium fluoride (KF) potassium chloride (KCl) potassium bromide (KBr) potassium iodide (KI) sodium fluoride (NaF) other combinations of sodium, cesium, rubidium, or lithium ions with fluoride, bromide, chloride or iodide ions These solids tend to be quite hard and have high melting points, reflecting the strong forces between oppositely-charged ions. The exact arrangement of ions in a lattice varies according to the size of the ions in the crystal. A Case Study: NaCl The properties of NaCl reflect the strong interactions that exist between the ions. It is a good conductor of electricity when molten (melted state), but very poor in the solid state. When melted, the mobile ions carry charge through the liquid. NaCl crystals are characterized by strong absorption of infrared (IR) radiation, and have planes along which they cleave easily. Structurally, each ion in sodium chloride is surrounded by six neighboring ions of opposite charge. The resulting crystal lattice is of a type known as “simple cubic,” meaning that the lattice points are equally spaced in all three dimensions and all cell angles are 90°. NaCl crystal structure: Spheres represent the Na+ and Cl- ions. Each ion is surrounded by six other ions of opposite charge, therefore NaCl is described as having (6,6) coordination. How can one sodium ion surrounded by six chloride ions (or vice versa) be consistent with the simplest (empirical) formula NaCl? The answer is that each of those six chloride ions sits at the center of its own octahedron, whose vertices are defined by six neighboring sodium ions. This might seem to correspond to Na6Cl6, but note that the central sodium ion shown in the diagram can claim only a one-sixth share of each of its chloride ion neighbors. Therefore, the formula NaCl is not just the simplest formula, but correctly reflects the 1:1 stoichiometry of the compound. As in all ionic structures, there are no distinguishable “molecular” units that correspond to the NaCl simplest formula. Sodium chloride, like virtually all salts, is a more energetically favored configuration of sodium and chlorine than the elements individually. Halite: Halite, or rock salt, is the mineral form of sodium chloride. Halite forms cubic crystals. It occurs in evaporite minerals that result from the drying up of enclosed lakes and seas. This picture was taken in Wieliczka, Poland, one of the world's oldest salt mines. Energy of Formation of Ionic Salts Since ionic salts have a lower energetic configuration than their individual elements, reactions forming ionic solids tend to release energy. For example, when sodium and chlorine react to form sodium chloride: $\text{Na(s)} + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl(s)} + 404 \text{ kJ}$ The release of 404 kJ of energy shows that the formation of solid sodium chloride is exothermic. Due to the Second Law of Thermodynamics, the released energy spreads out into the environment and is therefore unavailable to drive the reverse reaction. This irreversibility is the main reason that sodium chloride is more stable than its component elements. Lattice Energy When sodium and chloride ions react to form NaCl, 787 kJ/mol of energy is released: $\text{Na+(g)} + \text{Cl-(g)} \rightarrow \text{NaCl(s)} + 787 \text{ kJ}$ This large magnitude arises from the strength of the coulombic force between ions of opposite charge. This energy is one definition of lattice energy: the energy released when an ionic solid is formed from gaseous ions binding together. Note that the actual value of enthalpy change (ΔHo) is negative (- 787 kJ/mol). The exothermicity of such reactions results in the stability of ionic solids. That is, energy is needed to break apart the ionic solid into its constituent elements. (This is not to be confused with dissociation of a compound’s ions in solution. That is a different process.) This endothermic reaction gives rise to the other definition of lattice energy: the energy that must be expended to break up an ionic solid into gaseous ions. Lattice energy, while due mainly to coulombic attraction between each ion and its nearest neighbors (six in the case of NaCl) is really the sum of all the interactions within the crystal. Lattice energies cannot be measured directly, but they can be estimated from the energies of other processes. Close-packed Structures The most energetically stable arrangement of solids made up of identical molecular units are generally those in which there is a minimum of empty space. These are known as close-packed structures, and there are several kinds of them. In ionic solids of even the simplest 1:1 stoichiometry, the positive and negative ions usually differ so much in size that packing is often much less efficient. This may cause the solid to assume lattice geometries that differ from the one illustrated above for NaCl. Consider the structure of cesium chloride, CsCl. The radius of the Cs+ ion is 168 pm (compared to 98 pm for Na+), and cannot possibly fit into the octahedral hole of a simple cubic lattice of chloride ions (181 pm ionic radius). The CsCl lattice therefore assumes a different arrangement. CsCl structure: In CsCl, metal ions are shifted into the center of each cubic element of the Cl–ion lattice. Each cesium ion has eight nearest-neighbor chloride ions, while each chloride ion is also surrounded by eight cesium ions in (8,8) coordination. The two kinds of lattice arrangements exemplified by NaCl and CsCl are found in a large number of other 1:1 ionic solids, and these names are used generically to describe the structures of these other compounds. There are many other fundamental lattice arrangements (not all cubic), but the two described here are sufficient to illustrate the point that the radius ratio (the ratio of the radii of the positive to the negative ion) plays an important role in the structures of simple ionic solids. Atoms in covalent solids are covalently bonded with their neighbors, creating, in effect, one giant molecule. Discuss the properties of covalent crystals or network solids Key Takeaways Key Points Covalent (or network) solids are extended- lattice compounds, in which each atom is covalently bonded to its nearest neighbors. Because there are no delocalized electrons, covalent solids do not conduct electricity. The rearranging or breaking of covalent bonds requires large amounts of energy; therefore, covalent solids have high melting points. Covalent bonds are extremely strong, so covalent solids are very hard. Generally, covalent solids are insoluble due to the difficulty of solvating very large molecules. Diamond is the hardest material known, while cubic boron nitride (BN) is the second-hardest. Silicon carbide (SiC) is very structurally complex and has at least 70 crystalline forms. Key Terms covalent network solid: A solid formed when the atoms are bonded covalently in a continuous, extended network. covalent bond: A type of chemical bond where two atoms are connected to each other by the sharing of two or more electrons. diamond: a glimmering glass-like mineral that is an allotrope of carbon, in which each carbon atom is bonded to four others with a tetrahedral geometry. carbide: A compound composed of carbon and a less electronegative element. allotrope: A different form of an element. In graphite the carbons bond with each other in the trigonal planar arrangement. This difference accounts for the drastically different appearance and properties of these two forms of carbon. Diamond is also an allotrope of carbon. Diamond is the hardest material known, defining the upper end of the 1-10 scale known as Moh’s hardness scale. Diamond cannot be melted; above 1700 °C it is converted to graphite, the more stable form of carbon. The diamond unit cell is face-centered cubic and contains eight carbon atoms. Other Examples Boron nitride (BN) is similar to carbon because it exists as a diamond-like cubic polymorph as well as in a hexagonal form similar to graphite. Hexagonal boron nitride: Hexagonal boron nitride, a two-dimensional material, is similar in structure to graphite. Cubic boron nitride is the second-hardest material after diamond, and it is used in industrial abrasives and cutting tools. Cubic boron nitride: Cubic boron nitride adopts a crystal structure, which can be constructed by replacing every two carbon atoms in diamond with one boron atom and one nitrogen atom. Cubic boron nitride is the second-hardest material, after diamond. Recent interest in boron nitride has centered on its carbon-like ability to form nanotubes and related nanostructures. Silicon carbide (SiC) is also known as carborundum. Its structure is very much like that of diamond, with every other carbon replaced by silicon. Silicon carbide exists in about 250 crystalline forms. It is used mostly in its synthetic form because it is extremely rare in nature. It is found in a certain type of meteorite that is thought to originate outside of our solar system. The first light-emitting diodes (LEDs) used in high-efficiency lighting were based on SiC. When heated at atmospheric pressure, it decomposes at 2700 °C, but it has never been observed to melt. Structurally, silicon carbide is very complex; at least 70 crystalline forms have been identified. Its extreme hardness and ease of synthesis have led to a diversity of applications – in cutting tools and abrasives, high-temperature semiconductors and other high-temperature applications, the manufacturing of specialty steels and jewelry, and many more. Tungsten carbide (WC) is probably the most widely encountered covalent solid, owing to its use in carbide cutting tools and as the material used to make the rotating balls in ball-point pens. It has a high melting point (2870 °C) and a structure similar to that of diamond, although it is slightly less hard. In many of its applications, it is embedded in a softer matrix of cobalt or coated with titanium compounds. Silicon Carbide: Silicon carbide is an extremely rare mineral, and in nature is is mostly found in a certain type of meteorite. Molecules held together by van der Waals forces form molecular solids. Discuss the properties of molecular crystals. Key Takeaways Key Points A molecular solid is composed of molecules held together by van der Waals forces. Its properties are dictated by the weak nature of these intermolecular forces. Molecular solids are soft, often volatile, have low melting temperatures, and are electrical insulators. Classes of molecular solids include organic compounds composed of carbon and hydrogen, fullerenes, halogens (F, Cl, etc.), chalcogens (O, S, etc.), and pnictogens (N, P, etc.). Larger molecules are less volatile and have higher melting points because their dispersion forces increase with the larger number of atoms. Decrease in binding of outer electrons to the nucleus also increases van der Waals-type interactions of the atom due to its increased polarisability. Key Terms intermolecular force: Any of the attractive interactions that occur between atoms or molecules in a sample of a substance. Van der Waals force: Attractive forces between molecules (or between parts of the same molecule). These include interactions between partial charges (hydrogen bonds and dipole-dipole interactions), and weaker London dispersion forces. molecular solid: A solid composed of molecules held together by van der Waals intermolecular forces. doping: Intentionally introducing impurities into a sample of a substance in order to change its electrical properties. Recall that a molecule is defined as a discrete aggregate of atoms bound together sufficiently tightly by directed covalent forces to allow it to retain its individuality when the substance is dissolved, melted, or vaporized. The two words italicized in the preceding sentence are important. Covalent bonding implies that the forces acting between atoms within the molecule (intramolecular) are much stronger than those acting between molecules (intermolecular). The directional property of covalent bonding gives each molecule a distinctive shape which affects a number of its properties. Liquids and solids composed of molecules are held together by van der Waals (or intermolecular) forces, and many of their properties reflect this weak binding. Molecular solids tend to be soft or deformable, have low melting points, and are often sufficiently volatile to evaporate directly into the gas phase. This latter property often gives such solids a distinctive odor. Whereas the characteristic melting point of metals and ionic solids is ~ 1000 °C, most molecular solids melt well below ~300 °C. Thus, many corresponding substances are either liquid (water) or gaseous (oxygen) at room temperature. Molecular solids also have relatively low density and hardness. The elements involved are light, and the intermolecular bonds are relatively long and are therefore weak. Because of the charge neutrality of the constituent molecules, and because of the long distance between them, molecular solids are electrical insulators. Because dispersion forces and the other van der Waals forces increase with the number of atoms, large molecules are generally less volatile, and have higher melting points than smaller ones. Also, as one moves down a column in the periodic table, the outer electrons are more loosely bound to the nucleus, increasing the polarisability of the atom, and thus its propensity to van der Waals-type interactions. This effect is particularly apparent in the increase in boiling points of the successively heavier noble gas elements. Interactive: Charged and Neutral Atoms: There are two kinds of attractive forces shown in this model: Coulomb forces (the attraction between ions) and Van der Waals forces (an additional attractive force between all atoms). What kinds of patterns tend to form with charged and neutral atoms? How does changing the Van der Waals attraction or charging the atoms affect the melting and boiling point of the substance? Case Study: Phosphorus The term “molecular solid” may refer not to a certain chemical composition, but to a specific form of a material. For example, solid phosphorus can crystallize in different allotropes called “white”, “red” and “black” phosphorus. White phosphorus forms molecular crystals composed of tetrahedral P4 molecules. A molecular solid, white phosphorus has a relatively low density of 1.82 g/cm3 and melting point of 44.1 °C; it is a soft material which can be cut with a knife. Heating at ambient pressure to 250 °C or exposing to sunlight converts white phosphorus to red phosphorus, in which the P4 tetrahedra are no longer isolated, but are connected by covalent bonds into polymer-like chains. Heating white phosphorus under high (GPa) pressures converts it to black phosphorus, which has a layered, graphite-like structure. When white phosphorus is converted to the covalent red phosphorus, the density increases to 2.2–2.4 g/cm3 and melting point to 590 °C; when white phosphorus is transformed into the (also covalent) black phosphorus, the density becomes 2.69–3.8 g/cm3 with a melting temperature ~200 °C. Both red and black phosphorus forms are significantly harder than white phosphorus. Although white phosphorus is an insulator, the black allotrope, which consists of layers extending over the whole crystal, does conduct electricity. The structural transitions in phosphorus are reversible: upon releasing high pressure, black phosphorus gradually converts into the red allotrope, and by vaporizing red phosphorus at 490 °C in an inert atmosphere and condensing the vapor, covalent red phosphorus can be transformed back into the white molecular solid. Similarly, yellow arsenic is a molecular solid composed of As4 units; it is metastable and gradually transforms into gray arsenic upon heating or illumination. Certain forms of sulfur and selenium are each composed of S8 or Se8 units, and are molecular solids at ambient conditions. However, they can convert into covalent allotropes having atomic chains extending all through the crystal. Classes of Molecular Solids The vast majority of molecular solids can be attributed to organic compounds containing carbon and hydrogen, such as hydrocarbons (CnHm). Spherical molecules consisting of different number of carbon atoms, called fullerenes, are another important class. Less numerous, yet distinctive molecular solids are halogens (e.g., Cl2) and their compounds with hydrogen (e.g., HCl), as well as light chalcogens (e.g., O2) and pnictogens (e.g., N2). Conductivity of molecular solids can be induced by “doping” fullerenes (e.g., C60). Its solid form is an insulator because all valence electrons of carbon atoms are involved into the covalent bonds within the individual carbon molecules. However, inserting (intercalating) alkali metal atoms between the fullerene molecules provides extra electrons, which can be easily ionized from the metal atoms and make the material conductive, and even superconductive. Fullerene Crystals. Fullerene solid is an insulator, but it can become a superconductor when intercalating metal ions are inserted between the fullerene molecules (C60). Metallic crystals are held together by metallic bonds, electrostatic interactions between cations and delocalized electrons. Describe metallic crystals. Key Takeaways Key Points Atoms in metals lose electrons to form cations. Delocalized electrons surround the ions. Metallic bonds (electrostatic interactions between the ions and the electron cloud) hold the metallic solid together. Atoms are arranged like closely packed spheres. Because outer electrons of metal atoms are delocalized and highly mobile, metals have electrical and thermal conductivity. The free electron model can be used to calculate electrical conductivity as well as the electrons’ contribution to the heat capacity and heat conductivity of metals. Metals are ductile, or capable of plastic deformation. Hooke’s law describes reversible elastic deformation in metals, in which the stress is linearly proportional to the strain. Forces larger than the elastic limit, or heat, may cause an irreversible deformation of the object. In general, metals are denser than nonmetals. This is due to the tightly packed crystal lattice of the metallic structure. The larger the amounts of delocalized electrons, the stronger the metallic bonds are. Key Terms metallic bond: A chemical bond in which mobile electrons are shared over many nuclei; this leads to electrical conduction. metal: Any of a number of chemical elements in the periodic table that form a metallic bond with other metal atoms. It is generally shiny, malleable, and a conductor of heat and electricity. In a metal, atoms readily lose electrons to form positive ions (cations). These ions are surrounded by delocalized electrons, which are responsible for conductivity. The solid produced is held together by electrostatic interactions between the ions and the electron cloud. These interactions are called metallic bonds. Metallic bonding accounts for many physical properties of metals, such as strength, malleability, ductility, thermal and electrical conductivity, opacity, and luster. Metallic Bonding: Loosely bound and mobile electrons surround the positive nuclei of metal atoms. Understood as the sharing of “free” electrons among a lattice of positively charged ions (cations), metallic bonding is sometimes compared to the bonding of molten salts; however, this simplistic view holds true for very few metals. In a quantum-mechanical view, the conducting electrons spread their density equally over all atoms that function as neutral (non-charged) entities. Atoms in metals are arranged like closely-packed spheres, and two packing patterns are particularly common: body-centered cubic, wherein each metal is surrounded by eight equivalent metals, and face-centered cubic, in which the metals are surrounded by six neighboring atoms. Several metals adopt both structures, depending on the temperature. Metals in general have high electrical conductivity, high thermal conductivity, and high density. They typically are deformable (malleable) under stress, without cleaving. Some metals (the alkali and alkaline earth metals) have low density, low hardness, and low melting points. In terms of optical properties, metals are opaque, shiny, and lustrous. Melting Point and Strength The strength of a metal derives from the electrostatic attraction between the lattice of positive ions and the “sea” of valence electrons in which they are immersed. The larger the nuclear charge (atomic number) of the atomic nucleus, and the smaller the atom’s size, the greater this attraction. In general, the transition metals with their valence-level d electrons are stronger and have higher melting points: Fe, 1539°C Re, 3180 °C Os, 2727 °C W, 3380°C. The majority of metals have higher densities than the majority of nonmetals. Nonetheless, there is wide variation in the densities of metals. Lithium (Li) is the least dense solid element, and osmium (Os) is the densest. The metals of groups IA and IIA are referred to as the light metals because they are exceptions to this generalization. The high density of most metals is due to the tightly packed crystal lattice of the metallic structure. Electrical Conductivity: Why Are Metals Good Conductors? In order for a substance to conduct electricity, it must contain charged particles (charge carriers) that are sufficiently mobile to move in response to an applied electric field. In the case of ionic compounds in water solutions, the ions themselves serve this function. The same thing holds true of ionic compounds when melted. Ionic solids contain the same charge carriers, but because they are fixed in place, these solids are insulators. In metals, the charge carriers are the electrons, and because they move freely through the lattice, metals are highly conductive. The very low mass and inertia of the electrons allows them to conduct high-frequency alternating currents, something that electrolytic solutions cannot do. Electrical conductivity, as well as the electrons’ contribution to the heat capacity and heat conductivity of metals, can be calculated from the free electron model, which does not take the detailed structure of the ion lattice into account. Mechanical properties Mechanical properties of metals include malleability and ductility, meaning the capacity for plastic deformation. Reversible elastic deformation in metals can be described by Hooke’s Law for restoring forces, in which the stress is linearly proportional to the strain. Applied heat, or forces larger than the elastic limit, may cause an irreversible deformation of the object, known as plastic deformation or plasticity. Metallic solids are known and valued for these qualities, which derive from the non-directional nature of the attractions between the atomic nuclei and the sea of electrons. The bonding within ionic or covalent solids may be stronger, but it is also directional, making these solids brittle and subject to fracture when struck with a hammer, for example. A metal, by contrast, is more likely to be simply deformed or dented. Although metals are black due to their ability to absorb all wavelengths equally, gold (Au) has a distinctive color. According to the theory of special relativity, increased mass of inner-shell electrons that have very high momentum causes orbitals to contract. Because outer electrons are less affected, blue-light absorption is increased, resulting in enhanced reflection of yellow and red light. Gold: Gold is a noble metal; it is resistant to corrosion and oxidation.

what type of crystal structure do ionic compounds form. which property results from the crystal lattice structure of ionic compounds. the crystal lattice structure of ionic compounds is responsible for. crystal structure of metals vs ionic compounds. crystal structure of some ionic compounds. what is the structure of ionic compounds

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