

12.7: Types of Crystalline Solids

Learning Objectives

- Identify different types of solid substances.

As a society, we sometimes take things for granted. For example, it is often assumed that we will get electric power when we connect a plug to an electrical outlet. The wire that comprises that outlet is almost always copper, a material that conducts electricity well. The unique properties of the solid copper allow electrons to flow freely through the wire and into whatever device we connect it to. Then we can enjoy music, television, computer work, or whatever other activity we want to undertake. However, these activities—and the miracle of electricity itself—would not be possible without that copper wire!

Classes of Crystalline Solids

Crystalline substances can be described by the types of particles in them and the types of chemical bonding that take place between the particles. There are four types of crystals: (1) **ionic**, (2) **metallic**, (3) **covalent network**, and (4) **molecular**. Properties and several examples of each type are listed in the following table and are described in the table below.

Table 12.7.1: Crystalline Solids: Melting and Boiling Points

Type of Crystalline Solid	Examples (formulas)	Melting Point (°C)	Normal Boiling Point (°C)
Ionic	NaCl	801	1413
	CaF ₂	1418	1533
Metallic	Hg	-39	630
	Na	371	883
	Au	1064	2856
	W	3410	5660
Covalent Network	B	2076	3927
	C (diamond)	3500	3930
	SiO ₂	1600	2230
Molecular	H ₂	-259	-253
	I ₂	114	184
	NH ₃	-78	-33
	H ₂ O	0	100

Ionic crystals - The ionic crystal structure consists of alternating positively-charged cations and negatively-charged anions (see figure below). The ions may either be monatomic or polyatomic. Generally, ionic crystals form from a combination of Group 1 or 2 metals and Group 16 or 17 nonmetals or nonmetallic polyatomic ions. Ionic crystals are hard and brittle and have high melting points. Ionic compounds do not conduct electricity as solids, but do conduct electricity when molten or in aqueous solution.

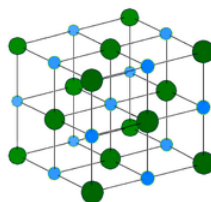


Figure 12.7.1: NaCl crystal.

Metallic crystal - Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons (see figure below). These electrons, also referred to as delocalized electrons, do not belong to any one atom, but are capable of moving through the

entire crystal. As a result, metals are good conductors of electricity. As seen in the table above, the melting points of metallic crystals span a wide range.

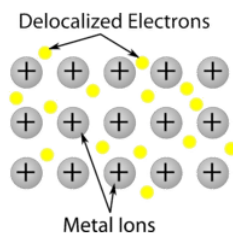


Figure 12.7.2: Metallic crystal lattice with free electrons able to move among positive metal atoms.

Covalent network crystals - A covalent network crystal consists of atoms at the lattice points of the crystal, with each atom being covalently bonded to its nearest neighbor atoms (see figure below). The covalently bonded network is three-dimensional and contains a very large number of atoms. Network solids include diamond, quartz, many metalloids, and oxides of transition metals and metalloids. Network solids are hard and brittle, with extremely high melting and boiling points. Being composed of atoms rather than ions, they do not conduct electricity in any state.

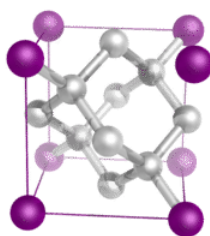


Figure 12.7.3: Diamond is a network solid and consists of carbon atoms covalently bonded to one another in a repeating three-dimensional pattern. Each carbon atom makes for single covalent bonds in a tetrahedral geometry.

Molecular crystals - Molecular crystals typically consist of molecules at the lattice points of the crystal, held together by relatively weak intermolecular forces (see figure below). The intermolecular forces may be dispersion forces in the case of nonpolar crystals, or dipole-dipole forces in the case of polar crystals. Some molecular crystals, such as ice, have molecules held together by hydrogen bonds. When one of the noble gases is cooled and solidified, the lattice points are individual atoms rather than molecules. In all cases, the intermolecular forces holding the particles together are far weaker than either ionic or covalent bonds. As a result, the melting and boiling points of molecular crystals are much lower. Lacking ions or free electrons, molecular crystals are poor electrical conductors.

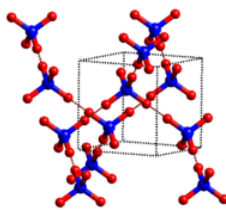


Figure 12.7.4: Ice crystal structure.

Some general properties of the four major classes of solids are summarized in Table 12.7.2

Table 12.7.2: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.			

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous
*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.			

✓ Example 12.7.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

- Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
- Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

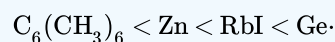
A. **Germanium** lies in the p block just under Si, along the diagonal line of semi-metallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a **covalent solid**.

RbI contains a metal from group 1 and a nonmetal from group 17, so it is **an ionic solid** containing Rb^+ and I^- ions.

The compound $C_6(CH_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form **a molecular solid** with no covalent bonds between them.

Zn is a d-block element, so it is **a metallic solid**.

B. Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is

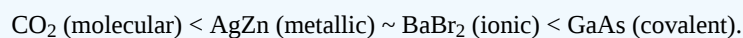


The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

? Exercise 12.7.1

Classify CO_2 , $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer



The actual melting points are: CO_2 , about -15.6°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

- Ionic crystals are composed of alternating positive and negative ions.
- Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons.
- Covalent crystals are composed of atoms which are covalently bonded to one another.
- Molecular crystals are held together by weak intermolecular forces.

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