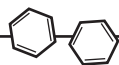


Summary Chart: Classification of Solid (Crystal) Structures

Type	Bonding Units	Bonding Strength	Factors	Examples
1. Atomic or Molecular Crystals	Neutral atoms or molecules (non-metallic elements)	Very Weak (Van der Waals) moderate to strong London Dispersion Forces	<ul style="list-style-type: none"> – surface area – Number of valence electrons – Symmetry – Polarity – "Hydrogen-bonding" (highest type of polarity) 	Ar, Kr, I ₂ C ₆ H ₁₂ O ₆ (sugar) H ₂ O
2. Metallic Crystals	Metal Atoms	moderate to strong "Delocalized Sea" of valence electrons surrounding + ions (kernels) – Bands aka Conduction Bands	<ul style="list-style-type: none"> – Ss size increases, down the Per. Chart, density of sea of e- decreases – Number of valence electrons 	Zn, U Pb, Fe Au, Na, Al,
3. Ionic Crystals	positive and negative ions Metals + Non-metals	Strong ionic bonds - arise from electrostatic attractions (opposite charges attract)	$F = k \cdot \frac{q_1 \times q_2}{d^2}$ → charges → distance between ions (nuclei)	NaCl, KBr, BaO, NiS etc.
4. Covalent Crystals	Atoms of C, Si, or Ge	Very strong Covalent bonds between atoms	<ol style="list-style-type: none"> 1. Network covalent or 2. planar covalent. structures 3. radius of atoms (as bond length increases, bond strength decreases) 	Carbon (graphite) Carbon (diamond) Quartz, mica. (Si) Sand (SiO ₂)

A. If one focuses on **Molecular crystals** (consisting of non-metallic atoms) first, one observes trends in their melting and subsequent boiling points related to their molecular size, molecular shape and polarity, as well as to the number of outer (valence) electrons on the molecule's surface (Please refer to their inclusion in the above chart.) In general, the attractions between neutral molecules increases as the size (surface area) increases. The amount of the molecular surface in "touch" with an adjacent molecule increases attractions to the surface electrons on the **adjacent** molecules. In addition, the more symmetrical the molecules, the closer together they can pack in to one another, and again, attractions between **adjacent** molecules' surfaces increases. The more outer (valence) electrons on the surface, the stronger the attractions tend to be. Polar molecules, by their very label, have positive and negative "poles" of charge on the molecule; the electron distribution is NOT symmetrical. Strong attractions result between these positive and negative regions of these molecules (dipole-dipole attractions). The stronger these attractions, the more energy that is required

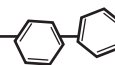


to separate these molecules into liquid phase and the higher the melting points. The same reasoning can be applied to the liquid molecules becoming independent gas molecules and their subsequent boiling points.

In polar molecules containing the highly electronegative atoms of fluorine, oxygen or nitrogen (and occasionally chlorine, in terminal positions on the molecule) the electronegativity differences may result in “hydrogen bonding.” This is the additional attraction of H atoms of one molecule to the F, O, or N (and occasionally Cl, in terminal positions) atoms on an adjacent molecule. “Hydrogen bonding” accounts for the fact that even though H_2S has the same shape and is a larger molecule than H_2O , the attractions between H_2O molecules are **MUCH** stronger, so much so that, at room temperature, water is a liquid with stronger inter-molecular attractions and a significantly higher boiling point, and that H_2S is a gas, indicating weaker inter-molecular attractions. “Hydrogen bonding” also accounts for water expanding as it freezes, instead of shrinking, (as metals most frequently do), as the water molecules align into crystals and occupy a larger volume, taking into account this additional “bond” between molecules in all three dimensions. Hence we can usually successfully predict (a favorite “science practice”) that molecules that include “hydrogen bonds” will typically have higher melting points and boiling points than similar molecules without these additional H-bonds.

B. If we investigate **Metallic crystals** next, we find correlations of properties here as well. The attractions between metallic atoms arise from the low ionization energies we typically observe in metals, which can give way to “delocalized” valence electrons - electrons no longer attracted to one specific nucleus but sufficiently delocalized into bands (conduction bands) surrounding the atoms that have become positive metal ions. Because Conduction Band Theory is not a part of the AP Chemistry curriculum, these electrons are often referred to as a delocalized “sea of electrons.” The more electrons a metal atom contributes to the band the stronger the force “wrapped around” the positive ions, the higher the energy needed to separate the atoms, and the higher the melting point of the metal. Within this band of loosely held electrons, the easy mobility of these electrons also leads to the properties of electrical and thermal conductivity that we find in metals as well. As the size of the metal atoms increases, moving down a column of the Periodic Table, we find the same number of valence electrons but the “sea of electrons” or band is spread out over atoms with more filled inner layers of electrons leading to atoms with larger volumes. This “blanket” of electrons is stretched over larger atoms, with more shielding of the nuclear charge, resulting in **weaker attractions** of the electrons in the outer band to the positive “kernels.” This accounts for the fact that we find that, with metal atoms, the melting points **decrease** as we move down the Periodic table. This is the opposite trend that we find with the halogen molecules, which are molecular solids. Very simply, these differences arise from the **differences in the nature or type of inter-molecular forces (IMF’s)**.

C. Next, we move to **Ionic Crystals**, which are made up of *positive and negative ions* organized into an array of crystal structures. The attraction arises from the fact that opposite charges attract, resulting in forces known as “electrostatic attractions.” The **greater the charges on the opposite ions, the stronger the attraction between the ions**, and the greater the energy required to separate the ions, leading to **higher melting points**. Conversely, **the larger the radius of the ions the greater the distance between the nuclei of the adjacent ions and the weaker the attraction** between oppositely charged ions. This results in lower melting points for ionic crystals with larger ions which typically result as we move down the Periodic Table. These can be summarized with an “inverse square law” relationship, Coulomb’s Law, shown in the chart above:



$$F = k \cdot \frac{q_1 \times q_2}{d^2} \begin{array}{l} \rightarrow \text{charges} \\ \rightarrow \text{distance between ions (nuclei)} \end{array}$$

where F is the force of attraction between ions, q = the amount of charge on the ions, and d = the distance between the nuclei (ions). For purposes here, k can be described as the proportionality constant that changes the proportional relationships into an equality. Again, we can often make useful predictions: we can predict, for example, that NaCl will have a higher melting point than CsBr, because although the charges are the same on the ions involved, the sizes are different, and the farther apart the ions are, the weaker the attraction between them.

D. Finally, we come to **Covalent crystals**, with the atoms most frequently involved found in the Upper IVA's of the Periodic Table: carbon, silicon and germanium. The two structures most frequently discussed are the planar covalent and network covalent crystals. In planar covalent crystals, the atoms have strong bonds within the plane, but much weaker bonds between planes of atoms, leading to the property of "cleavage," which we find in pencils. The incorrectly named pencil "leads" really consist of graphite, a planar covalent substance where the carbon readily rubs (cleaves) off onto the paper. This phenomenon occurs with mica (Si) as well, and, with the aid of a sharp fingernail or razor blade, one can peel off the layers of silicon atoms like the layers of an onion. With network covalent crystals, the atoms are strongly bonded in all three dimensions, leading to a network structure resulting in extraordinarily hard crystals that we find in diamond (carbon atoms) or quartz (silicon atoms). These strong bonds also explain the exceptionally high melting points we typically find in covalent solids, but who in their right mind would **melt** a diamond! We can apply this property to cutting tools. One thing that *can* cut a diamond is another diamond (used in the jewelry industry), and diamond cutting tools are frequently utilized in drilling processes or, in another era, were prized in phonograph record player needles.