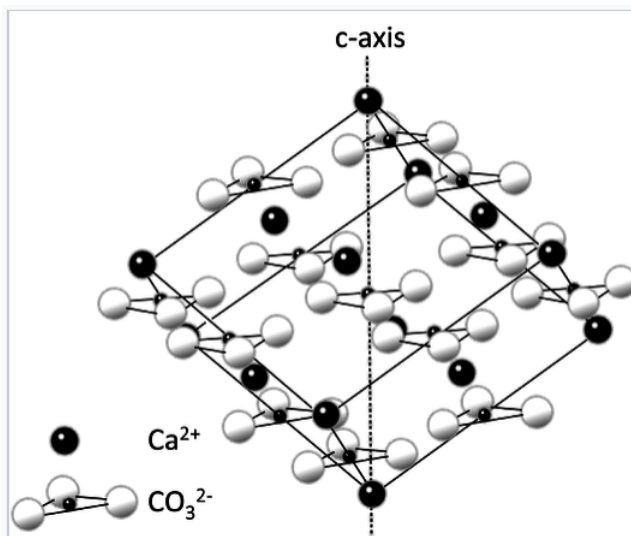


### 8.3: Structures Related to NaCl and NiAs

There are a number of compounds that have structures similar to that of NaCl, but have a lower symmetry (usually imposed by the geometry of the anion) than NaCl itself. These compounds include:

- $\text{FeS}_2$  (pyrite, "fools gold"):  $\text{S}_2^{2-}$  (disulfide) and  $\text{Fe}^{2+}$
- $\text{CaC}_2$  (a salt-like carbide):  $\text{Ca}^{2+}$  and linear  $\text{C}_2^{2-}$  anions
- $\text{CaCO}_3$  (calcite, limestone, marble):  $\text{Ca}^{2+}$  and triangular  $\text{CO}_3^{2-}$ .



The rhombohedral unit cell of the calcite crystal structure. The hexagonal c-axis is shown.

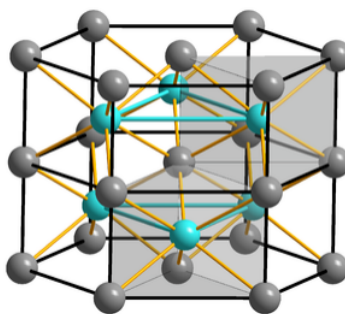
The **calcite** ( $\text{CaCO}_3$ ) crystal structure is shown above. Triangular  $\text{CO}_3^{2-}$  ions fill octahedral holes between the  $\text{Ca}^{2+}$  ions (black spheres) in a distorted NaCl lattice. As in NaCl, each ion is coordinated by six of the other kind. From this image we can see why the  $\text{CaCO}_3$  structure has a lower symmetry than that of NaCl. The fourfold rotation symmetry of the NaCl unit cell is lost when the spherical  $\text{Cl}^-$  ions are replaced by triangular  $\text{CO}_3^{2-}$  ions. Because of this symmetry lowering, transparent crystals calcite are birefringent, as illustrated below.



Calcite crystals are birefringent, meaning that their refractive indices are different along the two principal crystal directions. This gives rise to the phenomenon of double refraction.

#### NiAs structure

The NaCl structure can be described a face-centered cubic lattice with all of the octahedral holes filled. What if we start with a hexagonal-close packed lattice rather than a face-centered cubic lattice?



Nickel arsenide crystal structure. The  $\text{Ni}_6\text{As}$  trigonal prisms are shaded gray. One octahedron of six As atoms surrounding a Ni atom is shown in the center of the figure.

This is the structure adopted by **NiAs** and many other transition metal sulfides, phosphides, and arsenides. The cations are shown in gray while the anions are light blue in the figure at the right. The cations are in octahedral coordination, so each cation is coordinated to six anions. The anions are also coordinated to six cations, but they occupy trigonal prismatic sites. In terms of layer stacking, the NiAs structure is  $\text{AcBcAcBc}\dots$ , where the A and B sites (the hcp lattice) are occupied by the As atoms, and the c sites, which are eclipsed along the layer stacking axis, are occupied by Ni. Unlike the NaCl structure, where the anion and cation sites are interchangeable, NiAs has unique anion and cation sites. The layer stacking sequence for NiAs is shown below:

- ----- A
- ---c---
- ----- B
- ---c---
- ----- A
- ---c---
- ----- B
- ---c---

The NiAs structure cannot be adopted by ionic compounds because of the eclipsing cations, because the cation-cation repulsions would be internally destabilizing for an ionic compound. This structure is mainly adopted by covalent and polar covalent MX compounds, typically with "soft" X anions (S, Se, P, As,...) and low-valent transition metal cations. For example, some compounds with the NiAs structure are: MS, MSe, MTe (M=Ti, V, Fe, Co, Ni). Often these are nonstoichiometric or complex stoichiometries with ordered vacancies ( $\text{Cr}_7\text{S}_8$ ,  $\text{Fe}_7\text{S}_8$ ).

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