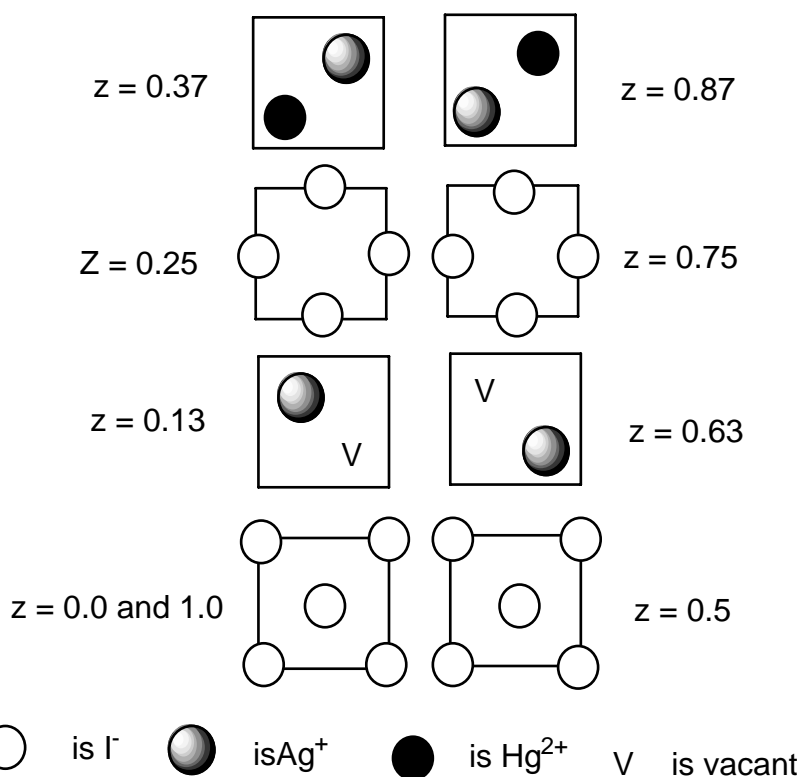


Solid-State Structure of an Interesting Material

The compound Ag_2HgI_4 is interesting because it shows a temperature-dependent change in its color and its conductivity. At temperatures below 50°C it is yellow and non-conducting and at temperatures above 50°C it is orange and conducting. Shown below are several cross-sections through the unit cell for Ag_2HgI_4 in its low temperature form:



Based on these cross-sections, answer the following questions:

- what is the coordination number for I^- (consider both cations)?

Each I^- has a coordination number of 3 as it touches 2 Ag^+ ions and 1 Hg^{2+} ion.

- what kind of packing do the iodide ions exhibit?

The iodide ions are in a face-centered cubic structure, but note that the unit cell consists of two such cubes stacked one upon the other.

- what is the coordination number for Ag^+ ?

The coordination number for Ag^+ is 4.

- what is the coordination number for Hg^{2+} ?

The coordination number for Hg^{2+} is 4.

- do the silver ions occupy tetrahedral holes or octahedral holes in the lattice of iodide ions? how about the mercury ions? do these agree with the radius-ratio rule? if no, then why do the cations fill tetrahedral holes? (see Appendix B.4 for ionic radii)

The radii of the ions are: 0.126 nm for Ag^+ , 0.110 nm for Hg^{2+} and 0.216 nm for I^- . This gives the ratio r_+/r_- as 0.583 for Ag^+/I^- and as 0.509 for $\text{Hg}^{2+}/\text{I}^-$. Both ratios suggest that the cations should be in octahedral holes. One limitation to the radius ratio rule is that ionic radii are not precise; that is, the radius of an ion is somewhat dependent on its environment, which includes the other ions in the compound.

- how many iodide ions, silver ions, and mercury ions are in a unit cell? Is this consistent with the compound's empirical formula?

For iodide there are 8 ions at the corners of the unit cell ($z = 0.0$ and 1.0), each contributing $1/8$ to the unit cell, 10 ions on faces ($z = 0.0, 0.25, 0.75$ and 1.0), each contributing $1/2$ to the unit cell, 4 ions on edges ($z = 0.5$), each contributing $1/4$ to the unit cell, and 1 ion in the center ($z = 0.50$), contributing all of itself to the unit cell. Together this gives 8 iodide ions per unit cell.

For silver there are 4 ions in tetrahedral holes, each contributing all of itself to the unit cell. Together this gives 4 silver ions per unit cell.

For mercury there are 2 ions in tetrahedral holes, each contributing all of itself to the unit cell. Together this gives 2 mercury ions per unit cell.

The stoichiometry is $\text{Ag}_4\text{Hg}_2\text{I}_8$, which simplifies to Ag_2HgI_4 ; thus, the unit cell is consistent with the compound's empirical formula.

In the high-temperature form the silver ions, the mercury ions and the vacancies are randomly distributed throughout the lattice formed by the iodide ions (this is called a disordered form). Speculate on why the disordered, high-temperature form is conductive, whereas the ordered, low-temperature form is not.

Having a random arrangement of ions suggests that the cations can jump around into vacancies. The ability of ions to move means that charge can move through the lattice, which is the meaning of conductivity.