16  \( I_x-VI_y \) compounds

16.0  Crystal structure and electronic structure

Among the \( I_x-VI_y \) compounds the oxides, sulfides, selenides and tellurides of copper and silver are of interest in semiconductor physics.

16.0.1  Copper compounds

The structure of \( \text{CuO} \), the natural tenorite mineral, is monoclinic; the tetramolecular cell has following parameters:

\[
\begin{align*}
    a &= 4.6927(4) \text{ Å}, \\
    b &= 3.4283(4) \text{ Å}, \\
    c &= 5.1370(6) \text{ Å}, \\
    \beta &= 99.546(9)^\circ.
\end{align*}
\]

The space group \( C_{2h}^6\text{-}C2/c \) has been ascribed to the structure of the tenorite. Each copper is coordinated to four coplanar oxygens at the corners of a parallelogram. The oxygen is coordinated to four coppers at the corners of a distorted tetrahedron. The six nearest oxygens to each copper complete a strongly distorted octahedron. The \( \text{CuO}_4 \) parallelograms form ribbons along [110] direction and alternating in [010] direction. Each ribbon is linked to adjacent chains of other groups by sharing corners (Fig. 16.0.1).

\( \text{Cu}_2\text{O} \) has a cubic structure, the cuprite (natural \( \text{Cu}_2\text{O} \) mineral) type, of space group \( T_{h}^2\text{-}Pn3 \) or \( O_{h}^4\text{-}Pn3m \) with following unit cell parameters: \( a = 4.27 \) Å at \( p = 0 \) GPa. Copper has two O neighbors, and the site symmetry is \( D_{3d} \). Oxygen has four Cu neighbors, and the site symmetry is \( T_d \). The lattice can be considered as two ice-type structures linked by Cu–Cu bonds (Fig. 16.0.2). Band structure: Fig. 16.0.5 (p.449).

\( \text{Cu}_2\text{S} \) occurs in several stoichiometric and nonstoichiometric (\( \text{Cu}_{2-x}\text{S} \)) modifications:

Orthorhombic chalcocite (= low temperature chalcocite or \( p\)-\( \text{Cu}_2\text{S} \)) space group: \( C_{2v}^{15}\text{-}Ab2m \). The unit cell contains 96 \( \text{Cu}_2\text{S} \) formula units. Lattice parameters \( a = 11.885 \) Å, \( b = 27.325 \) Å, \( c = 13.496 \) Å.

Left: Fig. 16.0.1. \( \text{CuO} \). Tenorite structure. Perspective view showing 4 unit cells. Spheres represent oxygen, ellipsoids are coppers. The numbers refer to different copper ions.

Right: Fig. 16.0.2. \( \text{Cu}_2\text{O} \). Cuprite structure. a) origin on an O site; b) origin on a Cu site.
**Hexagonal chalcocite:** $\beta$-Cu$_2$S is stable between 103.5°C and 435°C. The structure is hexagonal with the S atoms arranged in a nearly perfect close-packing and the Cu atoms distributed in the interstices in an almost fluid-like way. Space group: D$_6$h$^5$–P6$_3$/mmc. The unit cell contains 4 Cu$_2$S molecules. The lattice parameters are: $a = 4.005$ Å and $c = 6.806$ Å.

**Digenite:** The region of the copper sulfide system where the mineral digenite occurs, $1.74 < x < 1.95$, exhibits an intricate manifold of phases. There are only two discrete equilibrium forms of digenite, corresponding to compositions $x = 1.89$ and $x = 1.84$. A sequence of superlattice ordering transitions is reported in digenite-type crystals. Low temperature digenite is observed for $T < 80°C$ and $1.765 < x < 1.79$; space group is O$_h^7$–Fd3m. The cubic unit cell with an edge of $a = 27.71$ Å corresponds to a superstructure of an elementary cubic cell with $a = 5.54$ Å edge length. That phase seems to be unstable when pure and needs to be stabilized by Fe in the natural mineral digenite. High temperature digenite is observed for $T > 80°C$ and has the space group O$_h^5$–Fm3m. The unit cell corresponds to an edge length of $a = 5.57$ Å ($= a'$ of digenite LT). Cu atoms are distributed statistically; the range of existence is $1.73 < x < 1.84$, somewhat broader than for LT digenite.

**Djurleite** corresponds to $1.935 < x < 1.955$. The orthorhombic (or pseudo-orthorhombic) cell contains 128 Cu$_2$S formula units and parameters are: $a = 26.92$ Å, $b = 15.71$ Å, $c = 13.56$ Å.

Djurleite (Cu$_{1.938}$S) was also found to be monoclinic with space group P2$_1$/n and the following unit cell parameters: $a = 26.90$ Å, $b = 15.75$ Å, $c = 13.57$ Å, $\beta = 90°13'$. The monoclinic cell contains also 248 Cu and 128 S.

Cu$_2$Se has been classified in the cubic system with space group O$_h^5$–Fm3m in which four selenium ions occupy the 4(a) sites. Seven copper ions are statistically distributed over the 32(f) sites of this space group and the remaining copper ion is distributed over the 32(0) sites. An $\alpha$- $\rightarrow$ $\beta$-phase transition occurs at $T = 409$ K.

Cu$_2$Te undergoes four polymorphic transitions at 180°C, 305°C and 460...555°C. For the room temperature form a hexagonal structure has been suggested with cell parameters $a = 4.17$ Å, $c = 21.71$ Å.

### 16.0.2 Silver compounds

The properties of the silver oxides are comparable to those of the copper oxides, at least for the monovalent compounds. Several oxides are known, Ag$_2$O and AgO, but also Ag$_2$O$_3$ or Ag$_7$O$_{11}$ and Ag$_4$O$_3$.

**AgO:** Monoclinic AgO has the following unit cell parameters: $a = 5.85$ Å, $b = 3.47$ Å, $c = 5.49$ Å, $\beta = 107.5°$, and a space group C$_{2h}^5$–P2$_1$/c. This structure consists of a deformed face centered cubic metal atom arrangement with equal proportions of linearly coordinated Ag (I) and approximately square planar coordinated Ag (III) atoms, see Fig. 16.0.3 (p.448). Tetragonal AgO has the following unit cell parameters: $a = 6.833(3)$ Å, $c = 9.122(4)$ Å, and a space group I4$_1$/a. Tetragonal silver oxide shows structural features similar to those of monoclinic AgO. Its metal atom arrangement forms a distorted face-centered cubic substructure which contains two non equivalent Ag sites in equal proportion.

Ag$_2$O has the cuprite cubic structure, whose space group is T$_h^2$–Pn3, with $a = 4.72$ Å at 26°C or space group O$_h^4$–Pn3m with $a = 4.736$ Å at room temperature.

The silver sulfides, selenides and tellurides crystallize in several modifications:

**$\alpha$-Ag$_2$S.** The natural mineral acanthite is monoclinic with a tetramolecular unit with: $a = 4.23$ Å, $b = 6.91$ Å, $c = 7.87$ Å, $\beta = 99°35'$. Space group: C$_{2h}^5$–P2$_1$/n.