3.3.5 AB-INITIO SIMULATIONS FOR THE Cu-Sb-S SYSTEM

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Theoretical treatment of crystalline solids has become an indispensable tool to understand solid state materials; in particular, ion migration, ion substitution and local coordination for comparison with spectroscopic measurements. In this work, *ab-initio* calculations using DFT, as implemented in VASP, were used to optimize crystal structure. Additionally, with FEFF9 we were able to calculate XANES and EELS spectra using the optimized cell. The simulation of the spectra using *ab-initio* methods is crucial to interpret the excited states of the materials. A particular phase of the system Cu-Sb-S, designated by Tetrahedrite - $Cu_{12}Sb_4S_{13}$ was our focus. Tetrahedrites are an important group of economically valuable sulfosalt minerals which have the ideal simplified formula $(M^{1+})_{10},(M^{2+})_2\ (M^{3+})_4\ [S_{13}]$ where M^{1+} ions are mainly Cu^+ with some Ag^+, divalent ions are Cu^{2+}, Zn^{2+}, Fe^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, and trivalent ions Sb^{3+}, As^{3+}, Bi^{3+}. XANES experiments and simulations were performed to study the influence of the coordination geometry and nature of metal ions when bounded to sulfur. The cubic crystal structure of Tetrahedrite contains two formula units per unit cell. The atomic array derives from the arrangement in Sphalerite where each one of the constituting atomic species is surrounded by a tetrahedron of ions with opposite sign and leaving unoccupied four out of sixteen cubic close-packing anion positions, and further replacing this tetrahedral cluster of vacancies by one S-atom. This replacement process provides pyramidal and triangular coordination to some of the metal ions, and gives rise to a peculiar coordination and bonding situation for one out of thirteen sulphur atoms in the chemical formula. Such crystal chemical insight illustrates the decisive role that XANES, EELS and *ab-initio* simulations have in providing a comprehensive interpretation for Tetrahedrite behaviour. This has with significant economic implications since these structures are found in nature containing economically valuable elements that can be extracted.