

Experimental and Theoretical Investigation of the Electronic Structure of Transition Metal Sulfides: CuS, FeS₂, and FeCuS₂

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INTRODUCTION

Recent developments in instrumentation and synchrotron radiation sources give a new impulse to the study of the electronic structure of solids with the aid of soft X-ray emission spectroscopy (XES).¹⁻² As a result of the high brightness of third generation synchrotron sources, the intensity of fluorescence X-ray emission in the soft X-ray energy range (where non-radiative decay processes of core vacancy states dominant³) has increased. This makes it possible to study the electronic structure of impurity atoms in different materials.⁴⁻⁵ Use of tunable synchrotron radiation for excitation of XES has several advantages for the study of the electronic structure. First, selective excitation of XES avoids the overlap of satellites and valence spectra that originate from transitions into the spin-orbit split core levels ($L_{2,3}$, $M_{2,3}$, $M_{4,5}$ etc.). This is important for the analysis of the density of states (DOS) in the vicinity of the Fermi level in 3d, 4d and 5d transition metal alloys and compounds.⁶ Second, chemically identical atoms at inequivalent sites in the crystal can be subsequently excited as the excitation energy increases. Hence, the local electronic structure of atoms with electrons in states at slightly different binding energies can be determined.⁷⁻⁹

The present paper describes how tunable synchrotron radiation was used for selective excitation of inequivalent sulfur atoms in CuS. Thus, for the first time, the sulfur $L_{2,3}$ XES of S_1 atoms that form S_2 -dimers is measured separately. The obtained results compare favorably with the density of states determined from density functional band structure calculations. This study is an illustration of the power of combining XES and photoelectron spectroscopy (PES) with band calculations to determine the partial site-specific density of states.

RESULTS

While we made measurements and calculations on FeS₂, FeCuS₂, and CuS, we will just present our results for CuS to illustrate the point that combining XES and PES with calculations is a powerful method toward the elucidation of the electronic structure of a great number of materials. The details of the measurements and the calculations can be found in the publication.¹⁰

Our PES and XES measurements and our calculations were consistent with the assertion that in FeCuS₂ the sulfur atoms occupy the sulfur sites as single atoms, while in FeS₂ the sulfur atoms occupy the sulfur sites as dimers.

An excitation energy dependence of the sulfur $L_{2,3}$ x-ray emission spectra led us to make core photoemission measurements and calculations. LMTO calculations were used as an aid along with the measurements on the FeS_2 and FeCuS_2 compounds to aid in the interpretation of the energy dependence of the soft x-ray and photoelectron spectra. From these results we were led to the conclusion that two thirds of the sulfur atoms form dimers while the remaining sulfur atoms are single. The results of the calculations and the measurements for the XPS and XES are shown in the accompanying figure. In this figure the two different sulfur sites show up as a broadening of the sulfur L spectra taken at 163.5 eV. One can also see how the sulfur d states hybridize with the copper by comparing the copper L emission spectrum with the sulfur L: spectrum. This figure is an excellent example of how calculations and site specific spectroscopies can be used to map out a relative density of states of different symmetries. It would be an important contribution to be able to put these spectra on a absolute intensity scale and that serves as a future challenge.

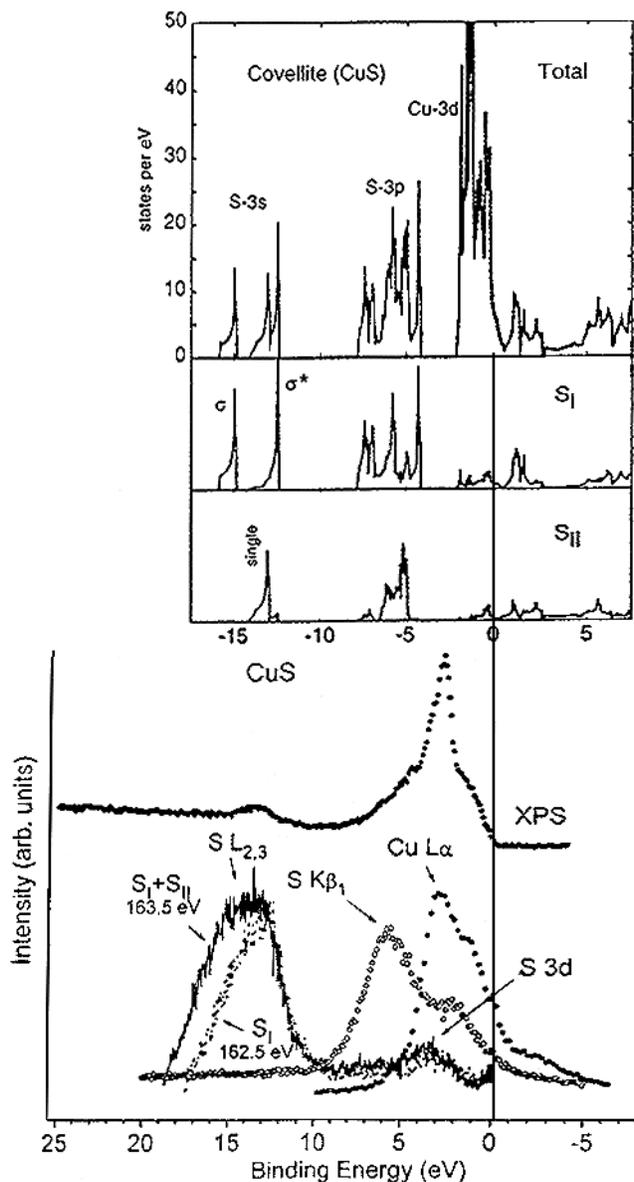


Figure 1. Photoemission and SX emission spectra for the Cu- L_1 , S-K, S_I - $L_{2,3}$ and (S_I+S_{II}) - $L_{2,3}$ spectra compared with calculated densities of states. The data show good agreement and clearly resolve the contributions of sulfur in two dissimilar sites.

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