Abstract

K edge XANES spectra of CuGaSe2, ZnGeAs2 and CuFeS2 are studied both experimentally and theoretically. While spectra of CuGaSe2 and ZnGeAs2 are remarkably similar, spectra of CuFeS2 differ significantly, especially in the pre-edge region. Full-potential band structure calculations without any core hole give essentially the same results as real-space multiple-scattering calculations for a muffin-tin potential with a core hole included; the notable exception is the Cu edge in CuGaSe2, where non-muffin-tin effects possibly occur. The distinct pre-peak in CuFeS2 has been interpreted as transitions to states of spatial distribution of the photoelectrons which participate in the formation of specific XANES features.

1. Introduction

Ternary semiconductors of the I-III-V1 and II-IV-V2 types share the same chalcopyrite structure. Their electronic properties were extensively studied in the past, both due to fundamental reasons (they offer an opportunity to study systematic variations of their properties with chemical composition) as well as due to their technological relevance. Among the techniques which probe the low-lying unoccupied states, X-ray absorption near-edge structure (XANES) spectroscopy holds a unique position as it offers a local view from a chemically specific site. Earlier XANES studies suggested that while spectra at analogous K edges of I-III-V1 compounds are quite similar to each other, the spectra of the “archetypal” chalcopyrite CuFeS2 exhibit remarkable differences, especially in the pre-edge region. To our knowledge, no XANES spectra of the II-IV-V2 compounds have been published so far.

When interpreting XANES spectra, it is often assumed that the pre-edge region corresponds to semi-bound states. In accord with this reasoning and with the results of band-structure calculations, the pre-peak in CuFeS2 has been interpreted as transitions to states arising from the Fe 3d band hybridized with the S and/or Cu states [1, 2, 3]. On the other hand, McKeown [4] suggested that the pre-peaks at the Cu and Fe K edge spectra may be caused by interference effects of the photoelectron wave function from the pre-peaks at the Cu and Fe K edge spectra of CuFeS2 arise from transitions to delocalized multiple-scattering resonances which are confined almost exclusively to the Fe sites.

2. Experimental and theoretical methods

The spectra of CuGaSe2 and ZnGeAs2 polycrystalline samples were measured using a two-crystal spectrometer and an X-ray spectrometry tube. The energy resolution varied from 0.36 eV for the Cu edge to 0.52 eV for the Se edge. The spectra were collected in a transmission mode, each measured data point represents an average of repeated measurements. The measured spectra were deconvoluted by the apparatus smearing function. The Cu and Fe K edge spectra of polycrystalline CuFeS2 were measured using synchrotron radiation at HASYLAB, Hamburg. Both edges were recorded in the transmission mode at the Al beamline with a two-crystal monochromator. The energy resolution of the monochromator was about 1 eV at 7 keV. The S K edge of CuFeS2 was digitized from the work [2].

Our results are summarized in Figs. 1–3. The energy ranges in these figures were set using the \( kR \sim \text{const} \) prescription, where \( k \sim \sqrt{2E} \) is the photoelectron wave vector and \( R \) is a typical interatomic distance in the given compound. The horizontal alignment of the theoretical spectra at different edges of the same compound was provided by the calculation itself, the block-wise alignment of the band-structure and the RSMS calculations as well as of the experimental spectra was performed by hand. The zero of the energy scale was set to the bottom of the conduction band of the pseudopotential calculation.

Theoretical spectra were obtained within the local density approximation framework, in a twofold way: via an all-electron full-potential band-structure calculation based on a pseudopotential technique and via a real-space multiple-scattering (RSMS) method involving a self-consistent muffin-tin potential. In the latter case, we investigated both the situation without a core hole (ground state) and with a relaxed and screened core hole. More details of our application of the pseudopotential formalism can be found in Ref. [5, 6], our implementation of the RSMS formalism was described in Ref. [6, 7].

In order to facilitate the interpretation of the pre-edge region in CuFeS2, wave function probability densities associated with the excited photoelectron were calculated in the formalism [8]. In that way, one can gain a well-defined picture of the spatial distribution of the photoelectrons which participate in the formation of specific XANES features.

3. Results and discussion

Our results are summarized in Figs. 1–3. The energy ranges in these figures were set using the \( kR \sim \text{const} \) prescription, where \( k \sim \sqrt{2E} \) is the photoelectron wave vector and \( R \) is a typical interatomic distance in the given compound. The horizontal alignment of the theoretical spectra at different edges of the same compound was provided by the calculation itself, the block-wise alignment of the band-structure and the RSMS calculations as well as of the experimental spectra was performed by hand. The zero of the energy scale was set to the bottom of the conduction band of the pseudopotential calculation.

The XANES spectra of CuGaSe2 and ZnGeAs2 are remarkably similar, spectra of CuFeS2 differ significantly, especially in the pre-edge region. The pre-peak in CuFeS2 has been interpreted as transitions to states which are confined almost exclusively to the Fe sites.
Fig. 1. K edge XANES spectra of Cu (dashed line), Ga (dotted line) and Se (full line) in CuGaSe$_2$, as provided by the experiment (uppermost panel), by the band structure calculation (middle panel) and by the RSMS calculation (lowermost panel).

Fig. 2. Experimental and theoretical Zn, Ge and As K edge XANES spectra of ZnGeAs$_2$.

Fig. 3. Experimental and theoretical Cu, Fe and S K edge XANES spectra of CuFeS$_2$. The pre-peak is marked by an arrow.

the II-IV-V$_2$ compounds will be similar as well. The CuFeS$_2$ case then stands out quite prominently.

The RSMS curves presented here have been obtained for a potential which accounts for the core hole. The ground-state potential gives rise to spectra which are quite similar to those shown here, just their peak heights at the low energy side are typically about 10% smaller. Therefore, we do not show them here for brevity. The results of the band structure calculation and of the RSMS calculation generally agree. Interestingly, the RSMS calculation does not correctly reproduce the Cu edge of CuGaSe$_2$ – the intensity of the first maximum at $E \approx 10$ eV in Fig. 1 is too low, being on par with the middle peak at $E \approx 13$ eV which itself is hardly distinguishable in the experiment. Our band-structure calculation seems to describe the Cu spectrum of CuGaSe$_2$ better. As suggested earlier [11], this difference may be a manifestation of the muffin-tin approximation, which was imposed on the RSMS calculation but not on the pseudopotential band-structure calculation.

Let us now concentrate on CuFeS$_2$ and its distinctiveness. The largest difference between CuFeS$_2$ and CuGaSe$_2$ or ZnGeAs$_2$ spectra occurs in the pre-edge region; there are no pre-peaks in the CuGaSe$_2$ or ZnGeAs$_2$ spectra, in contrast to CuFeS$_2$, where a well-defined pre-peak appears at each of the three edges (Fig. 3). The reproduction of this pre-peak by the theory is not perfect, nevertheless, it is good enough to substantiate a theory-based investigation of the mechanism of its formation. The differences between CuFeS$_2$ and CuGaSe$_2$ or ZnGeAs$_2$ spectra occur in the main peaks region as well, however, they are not so marked as at the pre-peak.

The relative roles of individual atomic sites in the formation of a particular spectral peak can be quantitatively assessed by comparing the wave function probability densities (WFPD) around those sites [8]. By performing this analysis for all the three edges, we found that the excited photoelectron is located almost exclusively on Fe atoms at the pre-peak energy; the calculated WFPD around the Fe sites is by three orders of magnitude higher than around any of the Cu or S sites. This is remarkably different from the main peak region, where the photoelectron WFPD is more-or-less uniformly spread among all the sites of the cluster.
Similarities and Differences Between XANES Spectra

as one would expect for a truly multiple-scattering resonance (we
do not plot the corresponding curves here for brevity). The strong
dominance of Fe sites in the WFPD distribution at the pre-edge
energy is consistent with the interpretation of the pre-peak as
transition to unoccupied Fe 3d states hybridized with Cu and/or S
states [1, 2, 3]; however, these states are located on many Fe atoms
simultaneously, not just a single one, and hence they correspond
to a resonance which arises from multiple scattering by the Fe
atoms. In this respect, it represents a crystal structure interference
effect as well [4]. So both views on the origin of the pre-peak in
the XANES of CuFeS$_2$ can be related and reconciled within the
WFPD concept.

4. Conclusions

Analogous K edge XANES spectra of compounds of the I-III-VI$_2$
type (CuGaSe$_2$) and of the II-IV-V$_2$ type (ZnGeAs$_2$) are quite
similar to each other while spectra of CuFeS$_2$ differ. The spectra
can be reasonably well reproduced by one-electron calculations.
Full-potential band structure calculations without any core hole
give essentially the same picture as RSMS calculations for
a muffin-tin potential with a core hole included; the notable
exception is the Cu edge in CuGaSe$_2$, where significant non-
muffin-tin effects possibly occur. The distinctiveness of CuFeS$_2$
spectra is caused by the presence of Fe atoms. Pre-peak in the
XANES of CuFeS$_2$ arises from transitions to delocalized multiple-
scattering resonances which are confined almost exclusively to the
Fe sites.

Acknowledgement
This work was supported by the project 202/02/0841 of the Grant Agency of the
Czech Republic.

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