

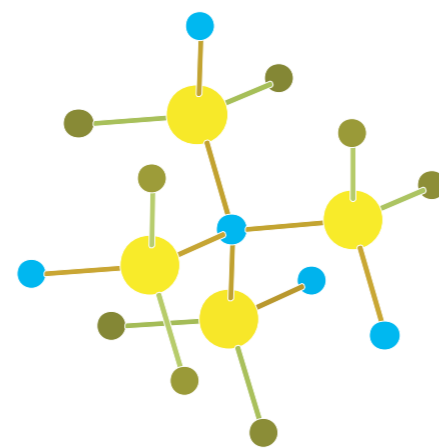
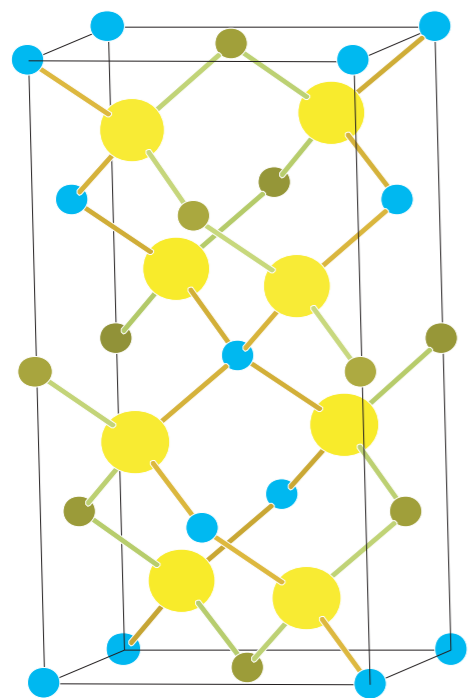
**Similarities and differences between XANES spectra
at analogous edges of ternary semiconductors
CuGaSe₂, ZnGeAs₂ and CuFeS₂**

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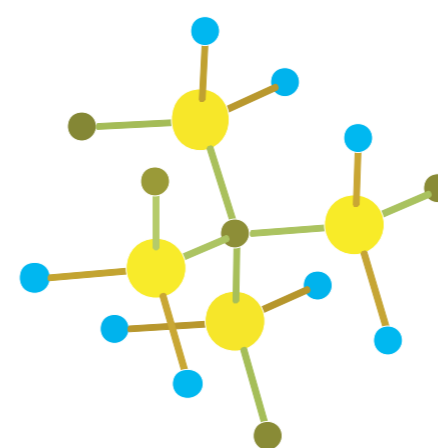
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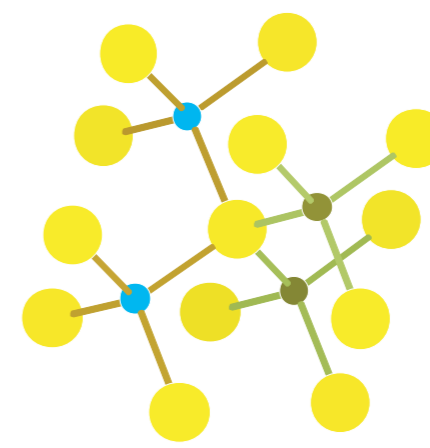
Structure of CuFeS_2 (and other ternary chalcopyrites and pnictides)



Cu coordination



Fe coordination



S coordination

State of art

- Ternary semiconductors of the I-III-VI₂ (CuGaSe₂) and II-IV-V₂ types (ZnGeAs₂) share the same chalcopyrite structure
- Compounds belonging to the I-III-VI₂ group have similar XANES spectra (CuGaSe₂, CuGaS₂, CuInSe₂, ZnSe).
- Spectra of binary analogs of the I-III-VI₂ and II-IV-V₂ types, ZnSe and GaAs, are similar to each other as well.
- Yet the archetypal chalcopyrite has got quite different XANES spectra than the rest of the family (cf. especially the pre-peak).

Dispute to be resolved

There is a general understanding that the key to the peculiarity of CuFeS₂ lies with the presence of Fe atoms in the compound. The question is **how do they technically achieve that?**

Two views have been presented:

1. Pre-peak arises from transitions of photoelectrons to **semi-bound states** created through hybridization of Fe 3*d* electrons with S and/or Cu states (and they are quite numerous Fe 3*d* electrons around at those energies...).
2. Pre-peak may be caused by interference effects of the photoelectron wave function from the crystal structure, i.e., it corresponds to essentially **extended states** (and it indeed can be obtained from real-space multiple-scattering calculations).

Aim of this work

- Compare spectra of compounds of the I-III-VI₂ type and the II-IV-V₂ type. Will they indeed be similar?
- Compare the experimental spectra with *ab-initio* calculations (verify that such a theoretical treatment is justified and hence can tell us something about the underlying mechanisms).
- Have a look at the photoelectron wave function and check the degree of localization of the pre-peak in CuFeS₂.

More details on the experiment

- Spectra of CuGaSe₂ and ZnGeAs₂ polycrystalline samples measured using a two-crystal spectrometer and an x-ray spectrometry tube in a transmission mode. The energy resolution varied from 0.36 eV for the Cu edge to 0.52 eV for the Se edge.
- The Cu and Fe *K* edge spectra of polycrystalline CuFeS₂ were measured in the transmission mode using synchrotron radiation at the A1 beamline in HASYLAB 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 Sainctavit, Ph., Petiau, J., Flank, A. M., J. Ringissen, J. and Lewonczuk, S., Physica B **158**, 623 (1989).

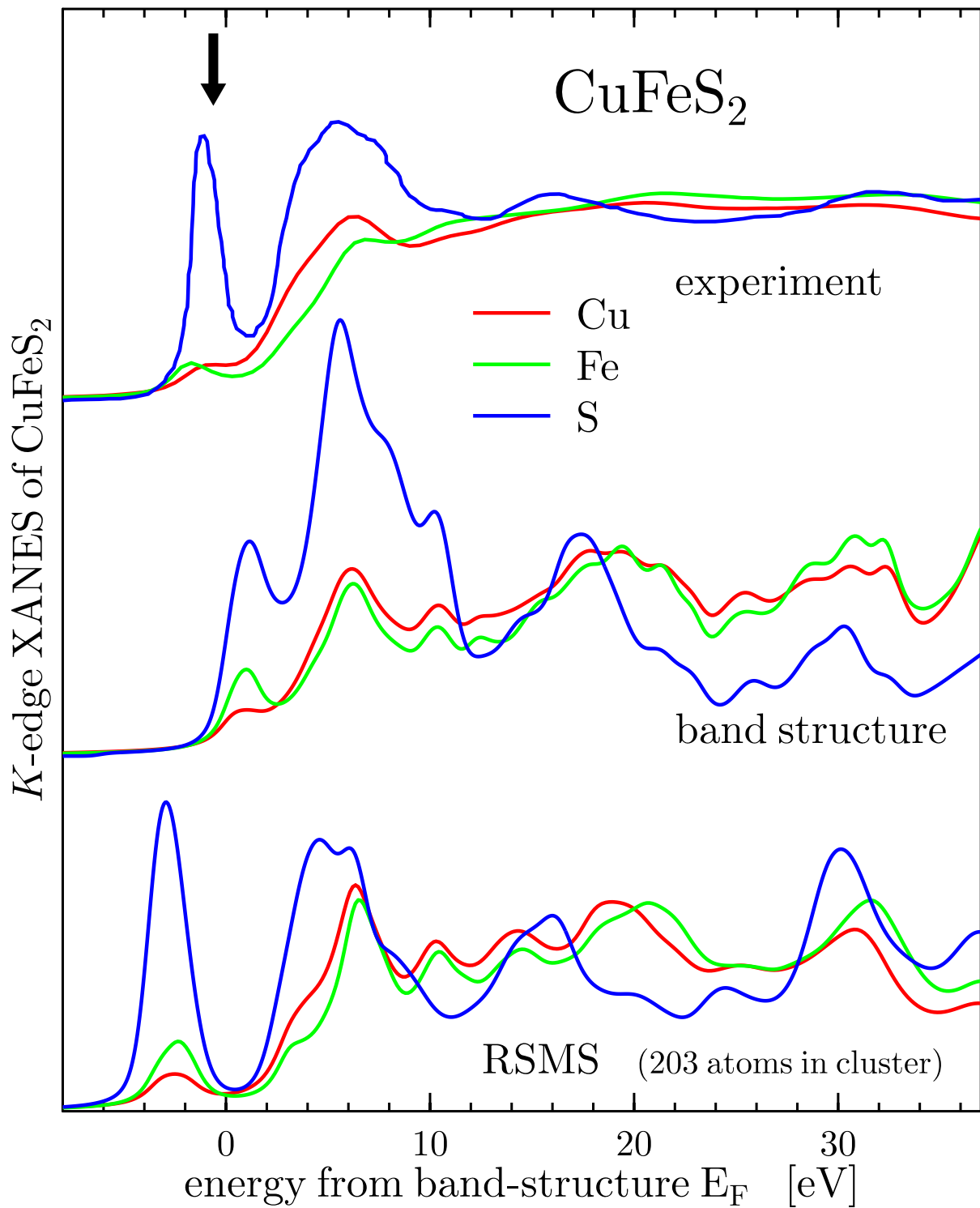
More details on the theory

- Theoretical spectra calculated *ab-initio* relying on the local density approximation, in a twofold way:
 1. via a full-potential band-structure calculation based on an **all-electron** pseudopotential technique [Vackář, J., Hyřha, M. and Šimůnek, A., Phys. Rev. B **58**, 12712 (1998)], and
 2. via a real-space multiple-scattering (RSM) method involving a self-consistent muffin-tin potential and a relaxed and screened core hole [Šipr, O. and Šimůnek, A., J. Phys.: Condens. Matter **13**, 8519 (2001)].

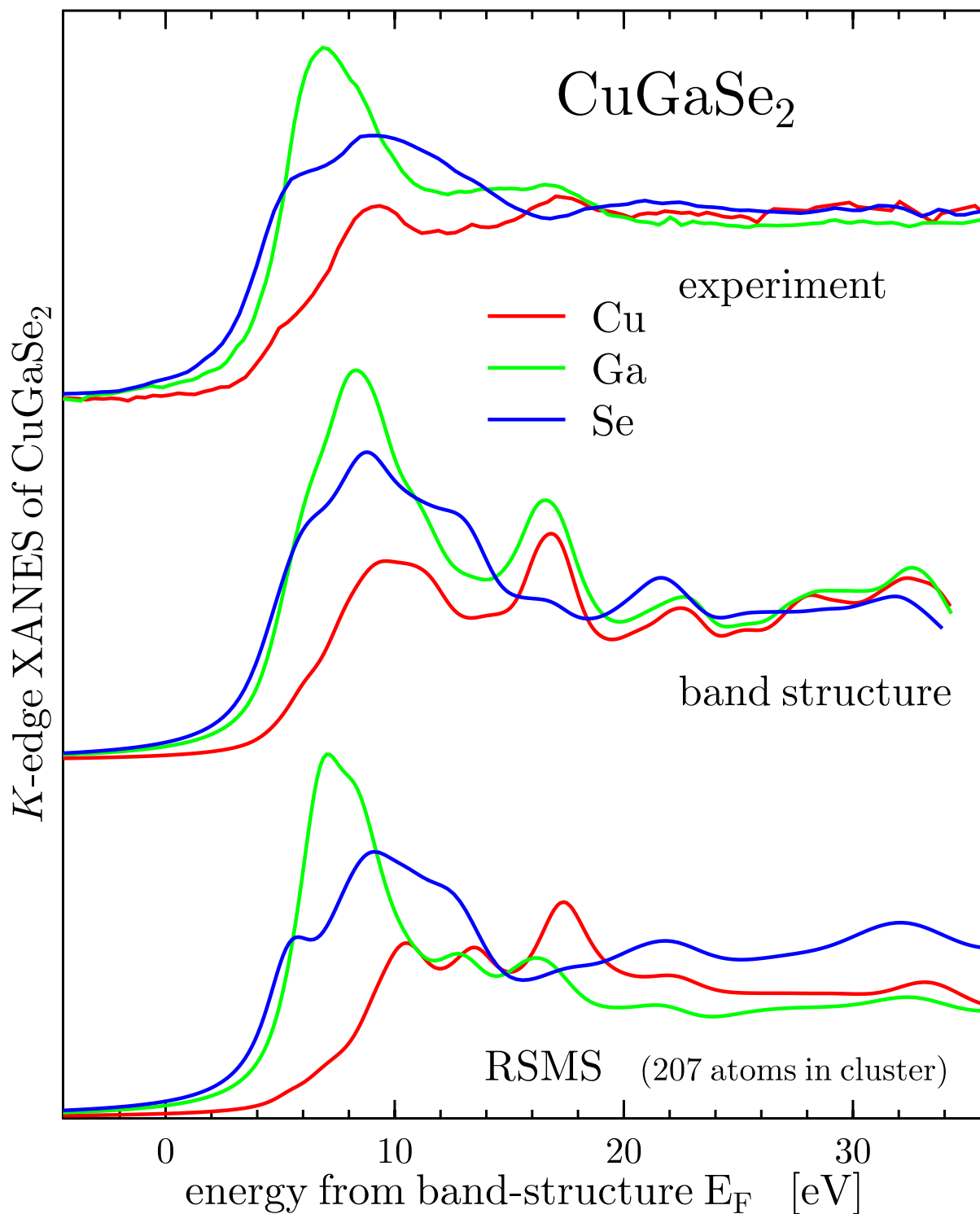
- Wave-function probability density associated with the excited photoelectron,

$$P(\mathbf{r}) = \frac{1}{\sigma_{\text{XAS}}} \int d^3\mathbf{k} \frac{d\sigma}{d\Omega d\mathbf{k}} |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2$$

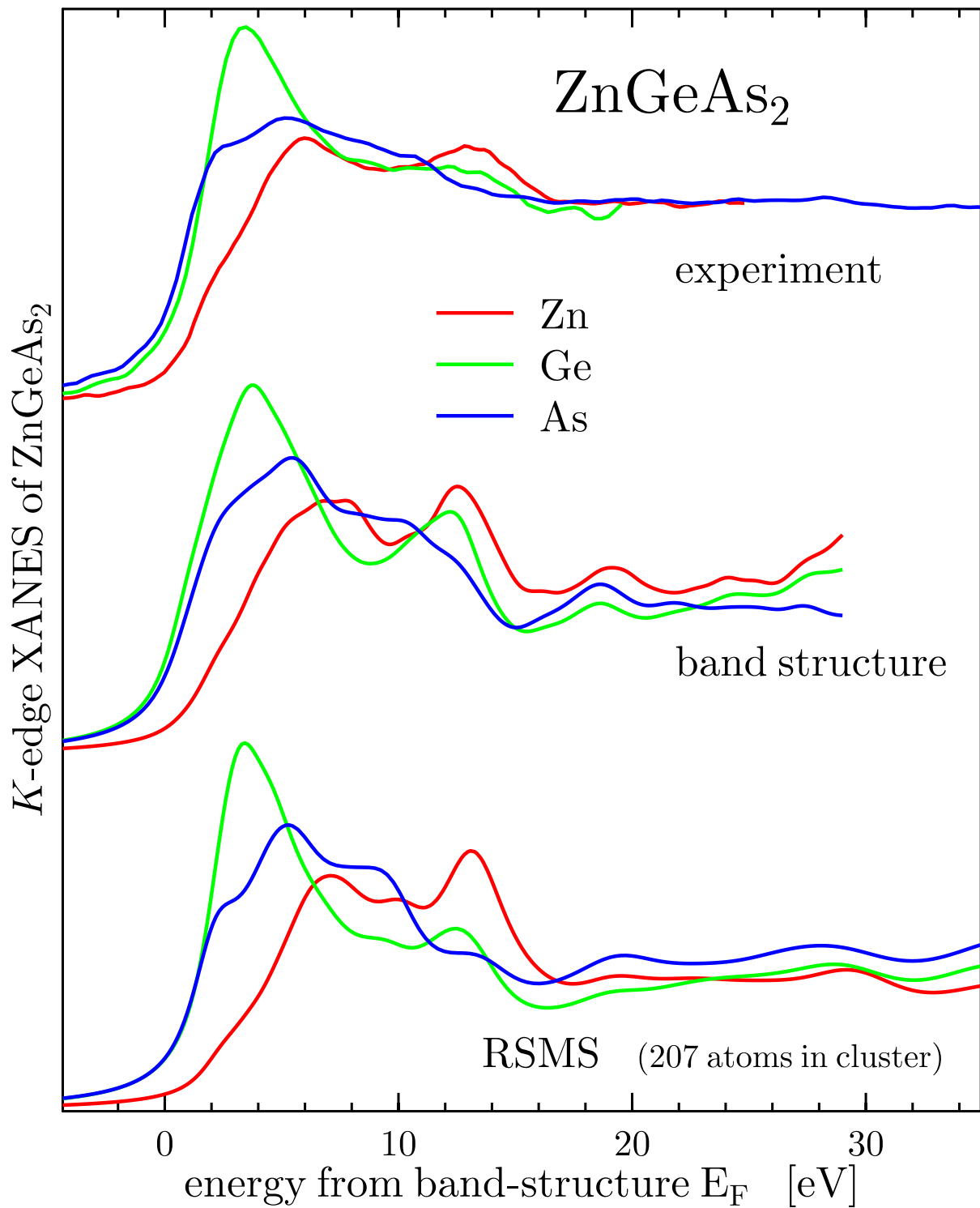
was calculated around each of the atomic sites [Šipr, O., Phys. Rev. B **65**, 205115 (2002)].



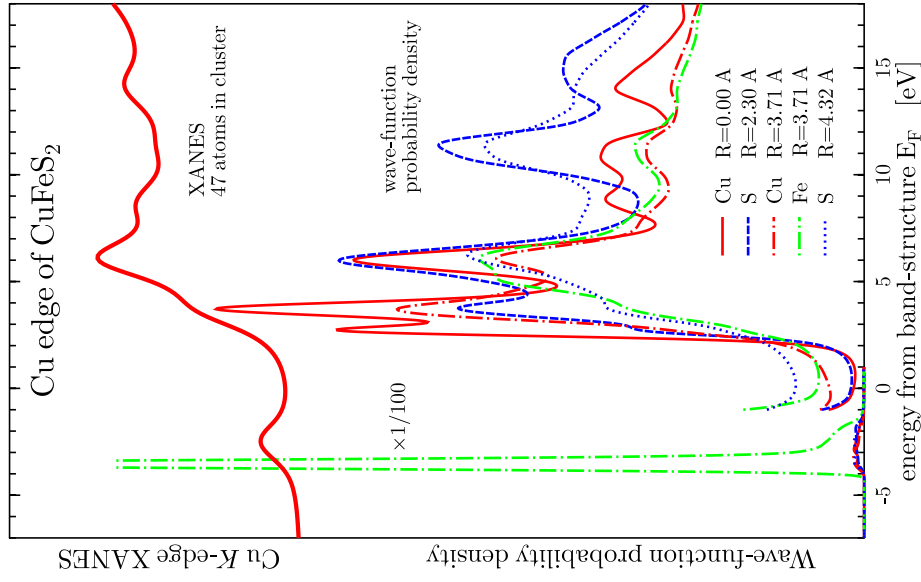
K edge XANES spectra of Cu, Fe and S in CuFeS₂, as provided by the experiment, by the band structure calculation and by the RSMS calculation. [The S *K* spectrum was digitized from the work Sainetavit, Ph., Petiau, J., Flank, A. M., J. Ringeissen, J. and Lewonczuk, S., Physica B **158**, 623 (1989).]



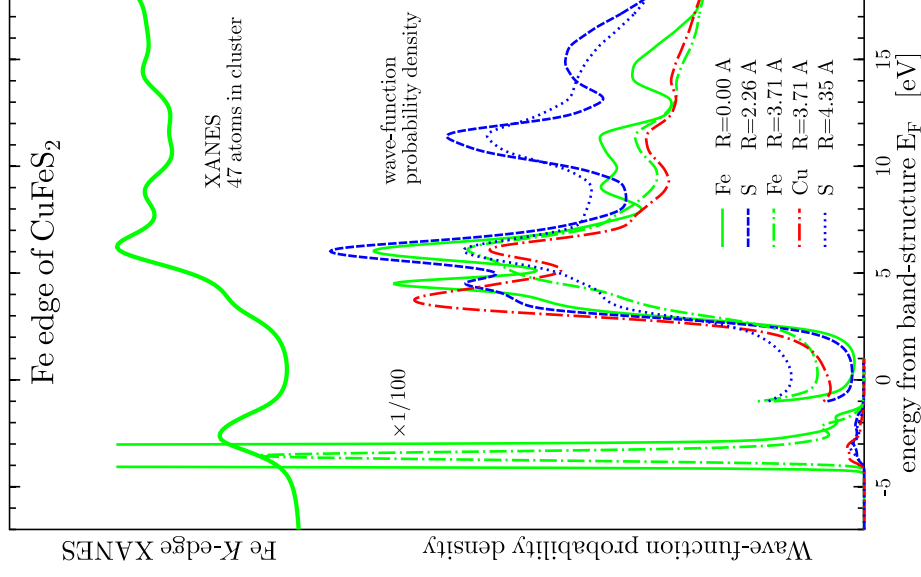
K edge XANES spectra of Cu, Ga and Se in CuGaSe₂, as provided by the experiment, by the band structure calculation and by the RSMS calculation.



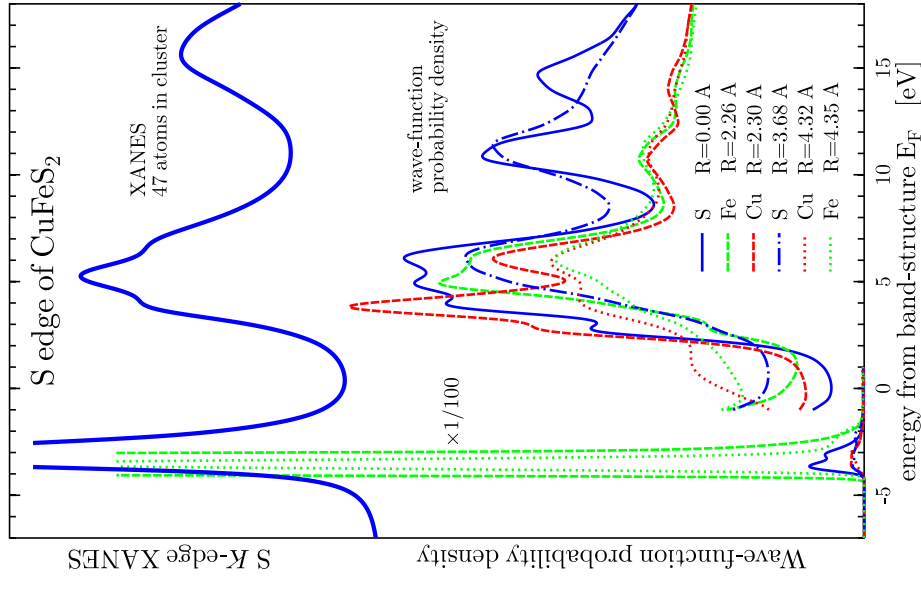
K edge XANES spectra of Zn, Ge and As in ZnGeAs_2 , as provided by the experiment, by the band structure calculation and by the RSMS calculation.



Photoelectron wave-function probability density associated with Cu *K* edge XANES spectra of CuFeS₂ around selected atomic sites, as provided by a RMS calculation for a cluster of 47 atoms.



Photoelectron wave-function probability density associated with Fe *K* edge XANES spectra of CuFeS₂.



Photoelectron wave-function probability density associated with S *K* edge XANES spectra of CuFeS₂.

Localization *vers.* delocalization of pre-peak-generating states

A truly post-modern solution: **Both views are valid !**

- At pre-peak energies, the excited photoelectron is localized around all Fe atoms (the share of Cu and S atoms is by two orders of magnitude smaller).
- It is the Fe 3d electrons who run the show. Nevertheless, the photoelectron states are created via multiple-scattering (interference from crystal structure) between the Fe atoms.
- The concept of photoelectron wave-function probability density joins the ~~nations~~ different interpretations of XANES features.

Other points to mention

- Pseudopotential formalism is suitable for describing x-ray absorption spectra — provided you use all-electron pseudopotentials.
 - Possibly the breakdown of muffin-tin approximation can be seen at the Cu *K* edge of CuGaSe₂ (which is not exactly the place where you would be looking for it).
 - A relaxed and screened core hole appears to make no big difference (we checked it explicitly with RSMS calculations but do not want to tire you with too many graphs).
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