

Electronic structure of BeS studied by resonant inelastic x-ray scattering

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INTRODUCTION

Due to their large energy gap and hardness, beryllium chalcogenides are interesting materials for improving the lifetime of optical devices made of other II-VI-semiconductors by forming multinary alloys [2]. Amongst them, beryllium sulfide (BeS) is an indirect semiconductor with a band gap of 7.4 eV direct and 4.7 eV indirect [1]. BeS, which is presently only available in powder form, is the only sulfur-containing II-VI-compound without any published experimental information about its electronic structure. This is due to the fact that the commonly employed method of choice (photoelectron spectroscopy) cannot be applied to an insulating powder because of charging effects, the lack of a suitable surface preparation method, and the fact that no sufficiently large single crystals are available.

We have therefore performed a combined soft x-ray absorption (NEXAFS) and resonant inelastic X-ray scattering (RIXS) study to investigate the electronic band structure of BeS powder using high brightness synchrotron radiation in the soft x-ray regime. RIXS is a bulk-sensitive photon-in-photon-out-process and therefore unaffected by charging effects as well as, to a large extent, by surface contaminations. Both NEXAFS and RIXS spectra were collected utilizing the high-flux capabilities of beamline 8.0 and the SXF endstation.

NEXAFS

Figure 1 presents NEXAFS spectra of four differently treated BeS and BeO samples. Due to the insulating properties of BeS, electron-yield detection does not provide a reliable absorption signal. We therefore have recorded the partial fluorescence yield between 98 and 110 eV, covering emission from the complete valence band region and avoiding the contribution of the large elastically scattered peak for excitation energies above 110 eV. The bottom three spectra were taken from a commercial BeS-powder (Alfa Aesar) with a purity of 99% and a grain size smaller than 150 microns, mounted on carbon tape. The powder was shipped under Ar atmosphere, and spectrum a) was taken right after breaking the Ar seal. Spectrum b) was recorded after a 9-month storage in air, and spectrum c) after an additional sputtering step with 2 keV Argon ions (3 hours, 4 μ A

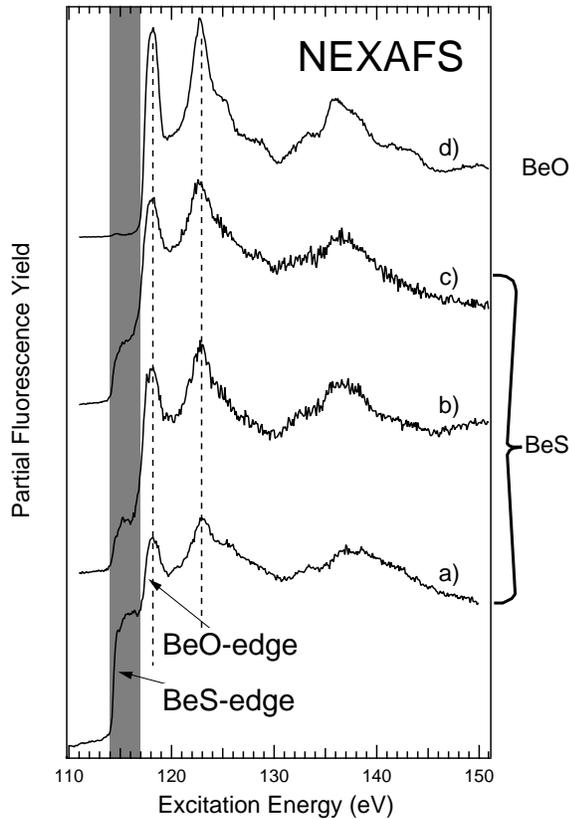


Figure 1: Be 1s NEXAFS-spectra for differently prepared samples.

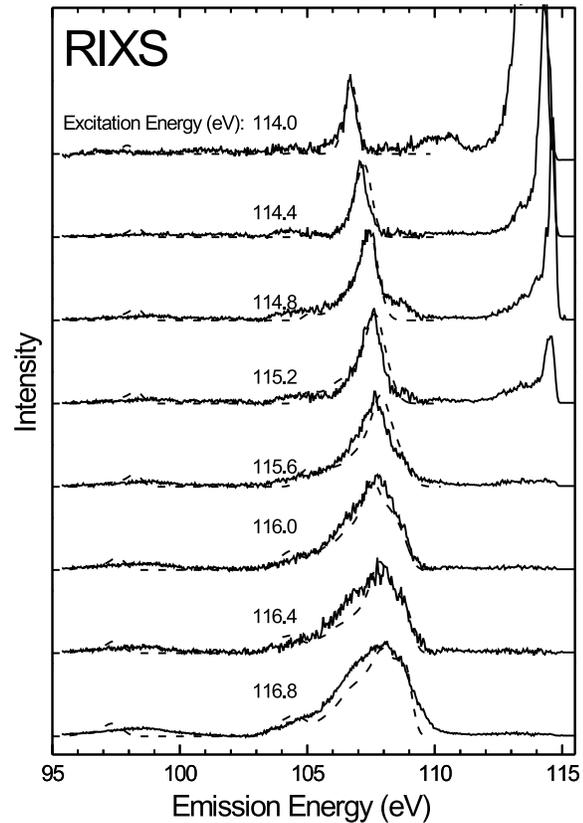


Figure 2: RIXS-spectra of BeS (solid lines) at excitation energies from 114 to 117 eV and simulated spectra based on an LDA-calculation (dashed lines).

sample current). Spectrum d) was taken from a BeO-reference sample, in order to identify the contributions from surface oxidation of the BeS-powder. While a comparison of the BeS- and BeO-spectra reveals a substantial contribution of oxide even for the fresh BeS powder, presumably due to humidity in the Ar atmosphere ($\text{BeS} + \text{H}_2\text{O} \rightarrow \text{BeO} + \text{H}_2\text{S}$), we can nevertheless identify an excitation energy range (114-117 eV), in which only transitions into the conduction band of BeS are possible (gray region in figure 1). This is due to the fact that the band gap of BeO is substantially larger (11 eV direct band gap [3]) than that of BeS.

RIXS

Figure 2 shows the RIXS spectra (solid lines) recorded for the energy regime in which a resonant excitation into the BeS conduction band is possible (114-117 eV). The spectral shapes show an obvious dependance on the excitation energy revealing detailed information about the band structure of BeS. The theory for a detailed interpretation of such effects was first developed by Y. Ma [4] and is briefly outlined here. The excitation and de-excitation of the intermediate (undisturbed) state have to be considered as a combined one-step process which preserves crystal momentum, i.e., both the exciting and

the emitted photon interact with the solid state band structure at the same \vec{k} -vector of the Brillouin zone if one neglects the momentum transfer of the photons [4]. This one-step scattering process can be described by the 'Kramers Heisenberg' formalism. This is generally applied for a description of Raman scattering processes and indicates the visualization of RIXS as an electronic Raman scattering process. In case of a 'disturbing' event during the RIXS process (e.g. phonon scattering), the 'coherence' of the excitation and emission process is lost and the momentum is no longer preserved, i.e. emission appears from almost all regions of the Brillouin zone. In consequence, an experimental XES spectrum is always composed of two components: a *coherent* and an *incoherent* fraction. The latter resembles an emission spectrum excited far above the absorption edge where conduction band states are available almost all over the Brillouin zone. This fact was used to isolate the coherent fraction of the experimental spectra by subtracting a spectrum at high excitation energy (in this case at 150 eV) from the original data.

The coherent part which is shown in figure 2 (solid lines) can be simulated with the help of a three-dimensional band structure calculation. Such simulated RIXS-spectra were computed based on an LDA band structure calculation of BeS [1]. The calculations simulate the RIXS process by taking the full matrix element into account. Thus, they utilize a three-dimensional \vec{k} -space representation of the occupied and unoccupied states as well as the dipole operator, leading to the application of dipole selection rules. Also, the band gap of the LDA band structure was corrected by suitable GW-calculations. The LDA-based results are presented as dashed lines and show good agreement with the experimental data. The broadening of the emission spectrum to lower as well as to higher emission energies with rising excitation energy indicates the dispersion of the valence states typical for a material with indirect band gap. In the present case, the broadening is due to probing the states between the conduction band minimum at the X-point and other high symmetry points (Γ - and W-point). At energies above 117 eV one should be able to excite electrons into unoccupied states at high symmetry points other than the X-point. This should result in strong resonances in the RIXS-spectra. For examinations at these energies, a BeS sample with very low surface oxidation is needed.

CONCLUSIONS

RIXS is a uniquely suited tool for studying the electronic structure of *insulating* BeS powder. By exciting within the band gap of BeO-surface contaminations, it is possible to probe the occupied and unoccupied states of the BeS bulk. A comparison with calculated spectra based on three-dimensional LDA gives very good agreement with the coherent part of the experimental RIXS spectrum.

References

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