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Sulfate speciation analysis using soft x-ray emission spectroscopy

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ABSTRACT: The chemical and electronic structure of fifteen different sulfates is studied using S $L_{2,3}$ soft x-ray emission spectroscopy (XES). Sulfur $L_{2,3}$ XES spectra of sulfates are distinctively different from those of other sulfur compounds, which make XES a powerful technique for sulfate detection. Furthermore, subtle but distinct differences between the spectra of sulfates with different cations are observed, which allow a further differentiation of the specific compound. Most prominently, the position and width of the emission from "S 3s" derived bands systematically varies for different compounds, which can be understood with electronic structure and spectra calculations based on density functional theory.

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INTRODUCTION

Sulfur compounds play important roles in a large number of applied material systems. They are used, e.g., as active materials in lithium-sulfur batteries[1], CdTe- or Cu(In,Ga)(S,Se)$_2$-based thin-film solar cells[2], metal sulfide catalysts[3] (e.g., FeS[4], CuS[5], CoS[6]), and also have high relevance in geology, the coal and oil industries, and many other fields. To understand and optimize these materials, a detailed knowledge of their chemical structure (including secondary phases) is important, in particular as a function of external parameters under operating conditions. This includes surface phases, diffusion processes in multilayer structures, as well as surface stability under operation, and calls for a thorough characterization of the different sulfur-containing phases in the material.

Often, the materials are exposed to environments that contain oxygen and/or humidity, possibly under illumination, which in turn can lead to the formation of sulfate phases. These sulfate phases are important to detect and characterize, as they can impact the device performance. As an example, sulfate formation can be observed for Cu(In,Ga)(S,Se)$_2$ thin-film solar cells after exposure to humidity and light[7-9] in experiments that investigate the long-term stability of the cells. Sulfates also play an important role as part of the electrolyte in a number of electrochemical applications, in which the interaction and absorption of sulfates on the material's surface also need to be taken into account[10].

For a chemical speciation of the involved compounds, photoelectron spectroscopy is a very powerful and surface-sensitive tool that has been intensively employed in the past. Significant core level shifts are observed in S 2p x-ray photoelectron spectroscopy (XPS) for different sulfur compounds, loosely following the formal sulfur oxidation state[11,12]. Particularly, the shift between sulfides and sulfates is found to be on the order of 7 eV. Several groups have also attempted to differentiate between sulfates with different cations using XPS and Auger electron spectroscopy[13-16]. Systematic shifts in S 2p binding and Auger kinetic energies in dependence on the specific sulfate compounds were described[13,15]. However, comparing the different studies and further literature values from the NIST data base[12], the available data are inconsistent. This might be related to the large band gap of sulfates, which can lead to charging in the experiments and also gives a high variability in binding energy depending on the Fermi level position within the band gap. Thus, the modified Auger parameter α' of sulfur, which is not affected by charging and Fermi level variations, was also investigated; unfortunately, it exhibits only small variations between the different sulfates[13,15]. Finally, the XPS valence band spectra of a variety of sulfates and bisulfates were explored[13,14,16]. After careful subtraction of the valence band contributions of the cations, small absolute[13,14,16] and relative[14] energy shifts were observed. However, while such

an analysis works reasonably well with well-defined surfaces of reference compounds, a similar analysis becomes very challenging in a more complex "real-world" system, where many other contributions in the valence region are present.

To analyze the electronic and chemical structure of sulfur compounds with bulk sensitivity, x-ray spectroscopy techniques are a uniquely suited choice. Most commonly, the S K edge has been investigated in the past using both x-ray absorption[17,18] (XAS) and emission spectroscopy[17,19] (XES). In these studies, significant energetic shifts of the absorption edge and the K_α x-ray emission energy are observed, which follow the formal oxidation state of the respective compound[17,19]. *Among* the sulfates, changes are much less pronounced; small energy shifts and changes in spectral shape are observed in XAS, while the energy position as well as the shape of the S K_α XES spectra are mostly independent of the cation[17].

The information content of XES increases significantly as compared to core to core transitions as in S K_α when investigating transitions involving *valence* states, i.e., for S K_β[20–25] (probing states with p symmetry) and S $L_{2,3}$ (probing states with s and d symmetry) XES[7,26,27]. In addition to the observed chemical line shifts, the spectral shapes now vary for different compounds offering high sensitivity for the differentiation of sulfur compounds. Together with the suitable photon attenuation lengths in the soft x-ray range, this makes S $L_{2,3}$ XES a very versatile technique for the investigation of fundamental and applied material systems like thin-film solar cells[7,8,26–29], CdS nanoparticles[30], or CdS/ZnSe superlattices[31].

Already in early pioneering work, the S $L_{2,3}$ XES spectra of sulfates were investigated and found to be very distinct from other sulfide compounds[32–35]. In later studies, improved energy resolution allowed a better distinction between different sulfur species, but the spectra of different sulfates still are very similar[7], as is the case for their K_β spectra[22–25]. This is understandable, given the fact that XES is a very local probe (as defined by the wave function of the initial core hole) and that sulfates are ionic compounds, with the sulfur located in the center of the sulfate ion, i.e., not in direct proximity to the cation partner. Notably, small but distinct energy shifts and changes in line width have been observed in the S K_β XES spectra of different sulfates[21].

In this paper, we present an in-depth experimental and theoretical study of the S $L_{2,3}$ XES spectra of a variety of different sulfates. We show that sulfates not only exhibit very specific S $L_{2,3}$ XES spectra when compared to other sulfur-containing compounds, but that there are distinct differences among the spectra of different sulfates that allow a more detailed and insight-based identification of the particular compound.

EXPERIMENT

Sulfate powders were purchased from Spectrum Chemical (K_2SO_4) and Alfa Aesar (all other sulfates). In most cases, anhydrous materials were available, with the exception of $ZnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$. The powders were unpacked and further processed in a nitrogen-filled glove box. From the pure powders, pellets were pressed using pressures between 50 and 300 bars. The pellets were then mounted on a sample holder using double-sided tape compatible with ultra-high vacuum. The $ZnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$ pellets were afterwards degassed in the rough vacuum of the glove box loading chamber for several hours, presumably losing a good fraction of the water of crystallization. Samples were afterwards transported in a nitrogen-filled container from the glove box to the experimental station and introduced into the loading vacuum chamber of the experimental station with a short air exposure of approx. 10 seconds. The base pressure of the experimental station was better than 10^{-8} mbar.

XES experiments were performed at beamline 8.0.1 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (Berkeley, USA) with the dedicated Solid And Liquid Spectroscopic Analysis (SALSA) roll-up experimental station[36]. Spectra were collected using a high-transmission soft x-ray spectrometer[37] with a variable line space (VLS) grating, achieving a resolving power E/ΔE of about 1500. The energy scales of the beamline and the spectrometer were carefully calibrated using the well-documented absorption energies of highly oriented pyrolytic graphite (HOPG)[38], TiO_2[39], and N_2[40] references. The necessary x-ray absorption scans were measured using the iRIXS endstation[41] at beamline 8.0.1. The detailed calibration procedure is described in the supporting information; it results in an emission energy scale that is precise to better than 0.1 eV in absolute energies and 0.03 eV in relative energies between the measurements.

In earlier studies at beamline 8.0.1, it was observed that prolonged exposure of sulfates (here: $CdSO_4$) can cause radiation damage, and a small fraction of sulfide (here: CdS) was found after several tens of minutes of exposure[42]. For the present study, such possible changes were characterized for $CaSO_4$ after exposing the sample to increasing radiation doses, as described in more detail in the supporting information. For high radiation doses, we find beam-induced sulfite and a small degree of sulfide formation. We avoid this by reducing the exposure time per sample spot to one second by

continuously scanning the sample under the synchrotron beam. While no additional sulfite formation can be observed at these settings, a small sulfite signal remains (visible for the alkali and alkaline earth metal sulfates, as well as $FeSO_4$), which we attribute to sulfite species present in the as-prepared samples.

THEORY

For a detailed understanding of the experimental spectra, we use electronic structure and spectra calculations based on density functional theory (DFT). For this we have approached the sulfates from two "directions": First, the XES spectrum of an isolated SO_4^{2-} ion was calculated using the StoBe-DeMon 3.1 DFT code.[43] Second, the investigated sulfates were described correctly as periodic crystals, and their electronic structure and XES spectra were calculated using the Wien2k program package[44].

StoBe-DeMon is based on self-consistent solutions of the Kohn-Sham DFT equations using Linear Combinations of (Gaussian type) Atomic Orbitals (LCAO). For our XES calculations, we used the Becke Perdew gradient-corrected exchange and correlation functionals[45-47]. The valence electrons were described with triple ζ bases[48] and effective core potentials (ECPs)[49] with 7111/411/1 and 73111/6111/1 basis sets for oxygen and sulfur, respectively. The auxiliary basis sets were comprised of five s and two spd functions for oxygen, and five s and four spd functions for sulfur, to fit the Coulomb and exchange-correlation potentials. The XES transition probabilities were calculated based on dipole matrix elements and the ground state Kohn−Sham eigenstates.

WIEN2k is based on the full-potential augmented plane wave plus local orbitals (APW+lo) method to solve the Kohn-Sham DFT equations[44]. To describe the electronic exchange-correlation effects, the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE)[50] was used. The plane-wave cutoff was defined by setting the product of the smallest atomic sphere radius R_{MT} times the largest K-vector K_{max} to 7. The self-consistent field (SCF) cycle was run with 1000 k points, while 10000 k points were used for calculating the projected density of states (PDOS) and the XES spectra. XES spectra were calculated in the dipole approximation using Fermi's golden rule with the formalism described by Neckel, Schwarz, et al.[51-53] and implemented in WIEN2k. While delivering no absolute emission energies, this "ground state approach" leads to a very good description of the XES spectra, since the core-hole is filled and the valence-hole well screened in the final state[44]. The crystal structures of the investigated sulfates were obtained from the Materials Projects Database[54].

RESULTS AND DISCUSSION

The S $L_{2,3}$ XES spectra of all investigated sulfates are shown in Figure 1 and compared with the spectrum of an isolated SO_4^{2-} as calculated with the StoBe-DeMon package. Due to the ionic nature of sulfates, all spectra contain the same main features, independent of the cation. In the following, we first assign these features based on the calculated spectrum of the tetrahedral SO_4^{2-} ion (point group T_D) in a molecular orbital picture. This is similar to the early work by Dolenko et al.[34], who investigated the electron-excited S K, O K, and S $L_{2,3}$ XES spectra of Li_2SO_4 and $(NH_4)_2SO_4$. The subsequent discussion of the differences between the spectra of the different sulfates will then need to take into account the respective cation and the band nature of the valence states.

Figure 1: S $L_{2,3}$ XES spectra of the investigated fifteen sulfates, normalized to the maximum of the "S 3d" emission line at ~162 eV. An excitation energy of 200.9 eV was used in all cases, with the exception of $ZnSO_4$, for which an excitation energy of 184.5 eV was used. Up to an emission energy of 148 eV, the spectra are also shown magnified by a factor of 5 (red). On the bottom, the calculated spectrum for the SO_4^{2-} ion is shown for comparison. The calculated energy positions and intensities are depicted by red (L_3) and blue (L_2) bars. The green curve is calculated by including a symmetric Voigt-shaped line broadening. Above the calculated spectrum, the isodensity surfaces of selected orbitals are shown (colors denote the sign of the wave function).

The molecular valence orbitals of the SO_4^{2-} ion are formed by hybridization of the O 2s, O 2p, S 3s, S 3p, and S 3d atomic orbitals, forming the $4a_1$, $3t_2$, $5a_1$, $4t_2$, $1e$, $5t_2$, and $1t_1$ molecular valence orbitals. In the S $L_{2,3}$ XES spectrum, only orbitals with an appreciable overlap with the S 2p core levels and s and d symmetry (to obey the dipole selection rules) will be seen, i.e., only those molecular orbitals that have significant contributions from the S 3s and S 3d atomic orbitals.

We find that the calculated XES spectrum gives a reasonable qualitative description of the experimental spectra. Most prominently, the line doublet at ~155 eV can be assigned to transitions involving the $5a_1$ molecular orbital, which, while dominated by O 2s and O 2p (see discussion of Figure 3), also includes contributions from the S 3s atomic orbital and thus is denoted as "S 3s" derived states or bands. Due to the spin-orbit splitting of the S 2p core levels, this one valence state leads to two spectral lines (L_3 and L_2 emission) that are separated by the S 2p spin-orbit splitting of 1.20 eV[55,56] and have an intensity ratio of about 2:1 (L_3:L_2), according to the $2j+1$ multiplicity of the core levels. Generally, all spectral features show this splitting, but only the $5a_1$ line is sufficiently narrow that the two lines are clearly separated.

Similarly, the broad peak at ~162 eV can be assigned to transitions involving the $1e$ and $5t_2$ molecular orbitals, which both have S 3d contributions. We will hence also denote this as "S 3d" derived states/bands in the following. Furthermore, we find two weak and very broad peaks at ~140 eV and ~144 eV (in the experimental spectra), which can be assigned to the $4a_1$ and $3t_2$ molecular orbitals, respectively. The $4a_1$ orbital contains S 3s and O 2s contributions. The $3t_2$ orbital is dominated by O 2s and S 3p contributions, but also has some admixture of S 3d[57]. In a simplified picture, these two orbitals will be denoted as "O 2s" derived states/bands.

While the calculated spectrum of SO_4^{2-} allows the above assignment of the main spectral features and gives a qualitative agreement with the experimental spectra, distinct quantitative differences are found. The SO_4^{2-} calculation shows a significantly lower relative "S 3d" intensity than is found in the respective spectral region of the experimental spectra. Similarly, the intensity of the $3t_2$ feature at ~144 eV, relative to the $4a_1$ feature at ~140 eV, is stronger in the experimental spectrum than predicted for the ion.

Most strikingly, the experiment shows distinct differences between the spectra of the different sulfates, which naturally cannot be explained by the simplified picture of an isolated SO_4^{2-} ion. We find that the emission energy and widths of the "S 3s" emission lines vary significantly (the corresponding values are given in Table S1 in the supporting information). Furthermore, more subtle shape changes can be observed for the "S 3d" and the "O 2s" emission. The intensity ratios of these features also vary for the different compounds, most prominently for Cs_2SO_4 and $BaSO_4$, where it is strongly reduced. All these changes create a powerful tool to distinguish the different sulfates. They can only be understood by correctly describing the compounds as crystalline solids with different cations, as will be discussed in the following.

While the variations of the relative intensities of the "S 3d" and "O 2s" emission could contain information on variations in the hybridization between the S and O bands, we find that in the present case the intensity changes are dominated by different degrees of self-absorption, which describes the absorption of the incoming and outgoing photons[58,59]. This modifies the XES intensity by a factor c_λ, which depends on the absorption lengths of the incoming (λ_i) and outgoing photons (λ_{out}) in the following way:

$$c_\lambda = \frac{\cos\theta_i}{\lambda_i} \int_0^\infty \exp\left(\frac{-x\cos\theta_i}{\lambda_i}\right) \exp\left(\frac{-x\cos\theta_{out}}{\lambda_{out}}\right) dx$$

$$\dot{c} \; \frac{\lambda_{out}}{\lambda_{out} + \frac{\cos\theta_{out}}{\cos\theta_i}\lambda_i}$$

where θ_i and θ_{out} are the angles between the sample surface normal and the directions of the in- and out-going photons, respectively. For the geometry in our experiment ($\theta_i = 0°$ and $\theta_{out} = 45°$), c_λ becomes $\lambda_{out}/(\lambda_{out} + \sqrt{2}\lambda_i)$. Both, λ_i and λ_{out}, are different for the different sulfates; in addition, λ_{out} also varies as a function of emission energy across the spectrum. In the case of Cs_2SO_4 and $BaSO_4$, λ_{out} is significantly smaller at ~140 eV than at 162 eV, which leads to the observed suppression of the "O 2s" emission. Using tabulated values for λ[60], this is quantified for all samples in Figure 2, where the intensity ratio

between the "O 2s" and the "S 3d" emissions is plotted as a function of $c_\lambda(\text{O 2s})/c_\lambda(\text{S 3d})$.

Figure 2: Blue data points represent the intensity ratio of the "O 2s" and "S 3d" emission lines as a function of $c_\lambda(\text{O 2s})/c_\lambda(\text{S 3d})$. The red line shows a linear fit of the data (including the origin). Next to the data points, the corresponding compounds are given.

In most cases, λ_{out} increases as a function of emission energy (i.e., from 140 to 162 eV) and $c_\lambda(\text{O 2s})/c_\lambda(\text{S 3d})$ is smaller than 1, reducing the relative intensity of the "O 2s" emission. The exceptions are Rb$_2$SO$_4$ and SrSO$_4$, for which $\lambda_{out}(\text{O 2s})$ is *larger* than $\lambda_{out}(\text{S 3d})$, due to the Cooper minimum in the ionization cross section of the nearby Rb and Sr M$_{3,4}$ absorption edges[61]. We find that the data points all lie close to a line that includes the origin, which suggests that self-absorption is indeed the dominating factor causing the observed intensity behavior. The slope of this line (0.69) then corresponds to the corrected average intensity ratio of the "O 2s" and "S 3d" emission in the investigated sulfates. We note that this is a "matrix effect" – it does not primarily depend on the character of the emitting atom (or sulfate ion) and its immediate chemical environment, but rather on the composition of the "surroundings" that the outgoing photon needs to transverse on its way to the surface and the XES detector. Overall, the influence of self-absorption is too strong to allow to extract information on variations in the hybridization between the S and O bands for the different sulfates. These variations can be much better studied by K$_\beta$ XES where self-absorption plays a much smaller role. However, no variations in the relative intensity of the "O 2s" derived band is mentioned by Sugiura or visible in the data of his careful study on 12 different sulfates[21], indicating that this effect is indeed small.

For the further discussion of the spectra, we will now switch from describing the electronic structure with the simplified picture of the SO$_4^{2-}$ ion to the correct description of a crystal that also includes the electronic impact of the respective cations. To do this, we have calculated the electronic structure and the XES spectra of the investigated compounds using Wien2k. In the following, we will use the calculations in Figure 3 to exemplarily analyze the S L$_{2,3}$ emission of CaSO$_4$. At the bottom of the graph, the calculated band structure of CaSO$_4$ is shown with the energy relative to the valence band maximum (VBM) on the abscissa and the position in reciprocal (k-) space on the ordinate. The k-resolved band structures for all sulfates investigated in this paper are shown in the SI (Figures S5, S6, and S7). The bands show a comparably small dispersion, owing to the ionic nature of the crystal, and are bundled in small groups of bands that can be related/assigned to the corresponding states in the molecular SO$_4^{2-}$ picture discussed above.

Above the band structure, the electronic density of states projected onto the three atomic species of the compound ("PDOS") is depicted. We find that the PDOS is dominated by the contribution of the oxygen atoms. In the region of the upper valence bands (between 10 and 0 eV), only a very small sulfur and nearly no calcium contribution is present. At higher binding energies, the situation is similar, but significant contributions from calcium are visible that can be attributed to Ca 3p states that form a band with the 3t$_2$ states of the sulfate ion. Above the PDOS, the (small) contribution from S ("S PDOS") is shown magnified and further projected onto their orbital angular momentum (s, p, and d). The situation is analog to the situation of the molecular orbitals of SO$_4^{2-}$ discussed above, reflecting the sulfur atomic orbital contributions to the different bands (i.e., S 3s contributing to the bands around 8.5 eV and 23 eV, S 3p to the ones around 6 eV and 19 eV, and S 3d to the ones around 3 eV). From this, we can calculate an L$_3$ XES spectrum, shown in red above ("calc. (L$_3$)"). The L$_2$ contribution can be included by adding a scaled (x0.5) and shifted (by 1.2 eV) version of the L$_3$ spectrum. Here, the result was convoluted with Voigt functions to account for experimental and lifetime broadening ("calc. (L$_{2,3}$ with broadening)"); the Gaussian widths were set to the experimental resolution (0.1 eV) and the Lorentzian widths were adjusted to fit the experimental spectrum. We find a good agreement between the calculated and experimental spectra. This calculations now includes the dispersive nature of the bands and is in particular improved with respect to that of the SO$_4^{2-}$ calculation in terms of relative intensities and shapes of the spectral features. To correctly reproduce the relative energy separations, the

energy scale of the calculated spectrum had to be stretched by a factor of 1.06.

On the low energy side of the "S 3s" emission, we find a small contribution from $CaSO_3$ contamination (labeled in Figure 3), which is discussed in the experimental section and the supporting information.

Figure 3: Analysis of the S $L_{2,3}$ XES spectra of $CaSO_4$ and comparison with K_β XES. Lower panel from bottom to top: Calculated k-resolved band structure, density of states projected onto the different atomic species (PDOS), density of states projected onto s, p, and d symmetry for the sulfur atom (S PDOS), calculated S L_3 emission spectrum, calculated S $L_{2,3}$ emission spectrum including experimental and lifetime broadening, and the experimental spectrum (top, black). For better visibility, the S PDOS and the calculated L_3 spectrum is shown magnified by a factor of 3 for energies smaller than 22 eV (relative to the VBM). Note that the energy axis of the calculation was stretched by a factor of 1.06 relative to the experimental energy axis for optimal alignment. Upper panel: Experimental (black, digitized from Ref.[21]) and calculated (red, energy rel. VBM) S K_β XES spectrum of $CaSO_4$.

For comparison, the top panel of Figure 3 depicts the experimental (black, digitized from Ref.[21]) and our calculated (red) S K_β XES spectrum of $CaSO_4$. In contrast and complementary to S $L_{2,3}$ XES, which probes bands with s and d symmetry, the bands with p symmetry are probed by S K_β XES. This leads to two emission lines that can be attributed to the "O2s"/"3t$_2$" (hybridized with S 3p states) and "S 3p"/"4t$_2$" derived bands at 2453.8 eV and 2467.4 eV[21], respectively. The spectrum is well reproduced by our calculation (energy scales were aligned at the "S3p" peak and the scale of the calculation was stretched by a factor of 1.06).

The spectra of all investigated sulfates were calculated with the same procedure as described for $CaSO_4$ – Figure 4 gives a comparison of the experimental and calculated spectra. For each pair, the calculated spectra were shifted to align the emission energy of the "S 3d" derived bands (at ~162 eV) with that of the experiment. For all calculated spectra, the emission energy scale was stretched by the same factor of 1.06. In most cases, the calculation accurately reproduces the relative shift of the "S 3s" emission, which shifts by about 1 eV from $CdSO_4$ (L_3 at 154.65 eV) to Rb_2SO_4 (L_3 at 155.71 eV). This demonstrates that the lines shifts are related to the band structure of the specific compound, i.e., involving the specific cation.

In addition to the spectra, Figure 4 shows the DOS projected onto the cation for each compound, which allows to get an intuitive qualitative view of the observed "S 3s" line shifts. Whenever the cation contributes with significant PDOS below/above the "S 3s" derived band, the latter is shifted up/down, i.e., towards/away from the VBM. The closer the cation-induced state to the "S 3s" derived band, the stronger the shift. This can be nicely seen for the alkali and alkaline earth metal sulfates, where the p levels of the outer shell of the cation gradually approach the "S 3s" derived band, which also gradually shifts upwards. Eventually, in the case of Cs_2SO_4, the cation p levels cross the "S 3s" derived band, which then appears at a lower emission energy than for all other alkaline metal sulfates. Likewise, the lowest "S 3s" emission energy is observed for $CdSO_4$ where the "Cd 4d" derived band is just above the "S 3s" derived band.

In some cases, the cation-derived band hybridizes with the "S 3s" derived band, giving a wave function overlap with the S 2p core level, and consequently directly showing up in the S $L_{2,3}$ XES spectra. We observe this for Rb_2SO_4 and $BaSO_4$ as a shoulder on the low emission energy side, and for Cs_2SO_4, $ZnSO_4$, and $CdSO_4$ as additional intensity on the high emission energy side (see magnified regions in Figure 4). Note that for $ZnSO_4$ and, to a lesser extent, $CdSO_4$, the calculation places the "Zn 3d" and "Cd 4d" contributions at higher emission energies than we observe in the experiment. This is caused by an underestimation of the calculated binding energy

of d bands and has been discussed for other compounds earlier[62-65].

The energy shifts of the "S 3s" emission line thus create a sensitive tool to distinguish between different sulfate compounds. In practical applications, either the absolute emission energy of the "S 3s" emission line (as listed in Table S1), or the energy difference between the "S 3s" and the "S 3d" emission lines can be used to differentiate between different sulfates. Due to its narrow line width, the "S 3s" position can be determined more precisely (in particular for data with lower signal-to-noise ratio than presented here), but a good absolute energy calibration is required to compare with the values in Table S1. Nevertheless, this can be easily facilitated by measuring a suitable sulfate reference (e.g., $CaSO_4$) immediately before or after the sample that contains the unknown sulfate compound.

Figure 4: Experimental (black) and calculated (red) S $L_{2,3}$ XES spectra of a) alkali metal sulfates, b) alkaline earth metal sulfates, and c) other sulfates. Below each calculated spectrum, the DOS projected onto the respective cation is shown in blue. In the cases where the cation contributes with a significant PDOS outside of the plotted energy window, the corresponding state is given, together with the energetic distance (dE) to the "S 3s" band. To better visualize line shifts, vertical dashed lines mark the position of the "S 3s" and "S 3d" emission of Li_2SO_4.

Similar emission energy shifts have also been observed for the features in the K_β XES of different sulfates[21] and it is worth comparing these with the shifts of the "S 3s" feature in the $L_{2,3}$ emission. As shown in Figure S3, we find a linear correlation between the shifts of the "3s" feature of the $L_{2,3}$ emission and the "S 3p" feature of the K_β emission. The shifts of the "3s" feature are about double that of the "3p" feature, which together with the much smaller line width, make S $L_{2,3}$ the more sensitive tool for sulfate speciation. In analogy to the shifts of the "3s" S $L_{2,3}$ emission, the shifts of the "3p" feature in the K_β emission are cause by the influence of the electronic states of the cation on the band structure, For all sulfates in which data was available for both S $L_{2,3}$ and S K_β, this shifts the "S 3s" and "S 3p" derived bands (and thus emission lines) in the same direction as is visible in the band structure calculations presented in Fig. S5, S6, and S7. In the case of Cs_2SO_4 and $CdSO_4$, a different behavior is expected due to the position of the "Cs 5p" respectively the "Cd 4d" derived bands just above the "S 3s" derived band but no corresponding Cs_2SO_4 or $CdSO_4$ K_β data was available to us.

As mentioned above, we observe significant differences of the line widths of the "S 3s" emission lines for the different sulfates, which are shown in Figure 5. Factors that contribute to the line width are the experimental broadening, the band width of the "S 3s" derived band, and the lifetime broadening. While the experimental broadening is identical for all samples, the band width and the lifetime broadening can vary significantly. To understand this, we assume that the ("S 3 s")$^{-1}$ final state decays mainly through Auger transitions. With a simple phase-space

argument, more Auger channels become available for higher binding energies of the "S 3s" derived band (assuming that the bands above do not change considerably). This reduces the lifetime of the ("S 3s")$^{-1}$ state, leading to an increase in lifetime broadening. In fact, when plotting the width of the "S 3s" emission as a function of its emission energy in Figure 5, we find a decrease of the line width with increasing emission energy for most of the sulfates, which can even be described with a linear relationship (as indicated by the red fitted line). The line widths for the compounds that do not follow this trend ($FeSO_4$, $In_2(SO_4)_3$, $SnSO_4$, $BaSO_4$, and Rb_2SO_4) exclusively lay *above* the red line, which suggests that other broadening effects play a significant role in their case. In fact, all of these compounds exhibit a significantly stronger dispersion for the "S 3s" derived band than the other compounds (see Figures S5, S6, and S7). This is caused by a stronger hybridization with states contributed by the cation that are close in energy for these compounds and broadens the "S 3s" emission line. Again, similar changes in the line width of the "S 3p" emission in K_β XES has been observed[21] and we compare with this data in Fig. S4. A linear correlation between the FWHM of the "S 3s" → S 2p$_{3/2}$ and "S 3p" → S 1s transitions is observed, with the exception of the data points for $BaSO_4$, Rb_2SO_4, and $FeSO_4$, where the "S 3s" bands are affected by hybridization with cation bands.

CONCLUSIONS

We use a series of high-quality S $L_{2,3}$ XES spectra of fifteen different sulfates to describe and understand their spectral specificity, hence creating a unique tool for sulfate differentiation. The overall spectral signature of the sulfates is very unique, as compared to other sulfur compounds. Comparing with the calculated spectrum of an isolated SO_4^- ion, the main spectral features can be assigned based on a molecular orbital model. We find distinct differences between the spectra of the different sulfates, namely changes in relative peak intensities and the widths and positions of the "S 3s" derived emission line. These changes can be attributed to self-absorption, differences in valence hole lifetimes, and, based on the comparison with calculated spectra of the individual compounds, energy shifts of the "S 3s" derived band, respectively. In particular, the energy shifts of the "S 3s" derived band make S $L_{2,3}$ XES a direct and sensitive tool for the differentiation of sulfate species in a large variety of fundamental, natural, and applied material systems.

Figure 5: Line width of the "S 3s" → S 2p$_{3/2}$ transition as a function of its emission energy (blue filled circles). The compounds are given next to the data points. The red line shows a fit illustration of the linear dependency between width and line position excluding the data points of $FeSO_4$, $In_2(SO_4)_3$, $SnSO_4$, $BaSO_4$, and Rb_2SO_4.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
The supporting information gives details on the spectrometer and beamline calibration procedure, the characterization and mitigation of beam-induced spectral changes, a table summarizing emission energies, intensities, and widths, and the k-resolved electronic band structures of the investigated sulfates (PDF).

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REFERENCES

(1) Li, T.; Bai, X.; Gulzar, U.; Bai, Y.-J.; Capiglia, C.; Deng, W.; Zhou, X.; Liu, Z.; Feng, Z.; Zaccaria, R. P. A Comprehensive Understanding of Lithium–Sulfur Battery Technology. Adv. Funct. Mater. 2019, 29 (32), 1901730. https://doi.org/10.1002/adfm.201901730.

(2) Powalla, M.; Paetel, S.; Ahlswede, E.; Wuerz, R.; Wessendorf, C. D.; Magorian Friedlmeier, T. Thin-film Solar Cells Exceeding 22% Solar Cell Efficiency: An Overview on CdTe-, Cu(In,Ga)Se2-, and Perovskite-Based Materials. Appl. Phys. Rev. 2018, 5 (4), 041602. https://doi.org/10.1063/1.5061809.

(3) Wang, G.; Li, C.; Shan, H. Highly Efficient Metal Sulfide Catalysts for Selective Dehydrogenation of Isobutane to

Isobutene. ACS Catal. 2014, 4 (4), 1139–1143. https://doi.org/10.1021/cs5000944.

(4) Wang, W.; Xu, R.; Yu, B.; Wang, X.; Feng, S. Electrochemical Fabrication of FeS x Films with High Catalytic Activity for Oxygen Evolution. RSC Adv. 2019, 9 (55), 31979–31987. https://doi.org/10.1039/C9RA05343C.

(5) Xu, W.; Zhu, S.; Liang, Y.; Li, Z.; Cui, Z.; Yang, X.; Inoue, A. Nanoporous CuS with Excellent Photocatalytic Property. Sci. Rep. 2015, 5 (1), 18125. https://doi.org/10.1038/srep18125.

(6) Sun, Y.; Liu, C.; Grauer, D. C.; Yano, J.; Long, J. R.; Yang, P.; Chang, C. J. Electrodeposited Cobalt-Sulfide Catalyst for Electrochemical and Photoelectrochemical Hydrogen Generation from Water. J. Am. Chem. Soc. 2013, 135 (47), 17699–17702. https://doi.org/10.1021/ja4094764.

(7) Heske, C.; Groh, U.; Weinhardt, L.; Fuchs, O.; Holder, B.; Umbach, E.; Bostedt, C.; Terminello, L. J.; Zweigart, S.; Niesen, T. P.; Karg, F. Damp-Heat Induced Sulfate Formation in Cu(In,Ga)(S,Se)2-Based Thin Film Solar Cells. Appl. Phys. Lett. 2002, 81 (24), 4550. https://doi.org/10.1063/1.1525884.

(8) Heske, C.; Groh, U.; Fuchs, O.; Weinhardt, L.; Umbach, E.; Schedel-Niedrig, T.; Fischer, C. H.; Lux-Steiner, M. C.; Zweigart, S.; Niesen, T. P.; Karg, F. Monitoring Chemical Reactions at a Liquid-Solid Interface: Water on CuIn(S,Se)2 Thin Film Solar Cell Absorbers. J. Chem. Phys. 2003, 119 (20), 10467. https://doi.org/10.1063/1.1627328.

(9) Reichardt, J.; Bär, M.; Grimm, A.; Kotschau, I.; Lauermann, I.; Sokoll, S.; Lux-Steiner, M. C.; Fischer, C. H.; Heske, C.; Weinhardt, L.; Fuchs, O.; Jung, C.; Guclat, W.; Niesen, T. P.; Karg, F. Inducing and Monitoring Photoelectrochemical Reactions at Surfaces and Buried Interfaces in Cu(In,Ga)(S,Se)2 Thin-Film Solar Cells. Appl. Phys. Lett. 2005, 86 (17). https://doi.org/10.1063/1.1906309.

(10) Liang, Y.; Sherwood, P. M. A.; Paul, D. K. Valence and Core Photoemission of the Films Formed Electrochemically on Nickel in Sulfuric Acid. J. Chem. Soc. Faraday Trans. 1994, 90 (9), 1271–1278. https://doi.org/10.1039/FT9949001271.

(11) Fantauzzi, M.; Elsener, B.; Atzei, D.; Rigoldi, A.; Rossi, A. Exploiting XPS for the Identification of Sulfides and Polysulfides. RSC Adv. 2015, 5 (93), 75953–75963. https://doi.org/10.1039/C5RA14915K.

(12) Naumkin, A.; Kraut-Vass, A.; Gaarenstroom, S.; Powell, C. NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database Number 20, National Institute of Standards and Technology http://dx.doi.org/10.18434/T4T88K.

(13) Wahlqvist, M.; Shchukarev, A. XPS Spectra and Electronic Structure of Group IA Sulfates. J. Electron Spectrosc. Relat. Phenom. 2007, 156–158, 310–314. https://doi.org/10.1016/j.elspec.2006.11.032.

(14) Audi, A. A.; Sherwood, P. M. A. X-Ray Photoelectron Spectroscopic Studies of Sulfates and Bisulfates Interpreted by Xα and Band Structure Calculations. Surf. Interface Anal. 2000, 29 (4), 265–275. https://doi.org/10.1002/(SICI)1096-9918(200004)29:4<265::AID-SIA739>3.0.CO;2-3.

(15) Yu, X.-R.; Liu, F.; Wang, Z.-Y.; Chen, Y. Auger Parameters for Sulfur-Containing Compounds Using a Mixed Aluminum-Silver Excitation Source. J. Electron Spectrosc. Relat. Phenom. 1990, 50 (2), 159–166. https://doi.org/10.1016/0368-2048(90)87059-W.

(16) Fantauzzi, M.; Rigoldi, A.; Elsener, B.; Atzei, D.; Rossi, A. A Contribution to the Surface Characterization of Alkali Metal Sulfates. J. Electron Spectrosc. Relat. Phenom. 2014, 193, 6–15. https://doi.org/10.1016/j.elspec.2014.01.007.

(17) Alonso Mori, R.; Paris, E.; Giuli, G.; Eeckhout, S. G.; Kavčič, M.; Žitnik, M.; Bučar, K.; Pettersson, L. G. M.; Glatzel, P. Electronic Structure of Sulfur Studied by X-Ray Absorption and Emission Spectroscopy. Anal. Chem. 2009, 81 (15), 6516–6525. https://doi.org/10.1021/ac900970z.

(18) Flemmig, B.; Modrow, H.; Hallmeier, K. H.; Hormes, J.; Reinhold, J.; Szargan, R. Sulfur in Different Chemical Surroundings – S K XANES Spectra of Sulfur-Containing Heterocycles and Their Quantum-Chemically Supported Interpretation. Chem. Phys. 2001, 270 (3), 405–413. https://doi.org/10.1016/S0301-0104(01)00415-3.

(19) Sánchez, E.; Deluigi, M. T.; Castellano, G. Binding Effects in Sulfur Kα and Kβ X-Ray Emission Spectra. J. Anal. At. Spectrom. 2019, 34 (2), 274–283. https://doi.org/10.1039/C8JA00345A.

(20) Yasuda, S.; Kakiyama, H. Chemical Effects in X-Ray Kα and Kβ Emission Spectra of Sulfur in Organic Compounds. Spectrochim. Acta Part Mol. Spectrosc. 1979, 35 (5), 485–493. https://doi.org/10.1016/0584-8539(79)80164-6.

(21) Sugiura, C. S. C. Kβ X-Ray Emission and K X-Ray Absorption Spectra of Sulfur in Sulfate Compounds. Jpn. J. Appl. Phys. 1993, 32 (8R), 3509. https://doi.org/10.1143/JJAP.32.3509.

(22) Yarmoshenko, Yu. M.; Trofimova, V. A.; Kurmaev, E. Z.; Slater, P. R.; Greaves, C. X-Ray Emission Spectra of YSr2Cu3O7−δ Containing Sulphate and Phosphate Groups. Phys. C Supercond. 1994, 224 (3), 317–320. https://doi.org/10.1016/0921-4534(94)90268-2.

(23) Yarmoshenko, Yu. M.; Korotin, M. A.; Trofimova, V. A.; Galakhov, V. R.; Elokhina, L. V.; Kurmaev, E. Z.; Uhlenbrock, St.; Neumann, M.; Slater, P. R.; Greaves, C. Electronic Structure of Cuprates Containing Sulfur and Phosphorus Oxyanions. Phys. Rev. B 1995, 52 (16), 11830–11836. https://doi.org/10.1103/PhysRevB.52.11830.

(24) Holden, W. M.; Jahrman, E. P.; Govind, N.; Seidler, G. T. Probing Sulfur Chemical and Electronic Structure with Experimental Observation and Quantitative Theoretical Prediction of Kα and Valence-to-Core Kβ X-Ray Emission Spectroscopy. J. Phys. Chem. A 2020, 124 (26), 5415–5434. https://doi.org/10.1021/acs.jpca.0c04195.

(25) Qureshi, M.; H. Nowak, S.; I. Vogt, L.; H. Cotelesage, J. J.; V. Dolgova, N.; Sharifi, S.; Kroll, T.; Nordlund, D.; Alonso-Mori, R.; Weng, T.-C.; J. Pickering, I.; N. George, G.; Sokaras, D. Sulfur Kβ X-Ray Emission Spectroscopy: Comparison with Sulfur K-Edge X-Ray Absorption Spectroscopy for Speciation of Organosulfur Compounds. Phys. Chem. Chem. Phys. 2021, 23 (8), 4500–4508. https://doi.org/10.1039/D0CP05323F.

(26) Weinhardt, L.; Hauschild, D.; Heske, C. Surface and Interface Properties in Thin-Film Solar Cells: Using Soft X-Rays and Electrons to Unravel the Electronic and Chemical Structure. Adv. Mater. 2019, 31 (26), 1806660. https://doi.org/10.1002/adma.201806660.

(27) Duncan, D. A.; Kephart, J. M.; Horsley, K.; Blum, M.; Mezher, M.; Weinhardt, L.; Häming, M.; Wilks, R. G.; Hofmann, T.; Yang, W.; Bär, M.; Sampath, W. S.; Heske, C. Characterization of Sulfur Bonding in CdS:O Buffer Layers for CdTe-Based Thin-Film Solar Cells. ACS Appl. Mater. Interfaces 2015, 7 (30), 16382–16386. https://doi.org/10.1021/acsami.5b03503.

(28) Weinhardt, L.; Gleim, T.; Fuchs, O.; Heske, C.; Umbach, E.; Bär, M.; Muffler, H. J.; Fischer, C. H.; Lux-Steiner, M. C.; Zubavichus, Y.; Niesen, T. P.; Karg, F. CdS and

Cd(OH)2 Formation during Cd Treatments of Cu(In,Ga)(S,Se)2 Thin-Film Solar Cell Absorbers. Appl Phys Lett 2003, 82 (4), 571. https://doi.org/10.1063/1.1539553.

(29) Hauschild, D.; Mezher, M.; Schnabel, T.; Spiering, S.; Kogler, W.; Carter, J.; Blum, M.; Yang, W.; Ahlswede, E.; Heske, C.; Weinhardt, L. Intermixing at the InxSy/Cu2ZnSn(S,Se)4 Heterojunction and Its Impact on the Chemical and Electronic Interface Structure. ACS Appl. Energy Mater. 2019, 2 (6), 4098–4104. https://doi.org/10.1021/acsaem.9b00263.

(30) Barglik-Chory, C.; Buchold, D.; Schmitt, M.; Kiefer, W.; Heske, C.; Kumpf, C.; Fuchs, O.; Weinhardt, L.; Stahl, A.; Umbach, E.; Lentze, M.; Geurts, J.; Müller, G. Synthesis, Structure and Spectroscopic Characterization of Water-Soluble CdS Nanoparticles. Chem. Phys. Lett. 2003, 379 (5–6), 443–451. https://doi.org/10.1016/j.cplett.2003.08.068.

(31) Heske, C.; Groh, U.; Fuchs, O.; Weinhardt, L.; Umbach, E.; Grun, M.; Petillon, S.; Dinger, A.; Klingshirn, C.; Szuszkiewicz, W.; Fleszar, A. Studying the Local Chemical Environment of Sulfur Atoms at Buried Interfaces in CdS/ZnSe Superlattices. Appl. Phys. Lett. 2003, 83 (12), 2360. https://doi.org/10.1063/1.1609235.

(32) Siegbahn, M.; Magnusson, T. Zur Spektroskopie der ultraweichen Röntgenstrahlung. II. Z. Für Phys. 1934, 87 (5), 291–309. https://doi.org/10.1007/BF01333423.

(33) Fischer, D. W.; Baun, W. L. Effect of Chemical Combination on the Soft X-Ray L Emission Spectra of Potassium, Chlorine, and Sulfur Using a Stearate Soap Film Crystal. Anal. Chem. 1965, 37 (7), 902–906. https://doi.org/10.1021/ac60226a029.

(34) Dolenko, G. N.; Sadovskii, A. P.; Mazalov, L. N.; Gluskin, E. S.; Kochubei, V. A. X-Ray-Spectral Investigation of Sulfate Ion. J. Struct. Chem. 1974, 15 (3), 357–361. https://doi.org/10.1007/BF00747039.

(35) Taniguchi, K.; Henke, B. L. Sulfur L II,III Emission Spectra and Molecular Orbital Studies of Sulfur Compounds. J. Chem. Phys. 1976, 64 (7), 3021–3035. https://doi.org/10.1063/1.432563.

(36) Blum, M.; Weinhardt, L.; Fuchs, O.; Bär, M.; Zhang, Y.; Weigand, M.; Krause, S.; Pookpanratana, S.; Hofmann, T.; Yang, W.; Denlinger, J. D.; Umbach, E.; Heske, C. Solid and Liquid Spectroscopic Analysis (SALSA) - a Soft x-Ray Spectroscopy Endstation with a Novel Flow-through Liquid Cell. Rev. Sci. Instrum. 2009, 80 (12). https://doi.org/10.1063/1.3257926.

(37) Fuchs, O.; Weinhardt, L.; Blum, M.; Weigand, M.; Umbach, E.; Bär, M.; Heske, C.; Denlinger, J.; Chuang, Y. D.; McKinney, W.; Hussain, Z.; Gullikson, E.; Jones, M.; Batson, P.; Nelles, B.; Follath, R. High-Resolution, High-Transmission Soft x-Ray Spectrometer for the Study of Biological Samples. Rev. Sci. Instrum. 2009, 80 (6), 63103. https://doi.org/10.1063/1.3133704.

(38) Watts, B.; Ade, H. A Simple Method for Determining Linear Polarization and Energy Calibration of Focused Soft X-Ray Beams. J. Electron Spectrosc. Relat. Phenom. 2008, 162 (2), 49–55. https://doi.org/10.1016/j.elspec.2007.08.008.

(39) Lusvardi, V. S.; Barteau, M. A.; Chen, J. G.; Eng, J.; Frühberger, B.; Teplyakov, A. An NEXAFS Investigation of the Reduction and Reoxidation of TiO2(001). Surf. Sci. 1998, 397 (1–3), 237. https://doi.org/16/S0039-6028(97)00740-1.

(40) Kato, M.; Morishita, Y.; Oura, M.; Yamaoka, H.; Tamenori, Y.; Okada, K.; Matsudo, T.; Gejo, T.; Suzuki, I. H.; Saito, N. Absolute Photoionization Cross Sections with Ultra-High Energy Resolution for Ar, Kr, Xe and N2 in Inner-Shell Ionization Regions. J. Electron Spectrosc. Relat. Phenom. 2007, 160 (1–3), 39–48. https://doi.org/10.1016/j.elspec.2007.06.003.

(41) Qiao, R.; Li, Q.; Zhuo, Z.; Sallis, S.; Fuchs, O.; Blum, M.; Weinhardt, L.; Heske, C.; Pepper, J.; Jones, M.; Brown, A.; Spucces, A.; Chow, K.; Smith, B.; Glans, P.-A.; Chen, Y.; Yan, S.; Pan, F.; Piper, L. F. J.; Denlinger, J.; Guo, J.; Hussain, Z.; Chuang, Y.-D.; Yang, W. High-Efficiency in Situ Resonant Inelastic x-Ray Scattering (IRIXS) Endstation at the Advanced Light Source. Rev. Sci. Instrum. 2017, 88 (3), 033106. https://doi.org/10.1063/1.4977592.

(42) Heske, C.; Groh, U.; Fuchs, O.; Umbach, E.; Franco, N.; Bostedt, C.; Terminello, L. J.; Perera, R. C. C.; Hallmeier, K. H.; Preobrajenski, A.; Szargan, R.; Zweigart, S.; Riedl, W.; Karg, F. X-Ray Emission Spectroscopy of Cu(In,Ga)(S,Se)2-Based Thin Film Solar Cells: Electronic Structure, Surface Oxidation, and Buried Interfaces. Phys. Status Solidi A 2001, 187 (1), 13. https://doi.org/10.1002/1521-396X(200109)187:1<13::AID-PSSA13>3.0.CO;2-D.

(43) Hermann, K.; Pettersson, L. G. M.; Casida, M. E.; Daul, C.; Goursot, A.; Koester, A.; Proynov, E.; St-Amant, A.; Salahub, D. R. Contributing Authors: Carravetta, V.; Duarte, H.; Friedrich, C.; Godbout, N.; Guan, J.; Jamorski, C.; Leboeuf, M.; Leetmaa, M.; Nyberg, M.; Patchkovskii, S.; Pedocchi, L.; Sim, F.; Triguero, L.; Vela, A. StoBe-DeMon Version 3.1 (2011).

(44) Blaha, P.; Schwarz, K.; Tran, F.; Laskowski, R.; Madsen, G. K. H.; Marks, L. D. WIEN2k: An APW+lo Program for Calculating the Properties of Solids. J. Chem. Phys. 2020, 152 (7), 074101. https://doi.org/10.1063/1.5143061.

(45) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A 1988, 38 (6), 3098–3100. https://doi.org/10.1103/PhysRevA.38.3098.

(46) Perdew, J. P. Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. Phys. Rev. B 1986, 33 (12), 8822–8824. https://doi.org/10.1103/PhysRevB.33.8822.

(47) Perdew, J. P. Erratum: Density-Functional Approximation for the Correlation Energy of the Inhomogeneous Electron Gas. Phys. Rev. B 1986, 34 (10), 7406–7406. https://doi.org/10.1103/PhysRevB.34.7406.

(48) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. Optimization of Gaussian-Type Basis Sets for Local Spin Density Functional Calculations. Part I. Boron through Neon, Optimization Technique and Validation. Can. J. Chem. 1992, 70 (2), 560–571. https://doi.org/10.1139/v92-079.

(49) Pettersson, L. G. M.; Wahlgren, U.; Gropen, O. Effective Core Potential Parameters for First- and Second-row Atoms. J. Chem. Phys. 1987, 86 (4), 2176–2184. https://doi.org/10.1063/1.452115.

(50) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77 (18), 3865–3868. https://doi.org/10.1103/PhysRevLett.77.3865.

(51) Neckel, A.; Schwarz, K.; Eibler, R.; Rastl, P.; Weinberger, P. Elektronische Struktur und Valenzbandspektren einiger metallischer Hartstoffe. In Siebentes Kolloquium über metallkundliche Analyse mit besonderer Berücksichtigung der Elektronenstrahl-Mikroanalyse; Zacherl, M. K., Ed.; Mikrochimica Acta; Springer: Vienna, 1975; pp 257–291. https://doi.org/10.1007/978-3-7091-8422-6_20.

(52) Schwarz, K.; Neckel, A.; Nordgren, J. On the X-Ray Emission Spectra from FeAl. J. Phys. F Met. Phys. 1979, 9 (12), 2509–2521. https://doi.org/10.1088/0305-4608/9/12/023.

(53) Schwarz, K.; Wimmer, E. Electronic Structure and X-Ray Emission Spectra of YS in Comparison with NbC. J. Phys. F Met. Phys. 1980, 10 (5), 1001–1012. https://doi.org/10.1088/0305-4608/10/5/028.

(54) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A Materials Genome Approach to Accelerating Materials Innovation. APL Mater. 2013, 1 (1), 011002. https://doi.org/10.1063/1.4812323.

(55) Durbin, T. D.; Lince, J. R.; Didziulis, S. V.; Shuh, D. K.; Yarmoff, J. A. Soft X-Ray Photoelectron Spectroscopy Study of the Interaction of Cr with MoS2(0001). Surf. Sci. 1994, 302 (3), 314–328. https://doi.org/10.1016/0039-6028(94)90836-2.

(56) Mullins, D. R.; Lyman, P. F.; Overbury, S. H. Interaction of S with W(001). Surf. Sci. 1992, 277 (1), 64–76. https://doi.org/10.1016/0039-6028(92)90612-A.

(57) Connor, J. A.; Hillier, I. H.; Saunders, V. R.; Barber, M. On the Bonding of the Ions PO43-, SO42-, ClO4-, ClO3- and CO32- as Studied by X-Ray Spectroscopy and Ab Initio SCF-MO Calculations. Mol. Phys. 1972, 23 (1), 81–90. https://doi.org/10.1080/00268977200100071.

(58) Tröger, L.; Arvanitis, D.; Baberschke, K.; Michaelis, H.; Grimm, U.; Zschech, E. Full Correction of the Self-Absorption in Soft-Fluorescence Extended x-Ray-Absorption Fine Structure. Phys. Rev. B 1992, 46 (6), 3283–3289. https://doi.org/10.1103/PhysRevB.46.3283.

(59) Eisebitt, S.; Böske, T.; Rubensson, J.-E.; Eberhardt, W. Determination of Absorption Coefficients for Concentrated Samples by Fluorescence Detection. Phys. Rev. B 1993, 47 (21), 14103–14109. https://doi.org/10.1103/PhysRevB.47.14103.

(60) Henke, B. L.; Gullikson, E. M.; Davis, J. C. X-Ray Interactions: Photoabsorption, Scattering, Transmission, and Reflection at E = 50-30,000 EV, Z = 1-92. At. Data Nucl. Data Tables 1993, 54 (2), 181–342. https://doi.org/10.1006/adnd.1993.1013.

(61) Yeh, J. J.; Lindau, I. Atomic Subshell Photoionization Cross Sections and Asymmetry Parameters: 1 ≤ Z ≤ 103. At. Data Nucl. Data Tables 1985, 32 (1), 1. https://doi.org/10.1016/0092-640X(85)90016-6.

(62) Fleszar, A.; Hanke, W. Dynamical Density Response of II-VI Semiconductors. Phys. Rev. B 1997, 56 (19), 12285–12289. https://doi.org/10.1103/PhysRevB.56.12285.

(63) Dröge, H.; Fleszar, A.; Hanke, W.; Sing, M.; Knupfer, M.; Fink, J.; Goschenhofer, F.; Becker, C. R.; Kargerbauer, R.; Steinrück, H. P. Complex Loss Function of CdTe. Phys. Rev. B 1999, 59 (8), 5544–5550. https://doi.org/10.1103/PhysRevB.59.5544.

(64) Weinhardt, L.; Fuchs, O.; Umbach, E.; Heske, C.; Fleszar, A.; Hanke, W. Resonant Inelastic Soft X-Ray Scattering, x-Ray Absorption Spectroscopy, and Density Functional Theory Calculations of the Electronic Bulk Band Structure of CdS. Phys Rev B 2007, 75 (16), 165207. https://doi.org/10.1103/PhysRevB.75.165207.

(65) Weinhardt, L.; Fuchs, O.; Fleszar, A.; Bär, M.; Blum, M.; Weigand, M.; Denlinger, J. D.; Yang, W.; Hanke, W.; Umbach, E.; Heske, C. Resonant Inelastic Soft X-Ray Scattering of CdS: A Two-Dimensional Electronic Structure Map Approach. Phys Rev B 2009, 79 (16), 165305. https://doi.org/10.1103/PhysRevB.79.165305.

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