X-Ray Absorption Fingerprints from Cs Atoms in Cs$_3$Sb

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X-ray absorption spectroscopy represents a valuable characterization tool for complex materials like multialkali antimonides. The interpretation of such experimental results greatly benefits from state-of-the-art theoretical references. In a first-principles work based on density-functional theory and many-body perturbation theory, the fingerprints of X-ray absorption near-edge structure (XANES) of Cs$_3$Sb from the Cs K- and L$_3$-edge are unraveled. From the electronic structure and the orbital character of the conduction bands, the contributions to the XANES spectra from the two inequivalent Cs atoms in the adopted stoichiometric unit cell are analyzed. The predominant weight of Cs s- and d-electrons in the unoccupied region anticipates the relatively high signal yielded by the L$_3$-edge. Clear atomic signatures, in the form of a pronounced excitonic peak, are visible in the Cs K-edge spectra. In the XANES from the L$_3$-edge, both Cs atoms yield similar contributions, which are yet distinguishable in the presented calculations. Quantitative analysis enabled by the adopted methodology reveals that electron–hole correlation effects manifest themselves mainly through a redistribution of the oscillator strength to lower energies, whereas exciton binding energies are on the order of a few hundred meV.

Multialkali antimonides are promising semiconducting materials for high-brightness electron sources in particle accelerators.[11–13] Most of the interest in these compounds has been mainly directed toward the deposition of photocathodes[4–7] with maximized quantum efficiency and minimized mean transverse energy,[8–11] with so far limited opportunities for a thorough characterization of the fundamental properties of the materials. The extreme sensitivity of alkali antimonides to atmospheric agents[12] requests ultra high-vacuum conditions during growth and diagnostics, which is typically performed via in situ monitoring.[9,11,13–17]

Among the techniques available for this purpose, X-ray spectroscopy occupies a leading role,[7,17,18] due to its sensitivity to the atomic species and their local environment,[19–27] including oxidation state and chemical bonding. While instrumentation for X-ray photoemission spectroscopy is typically available in laboratory facilities, X-ray absorption spectroscopy measurements, especially those probing deep core states, can be carried out only in synchrotron beamlines equipped with photocathode growth chambers. Even in these cases, identifying the spectral fingerprints of specific compounds and stoichiometries is not straightforward, especially due to the ultrashort excitation lifetimes in the hard X-ray region.

Ab initio many-body theory can provide a useful aid to identify atomic fingerprints in the X-ray near-edge absorption structure (XANES) spectra of multialkali antimonides. The approach based on all-electron density-functional theory (DFT) and many-body perturbation theory (MBPT)[28–30] offers unprecedented insight into the electronic structure of the materials and their response to electromagnetic radiation, without the need for empirical parameters. The electron–hole (e–h) correlation effects included in the Bethe–Salpeter equation (BSE) are the key ingredients to obtain an accurate description of the absorption features. This methodology has been successfully applied to study XANES in a number of materials, ranging from inorganic crystals,[22–25,28,31–34] to organic aggregates,[35] and hybrid materials.[36] The overall performance of the BSE approach for XANES depends on the underlying description of the electronic structure from DFT. For example, a semiempirical Hubbard correction may be needed to optimally describe multiplet effects in materials containing transition–metal atoms,[37–39] which, however, is not the case here.

In this letter, we unravel the X-ray absorption fingerprints of Cs$_3$Sb, one of the simplest and yet most representative alkali antimonides. From the calculation of the atom-projected density of states (PDOS), we determine the character of the unoccupied electronic bands, which are the final states of the resonant transitions from excited core electrons. By selectively exciting 1s and 2p$_{3/2}$ electrons of inequivalent Cs atoms in the unit cell of Cs$_3$Sb, we identify the fingerprints associated to each atom in the corresponding crystallographic position. The discussion about the e–h correlation effects corroborates the analysis and provides additional insight into the intrinsic electronic properties of Cs$_3$Sb. As the spin–orbit splitting between Cs 2p electrons with different $m$ quantum numbers is of the order of tens of
eV, excitations from 2p_{3/2} and 2p_{1/2} electrons can be treated independently.\[40\]

Cs_3Sb is modeled here in a stoichiometric face-centered cubic (FCC) unit cell including four atoms (see inset of Figure 1)\[41\] with optimized lattice parameter \(a = 9.38\ \text{Å}\). The crystal structure of Cs_3Sb was resolved as a cubic lattice of with 16 atoms per cell.\[40,41\] The FCC cell used here has been proven to reproduce well the electron structure of this material and related compounds (compare refs. \[42,43\]). The Sb atom is at the Wyckoff position (0,0,0), whereas Cs atoms have coordinates (1/2,1/2,1/2) and \(/C_6\ (1/4,1/4,1/4).\) We label the former Cs\(_2\) and the latter Cs\(_1\) and Cs\(_3\) (see inset of Figure 1). As Cs\(_1\) and Cs\(_3\) are crystallographically and chemically equivalent, in the following only Cs\(_1\) shall be considered.

The results presented in this work are obtained from DFT\[44,45\] and MBPT through the solution of the BSE, which is the equation of motion of the e–h correlation function.\[46\] In practice, the effective two-particle Schrödinger equation is mapped into a secular equation ruled by the BSE Hamiltonian, which includes the e–h Coulomb kernel accounting for both the bare exchange and the screened attractive e–h interaction.\[30\] Neglecting these terms restores the so-called independent-particle approximation (IPA), where only vertical interband transitions are accounted for. All calculations are performed with the all-electron full-potential code \(\text{\textit{exciting}}\),\[47\] implementing the family of augmented plane-wave plus local orbital methods. This approach offers an explicit treatment of core states as solutions of the Dirac equation in a spherically symmetric potential.\[28,47\] The \(\text{\textit{exciting}}\) code includes a state-of-the-art implementation of the BSE treating optical and core excitations on the same footing.\[30\]

DFT calculations are performed within the generalized gradient approximation for the exchange–correlation functional, in the Perdew–Burke–Ernzerhof parameterization.\[48\] The basis set size is determined by muffin-tin radii (\(R_{MT}\)) of 2.5 bohr assigned to both atomic species, and by the plane-wave cutoff satisfying the condition \(R_{MT}G_{\text{max}} = 8\). A homogeneous \(k\)-mesh with \(8 \times 8 \times 8\) points, reduced to 29 points by crystal symmetries, is adopted to sample the Brillouin zone (BZ). In the BSE calculations, a \(6 \times 6 \times 6\)-grid shifted from the \(\Gamma\)-point is used. Local-field effects are accounted for with 339 \(\mathbf{G} + q\) vectors. A total of 200 unoccupied bands are used to calculate the screening in the random-phase approximation and 80 empty states are included in the transition space, where the excited core electron is the only initial state. The absorption is described by the imaginary part of the macroscopic dielectric function (Im\(\varepsilon_M\)), which has only one distinct nonzero component in Cs_3Sb due to crystal symmetries. A Lorentzian broadening of 100 meV is applied to compute Im\(\varepsilon_M\) from the discrete spectrum of solutions of the BSE.\[30\] Although this value is unphysical to mimic the lifetime of deep core resonances,\[49\] it is adopted on purpose to visualize absorption features that cannot be resolved in raw experimental data.

The PDOS of Cs_3Sb is shown in Figure 1a. The adopted DFT approach underestimates the bandgap but captures well the character of the electronic states. Quantitative comparisons with experimental results\[50\] can be done with respect to the quasi-particle band structure – see ref. \[42\]. The valence region is dominated by Sb p-states hybridized with Cs s-, p-, and d-states. In the conduction region, the largest density pertains to Cs d-states, especially above 1 eV from the conduction band minimum (CBM). As discussed in ref. \[42\], the bottom of the conduction

\[Figure 1.\] a) Projected density of states of Cs_3Sb with atomic orbital-resolved contributions. The contributions of s-, p-, and d-electrons of each inequivalent Cs atom in the unoccupied region are reported in panel b), c), and d), respectively. Total contributions are given by solid lines, whereas those from Cs\(_1\) and Cs\(_2\) are given by dashed and dotted lines, respectively. The values referred to Cs\(_1\) are multiplied by 2 to account also for the contribution of Cs\(_3\). In all graphs, the bottom of the conduction band is set to zero. Inset: Ball-and-stick representation of the FCC unit cell of Cs_3Sb, with Sb atoms in black and Cs atoms in gray.
band has an almost parabolic dispersion which is associated with the s-like character of the corresponding Sb and Cs electrons. The p-states of both atomic species are also clearly visible in the unoccupied region (see Figure 1a).

Orbital-resolved contributions from inequivalent Cs atoms are shown in Figure 1b–d. Note the different scales of the y-axes, which are adjusted to enhance visualization. The PDOS from Cs s-states (Figure 1b) exhibits a weak shoulder at lowest energy, corresponding to the parabolic band at the bottom of the conduction region, bearing both Cs₁ and Cs₂ character. A sharp peak from Cs₂ is found about 1 eV above the CBM. At higher energies, the contributions from the s-electrons of Cs₁ become predominant. On the contrary, p-states start contributing about 0.5 eV above the CBM (see Figure 1c). In the low-energy part of the conduction region, the contributions from Cs₁ bear larger weight compared with those of Cs₂, which are mostly relevant between 2.5 and 4.0 eV. The p-states from Cs₁ mainly contribute between 1 and 4 eV above the CBM. Also, d-states are visible in the PDOS only 0.5 eV above the CBM (see Figure 1d). Contributions from inequivalent atoms are almost equal up to 1.5 eV above the onset, whereas states from Cs₁ are predominant from 3 eV on.

The analysis of the atom-resolved PDOS provides the key ingredients to interpret the XANES. The K-edge spectrum, which is analyzed first (see Figure 2), is obtained by exciting Cs 1s
electrons. Therefore, the final states of these transitions must include Cs p-character. In Figure 2a, the K-edge spectra computed from the solution of the BSE (solid lines) are plotted together with their independent-particle counterparts (shaded areas). The latter reflect the features in PDOS discussed earlier (see Figure 1c), with the contribution from Cs$_1$ (Cs$_2$) being more pronounced in the lower (higher) energy part of the examined spectral range. Note that the spectra computed for Cs$_1$ and Cs$_2$ have different onsets, owing to the core-level shift of 0.87 eV between the 1s electrons of these inequivalent atoms.\[42\]

In Figure 2a, excitation energies are scaled to the onset of the IPA spectrum from Cs$_2$, which is set to zero. The total XANES spectrum, obtained as the sum of all atom-resolved contributions (we recall that Cs$_2$ is equivalent to Cs$_3$), is also shown for reference. The comparison between BSE and IPA spectra highlights at a glance the e–h correlation effects. The BSE spectrum from Cs$_3$ (see Figure 2a) is characterized by a pronounced peak at the onset, which is formed by a set of 12 excitations spanning a range of 0.5 eV. For symmetry reasons, the first four excitations are double degenerate, whereas the fifth one is fourfold degenerate. This maximum dominates the lowest energy part of the total spectrum. This intense feature is, however, not the first excitation in the XANES. At lowest energy we find a very weak excitation, marked by a vertical bar in Figure 2a, which targets the CBM (see Figure 2b). Given the s-character of this electronic state (see Figure 1 and ref. [42]), the oscillator strength associated with this transition in the Cs K-edge spectrum is accordingly very low. The composition of the two higher energy excitations, plotted in Figure 2c,d, indicates that they both target states distributed over the entire BZ. Dominant contributions arise from the second unoccupied band at $\Gamma$ (Figure 2c), and again from the CBM, as well as from the bottom of the conduction band at $X$ (Figure 2d). The most intense excitation, giving rise to the sharp maximum in Figure 2a, corresponds mainly to transitions to the lowest unoccupied states at $X$ (Figure 2e). Among the excitations discussed earlier, only the lowest energy one, which is double degenerate, is a bound exciton. Its binding energy, computed as the difference with respect to the IPA absorption onset (an alternative definition of the exciton binding energy, given by the difference between the BSE and IPA excitation energy, is more appropriate in case of organic crystals.\[35\] layered materials\[51\] or complex heterostructures,\[52–54\] where individual excitations are clearly distinguishable), is equal to 150 meV, a low value for core excitations, which are typically more tightly bound.\[25,28,34–36\] However, the very different shape of the BSE spectrum compared to its IPA counterpart indicates the excitonic nature of the low-energy peak discussed earlier. The qualitatively different K-edge spectra obtained from Cs$_1$ and Cs$_2$ suggest that defects or substitutions on those crystallographic sites should be detectable in the XANES.

The spectrum from the K-edge of Cs$_2$ does not exhibit any strong peak but is instead characterized by very weak excitations at lowest energies, which are marked in Figure 2a by vertical bars of arbitrary, although relatively scaled, height. Interestingly, the first ten excited states are bound excitons with binding energies ranging from 150 to 85 meV. Due to the crystal symmetries, only four out of these ten excitations are nondegenerate. These states target mainly the CBM and the bottom of the conduction band at $X$ (see Figure 2f–g). The third and most intense excitation of this manifold corresponds to transitions delocalized over the entire BZ (Figure 2h). At higher energies, a broad onset with relatively intense excitations dominates the region between 0.5 and 3.0 eV also in the total spectrum. Again, the BSE result is overall qualitatively different from the IPA one: excitonic effects manifest themselves in the pronounced excitation strength toward the lower energy part of the spectrum.

We now turn to the XANES spectra computed from the Cs L$_2$-edge (Figure 3a). The corresponding excitations target unoccupied states with s- and d-character, which provide the dominant contributions to the PDOS in the conduction region (see Figure 1). Consequently, the absorption is three orders of magnitude larger compared with the XANES spectra from the Cs K-edge (see Figure 2a) and thus are expected to be much better resolved experimentally. Also in this case, the IPA spectra from Cs$_1$ and Cs$_2$ are offset with respect to each other, due to the core-level shift between the corresponding 2p$_{3/2}$ electrons.\[42\] The BSE spectra computed from both Cs$_1$ and Cs$_2$ are dominated by an intense peak at the onset, which are clearly visible and distinguishable also in the total spectrum summing up the contributions from all Cs atoms in the unit cell. The excitonic nature of these features is confirmed by the fact that none of them appears in the IPA spectra. In the spectrum from Cs$_3$, only the lowest energy exciton is actually bound and has a binding energy of 160 meV. The first excitation targets the CBM (see Figure 3b), as expected from the s-like character of this state (see Figure 1b and ref. [42]). Higher energy transitions, marked by dashed bars in Figure 3a, are more intense and rather delocalized in the BZ, with major contributions from the second unoccupied band around $\Gamma$ (see Figure 3c) and from the lowest empty state at $X$ (see Figure 3d). The highest energy excitation in this manifold is mainly delocalized over the second unoccupied band along the $X$–$W$–$K$ path (see Figure 3e).

Also, the XANES spectra computed from Cs$_2$ L$_2$-edge is dominated by a sharp peak at the onset, which is formed by 20 bound excitons (corresponding to six nondegenerate excitations) with binding energies ranging from 360 to 95 meV. The three excitations marked in Figure 3a by vertical bars target the CBM (Figure 3f), the bottom of the conduction band at $X$ (Figure 3g), and a number of higher energy states spread over the entire BZ (Figure 3h), respectively. The comparison with the spectra computed from the IPA reveals that in the latter the spectral density is almost uniformly spread over the explored energy range, reflecting the contributions from s- and d-states in the unoccupied region of the PDOS (see Figure 1b,d).

Before concluding, it is instructive to discuss the spectrum obtained from the Cs$_1$ L$_2$-edge in Cs$_3$Sb with respect to its counterpart computed for CsK$_2$Sb at the same level of theory (see ref. [34]). In CsK$_2$Sb, K atoms replace Cs$_1$ and Cs$_3$ at Wyckoff positions $\pm(1/4,1/4,1/4)$, whereas Cs$_2$ remains at $(1/2,1/2,1/2)$. The overall shape of the XANES spectrum is very similar in both materials, with a strong excitonic resonance dominating the onset and weaker absorption appearing at higher energies. This result indicates that, in this particular case, the XANES is not significantly affected by the chemical environment of the excited Cs$_2$ atom, at least in the FCC unit cell adopted in both calculations. This does not exclude, however, that in realistic samples including defects, nonstoichiometric compositions, and/or polycrystalline domains, atomic signatures in the
XANES can be identified based on the references presented here and in ref. [34] for the pristine materials. From a fundamental viewpoint, the coordination of Cs$_2$ with lighter K atoms reduces the electronic screening and thus enhances exciton binding energies up to 200 meV.

In summary, we have reported a detailed ab initio study of the XANES spectra from the Cs K- and L$_3$-edge of Cs$_3$Sb, a representative alkali antimonide material, unraveling the fingerprints of inequivalent atoms. The analysis of the PDOS reveals that the bottom of the conduction region has pronounced Cs s-like character, whereas, within the next few eV, Cs p- and especially d-states are predominant. The signal associated with the Cs L$_3$-edge is thus much stronger than the one from the Cs K-edge, and, as such, more suitable for experimental characterization. The fingerprints of inequivalent Cs atoms are clearly recognizable in the XANES from the Cs K-edge through the presence of a pronounced excitonic peak given by transitions from Cs$_1$. On the contrary, the L$_3$-edge XANES from both inequivalent Cs atoms are dominated by sharp resonances at the onset, making the two contributions hardly distinguishable in experiments, especially given the ultrashort lifetime of the corresponding excitations. In the ab initio results presented here, the two features are clearly discernible, also due to the energy onset between the two spectra, due to the core-level shift between the initial states.

Figure 3. a) Atom-resolved X-ray absorption spectra of Cs$_3$Sb from the Cs L$_3$-edge: BSE results are indicated by solid lines, IPA ones by shaded areas. The total contribution, computed as the sum of all atom-resolved spectra, is shown in the background. A Lorentzian broadening of 100 meV is applied to all spectra. Vertical solid bars mark bound excitons, whereas the dashed ones indicate selected unbound excitations. The energy scale is set to zero at the onset of the IPA spectrum from Cs$_2$. The target conduction states of these excitons are represented by the colored symbols (squares for Cs$_1$ and diamonds for Cs$_2$) in the band structures of panels b–h), where the CBM is set to zero. The contributions in panels c–e), g), and h) are magnified by a factor 20 compared with those in panels b) and f).
Excitonic effects are pronounced in all spectra, either via the presence of bound excitons or through a sizable redistribution of the oscillator strength to lower energies. This finding suggests that a many-body approach like the BSE outperforms the independent-particle approximation in correctly reproducing XANES features in these materials.

In conclusion, our results represent an important step forward toward the characterization of Cs$_3$Sb and, more generally, of multialkali antimonides. By providing a clear reference for the pristine material, our work paves the way to a deeper understanding of realistic samples, typically including defects, nonstoichiometric content, and polycrystalline domains. Combined efforts to interface XANES experiments with many-body ab initio calculations will lead to unprecedented understanding and control of the fundamental properties of these materials and, thus, to consolidating their role in the next generation of ultrabright electron sources.

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Conflict of Interest

The author declares no conflict of interest.

Keywords

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