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Surface X-ray emission from lanthanide metals

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Abstract

O₃ X-ray emission (XE) upon 5p_{3/2} electron-impact ionization of La(0001) and Sm(0001) metal surfaces exhibits up to 30% spectral intensity from the topmost atomic surface layer. The energy separation of surface and bulk XE peaks is explained by the surface core-level shift of La and the surface valence transition of Sm. While the bulk XE spectra are in reasonable agreement with theoretical sd partial density of states (DOS), the experimental access to the partial surface-layer DOS opens new opportunities in studying surface phenomena in lanthanide metals and compounds.

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One of the most important contributions of electron theory to surface science has been the calculation of *atomic-layer resolved* electronic structure, such as the layer-projected density of valence states (DOS). Density functional theory in local-density approximation [1,2] showed that the electronic structure near a metal surface turns rapidly bulk-like within a few sub-surface atomic layers. In particular, two characteristic properties of transition-metal surfaces have been identified: the presence of *surface states* in surface projected gaps of the bulk band structure [3], and the surface

band narrowing [4], which—in a tight-binding picture—may intuitively be expected from the reduced coordination of surface atoms. In transition metals with a less than half-filled valence band, band narrowing leads to a considerable down shift of the surface-band center, driven by the need of the semi-infinite surface-bulk system to maintain a common Fermi level [5]. As a consequence, the core-level binding energies (BE) of surface atoms are shifted by the well-known surface core-level shifts, which for lanthanide metals amount to 0.2–0.5 eV [6].

In the lanthanide metals the ubiquitous surface band narrowing has a particular consequence: while the bulk atoms in Sm metal assume a trivalent 4fⁿ(6s5d)³ configuration ($n = 5$), as do all lanthanide metals except Eu and Yb, the topmost Sm(0001) surface atoms remain divalent, 4fⁿ⁺¹(6s5d)², as in the gas phase. With their

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considerably larger radii, the divalent surface atoms induce a 5×5 lattice reconstruction of the Sm metal surface layer [7].

In many lanthanide metals valence electrons are known to mediate an indirect magnetic exchange coupling between the localized 4f moments, and the bulk magnetic properties are governed by the valence-band DOS. Yet, at the surfaces of lanthanide metals the magnetic properties (e.g. coupling strength) can differ considerably from the underlying bulk [8]. Even though some studies have aimed at relating them to the surface electronic structure at special points in electron-momentum space [9], up to now there has been *no experimental access* to the surface-layer projected DOS, neither for lanthanides nor for any other metallic system.

In this letter we present electron-excited O_3 X-ray emission (XE) spectra of La(0001) and Sm(0001) metal surfaces. The XE spectra allow a spectroscopic separation of surface and bulk partial densities of states. High surface sensitivity is reached via electron-impact ionization at low kinetic energies, down to a few eV above the 5p excitation threshold.

The experiments were performed using a spectrometer equipped with a toroidal-grating monochromator (for 12–28 eV photon energy), a position-sensitive photon detector with CsI-coated multichannel plates, and a Pierce-type electron gun [10]. The kinetic energy of the primary electrons was varied from 26 to 200 eV, and the energy resolution of the optical system was 0.15–0.3 eV, smoothly increasing with photon energy. Single-crystal films of La and Sm metal were grown by vapor deposition of high-purity metals on a W(110) substrate at a rate of ~ 0.1 nm/min. The base pressure was in the low 10^{-11} mbar range, rising during evaporation to low 10^{-10} -mbar. After annealing of the La films (deposited at 200 K) for 5 min at 550 K, sharp hexagonal LEED patterns appeared, indicating a well-ordered La(0001) surface. Sm films were grown at room temperature to achieve layer-by-layer growth, and subsequently annealed at 350 K to form the well-known 5×5 surface reconstruction [9].

Fig. 1 shows O_3 XE spectra of (a) La(0001) and (b) Sm(0001) for various primary electron energies E_0 . The spectra were normalized to equal

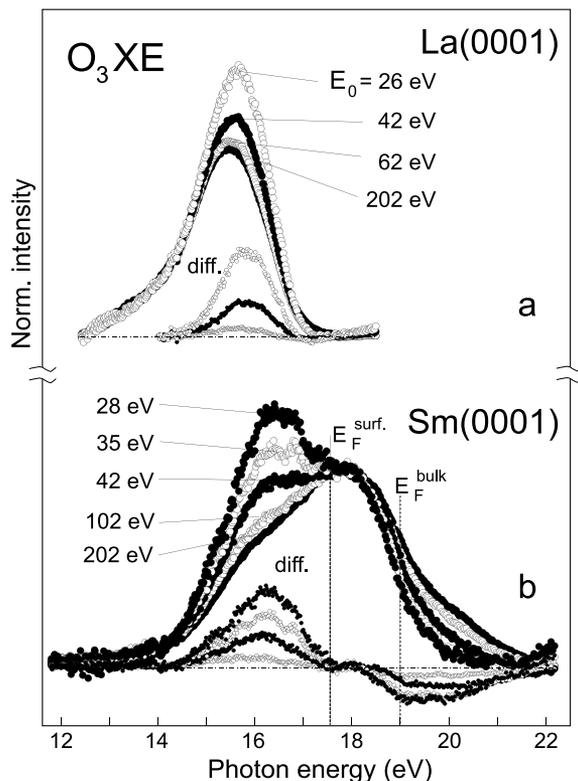


Fig. 1. O_3 XE spectra (large symbols) of (a) La(0001)/W(110) and (b) Sm(0001)/W(110) for various primary-electron energies E_0 . The spectra were normalized to equal bulk intensities, with a linear background subtracted. Difference spectra between the 202-eV spectrum and the others are given underneath (small symbols). Vertical lines in (b) correspond to XE from the Fermi level in case of surface atoms (E_F^{surf}) and bulk atoms (E_F^{bulk}). La (Sm) XE spectra (not shown here), recorded at $E_0 = 102$ eV (152 eV), are virtually identical with the 202 eV spectra.

background intensities before background subtraction.¹ For La, lowering E_0 leads to an increase in spectral intensity on the high-photon energy side. The Sm spectra, by contrast, reveal an even

¹ Auger decay is by far the dominant relaxation process of the shallow lanthanide 5p holes (10^4 times more likely than radiative decay); the many Auger electrons can lose energy via Bremsstrahlung. While Bremsstrahlung of primary electrons gives rise to an approximately linear background, see Ref. [11], the strong Auger decay channels in Sm involve 4f electrons and lead to an additional nonlinear background.

more pronounced enhancement with decreasing E_0 , yet on the low-photon energy side; the spectral shape on the high-energy side changes as well.

It is well known that the electron mean-free path λ in d-hole transition metals decreases considerably with increasing kinetic energy, staying as short as a few atomic layers below ~ 40 eV.² It may thus be tempting to attribute all E_0 dependent spectral changes in Fig. 1 to a change in relative contributions from the surface and sub-surface (bulk) layers. Yet let us first discuss other possible explanations for such changes. (i) Self-absorption: in lanthanides, the X-ray absorption coefficient near the O_3 threshold is typically some 5×10^5 cm⁻¹ [13]; thus, the emitted radiation is practically not absorbed in the sample. (ii) Radiative excitation/de-excitation processes (in photon-excited XE known as resonant inelastic X-ray scattering [14]) cannot generate the spectral changes observed here, because such effects occur only when the excitation energy is just a few eV above threshold. By contrast, the spectral changes in Fig. 1 are significant in a much wider range of excitation energies up to ~ 100 eV above 5p threshold. (iii) So-called satellite emission: it mainly arises from multiple-ionized core-hole states or it follows non-radiative decay of a deeper core hole. Due to a reduced screening of the nuclear charge for multiple-hole states, the associated XE (satellite) intensity is shifted to higher photon energies. It is important to note that the satellite intensity is expected to *decrease* rapidly with E_0 near the double-ionization threshold [15].

Let us first focus on La which is the most simple case with no 4f electrons being involved in the XE process ($4f^0$ configuration). The observed spectral changes in Fig. 1a indicate that the La XE spectra contain two subspectra, one from the *bulk* and

another one from the topmost atomic *surface layer*. This identification is readily suggested by the known 0.5-eV surface core-level shift of the $5p_{3/2}$ BE to higher energies [6]; consequently, the surface XE spectrum must appear at higher photon energies. We normalized the raw spectra to equal bulk intensity by assuming pure bulk emission at the low-energy end of the spectrum below $h\nu = 14$ eV (see Fig. 1a). Since only minor spectral changes are observed for excitation energies above 100 eV, we identify the 202 eV spectrum with bulk emission. Differences between the bulk spectrum and XE spectra for lower excitation energies are shown by small symbols (“diff.”) in Fig. 1a. Their shape is independent of E_0 , and we attribute them to 5p XE from the La(0001) surface layer.

The Sm XE spectra in Fig. 1b reveal a similar behavior as the La spectra, yet in the photon energy range below 18 eV. The energies 17.55 and 19.0 eV (vertical dashed lines) mark radiative transitions from surface- and bulk-valence states directly at the Fermi level, i.e. those of highest transition energy. We denote these photon energies as surface and bulk “Fermi level”. In analogy to the La spectra, we attribute the spectral changes below E_F^{surf} to an increase in surface sensitivity with lowering E_0 . Again, the difference spectra between the bulk-like 202 eV spectrum and those of lower E_0 are shown (small symbols in Fig. 1b), and the *positive* differences below E_F^{surf} are assigned to O_3 XE from the topmost Sm surface layer. This assignment has been confirmed by further experiments, where we varied the electron incidence angle at fixed impact energy E_0 : as expected the surface sensitivity is significantly higher for 10° grazing incidence than for normal electron incidence; it is most pronounced for Sm(0001) using $E_0 = 28$ eV.

In the Sm case we also find spectral changes that lead to *negative* differences in Fig. 1b. They show an opposite E_0 dependence and appear at higher photon energies (>18 eV) mainly above E_F^{bulk} . From the E_0 dependence and the energy position this part of the Sm XE spectrum can safely be identified as satellite XE from multiple-ionized core holes; see point (iii) above. We attribute the noticeable satellite intensity (up to 15%) in the Sm XE spectra to well-localized $\text{Sm } 4f^4 5p_{3/2}^5$

² In d-hole transition metals, the inelastic mean-free path λ does not follow the “universal curve”, but stays as short as 2–3 monolayers at kinetic energies below $\cong 40$ eV [12]. λ is particularly short in lanthanide metals, a fact that has been attributed to the large number of d-holes in these metals [20]. It is therefore reasonable to assume that in the energy range between 30 and 200 eV of the present experiment, λ decreases rather monotonically with increasing energy.

double-hole states; such f-hole states cannot exist in La. Note that no O_2 ($5p_{1/2}$) emission, which would be expected at 2.4 eV (5.4 eV) higher photon energy for La (Sm) [16], is discernible in the XE spectra in Fig. 1. Their absence is very likely due to intense non-radiative (Coster–Kronig) transitions, which do not exist for the shallower $5p_{3/2}$ hole.

In order to visualize our interpretation of the O_3 XE spectra, we show in Fig. 2 how the separation into bulk and surface contributions evolves with E_0 . For the La spectrum we use two components: bulk (dotted) and surface (solid curves). The surface contribution is the sum of the difference curves in Fig. 1a. For Sm we use three components, in accordance with the above analysis: bulk, surface, and a weak satellite contribution. To obtain a Sm ‘bulk’ spectrum, we remove the satellite intensity from the 202 eV spectrum by taking the 202 eV spectrum in the photon energy range below 18 eV and the 28 eV spectrum above. The least-squares fit analysis (Fig. 2) shows that the maximum of the surface emission is shifted with respect to the bulk emission by 0.3 eV to *higher* photon

energies for La(0001), but by as much as 1.4 eV to *lower* photon energies for Sm(0001). The surface contributions increase with decreasing E_0 and reach some 30% for both metals. The surface-to-bulk intensity ratio s/b (given in Fig. 2) changes exponentially with E_0 in approximately the same way in the two cases.

In order to compare the experimental XE spectra with partial DOS on a common energy scale, knowledge of the surface and bulk BE of the $5p_{3/2}$ level is required. To this end we recorded $5p$ core-level PE spectra (not shown) from La(0001) and Sm(0001); they yield a bulk (surface) BE of 16.3 eV (16.8 eV) for La $5p_{3/2}$, and 19.0 eV (17.55 eV) for Sm $5p_{3/2}$. The large negative shift of (-1.45 ± 0.08) eV in the case of Sm reflects the surface valence transition (see above). With these $5p_{3/2}$ BE values for bulk and surface, we arrive at a common energy scale for the surface and bulk XE spectra, shown in Fig. 3 (upper part). According to the electric-dipole (E_1) selection rule, $\Delta l = \pm 1$, for the one-electron orbital angular momentum, O_3 XE samples light from $s \rightarrow p$ and $d \rightarrow p$ transi-

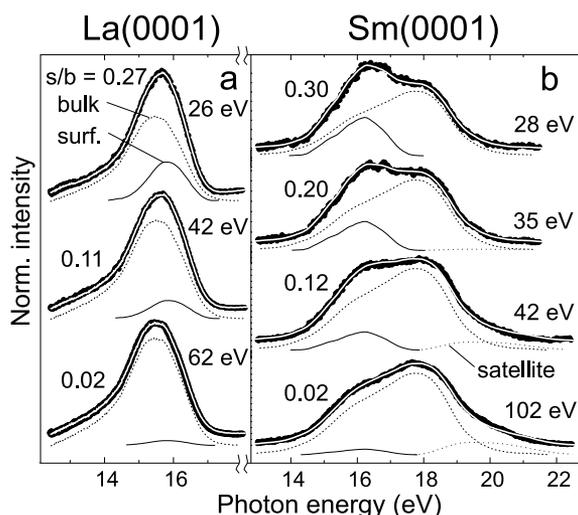


Fig. 2. Decomposition of the experimental O_3 XE spectra (filled dots) into bulk (dashed) and surface (solid) subspectra in the (a) La(0001) and (b) Sm(0001) case for various primary-electron energies (E_0). For Sm, satellite contributions (dotted) are included. White curves represent the sum of all subspectra and s/b denotes the surface-to-bulk intensity ratio.

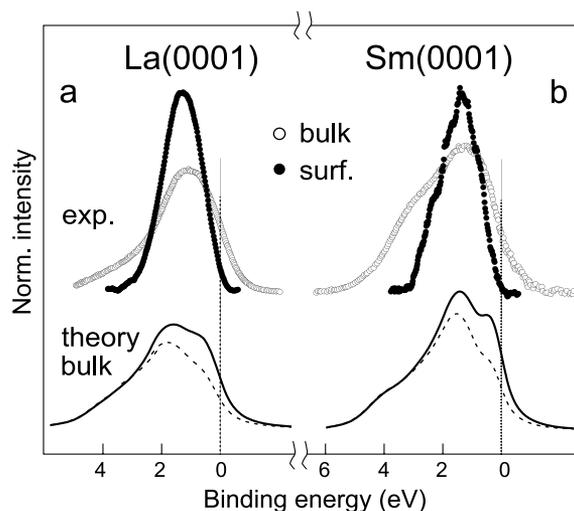


Fig. 3. Top panel: Experimental surface (solid dots) and bulk (open dots) XE spectra of (a) La(0001) and (b) Sm(0001). Bottom panel: Theoretical bulk sd-partial DOS with (dashed curve) and without (solid curve) valence-electron core-hole screening. To account for relative electric-dipole transition probabilities, the theoretical s- and d-DOS spectra were weighted by 3:1 (see text).

tions. Therefore, in absence of correlation effects between the valence electrons [17], the 5p XE spectra simply reveal the *partial* s and d DOS *weighted* by the E_1 transition probabilities. To account for the different numbers of valence electrons, we normalized the areas below the surface (solid symbols) and bulk (open symbols) curves in Fig. 3 to 1:1 (La) and 2:3 (Sm). It is evident that the *surface* DOS is much *narrower* in both metals: for La it reduces to 67%, and for Sm to 53% of the respective bulk width. We attribute the considerably stronger surface-band narrowing at the Sm surface to the larger interatomic distance between surface atoms in the reconstructed Sm surface layer.

For comparison of the bulk XE spectra with theory we show, in the lower part of Fig. 3, the sd partial bulk DOS extracted from band-structure calculations by Danzenbächer and Richter [19]. Theoretical spectra were convoluted with a Lorentzian and a Gaussian to simulate lifetime broadening and experimental resolution, respectively. Using the 3:1 relative probability for s and d partial DOS that we found analytically,³ the overall shape of the theoretical bulk DOS (solid curves) is in reasonable agreement with experiment. We note that identification of the experimental O_3 XE (upper curves in Fig. 3) with the weighted partial DOS (lower) is straightforward in the La case (empty 4f shell), but it might be more complicated in the Sm case due to the partially filled 4f shell. However, the good qualitative agreement between experimental and calculated bulk spectra for both metals indicates that the O_3 XE spectra are not strongly affected by correlation effects.

Finally, Fig. 3 shows a rather low surface DOS near the Fermi energy E_F . This may be surprising in light of the known La(0001) valence-band PE spectra showing a 5d-derived surface state right at E_F [18]. Yet this state cannot appear in the XE surface spectrum since analytical calculations³ of the electric dipole transition (E_1) probabilities

reveal that an s-like valence electron has a 15 times higher probability to fill a $5p_{3/2}$ core-hole (via E_1) than an electron from the surface state that is of d_{z^2} -symmetry [18]. Moreover, the valence-electron hole-screening model of Mahan [17] predicts a suppression of $d \rightarrow p$ transitions close to E_F . We included the predicted suppression by modifying the theoretical spectra (dashed curves) in Fig. 3. Their favorable comparison with the experimental bulk XE spectra suggests that such an additional suppression of $d \rightarrow p$ transitions in O_3 XE indeed exists in metals.

In summary, we have demonstrated for the example of the close-packed La and Sm metal surfaces, that electron-excited soft XE can reach sufficient surface sensitivity to allow a separation of XE spectra from the bulk solid and the topmost surface layer. We find good overall agreement of the experimental bulk O_3 XE spectra for La and Sm metal with theoretical s- and d-DOS weighted with electric dipole transition probabilities. This first observation of the weighted partial DOS of a surface layer gives experimental access to surface electronic properties of lanthanide metals and compounds. Calculations of the electronic properties of lanthanide metal surfaces, in particular the DOS, are clearly encouraged.

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