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Attenuation lengths of low-energy electrons in solids: The case of CoO

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The effective attenuation length (EAL) of low-energy electrons in CoO is investigated by photoemission spectroscopy experiments ($5 \leq h\nu \leq 19$ eV) by measuring the Ag Fermi-edge signal through a CoO overlayer of increasing thickness. The EAL is found to increase when lowering the electron energy, but the experimental values are much smaller than expected from the commonly used Seah–Dench formulas [Surf. Interface Anal. **1**, 2 (1979)].

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Photoemission spectroscopy (PES) is a versatile tool for the investigation of the electronic properties of solid systems. PES experiments are very surface sensitive and this becomes a strong limitation for the practical use of PES when the electronic properties at the surface are different from those of the bulk,[1] as for technologically important systems such as superconductors and materials exhibiting colossal magnetoresistance, and for the investigation of as-grown and capped samples. The surface sensitivity in PES is due to the short electron inelastic mean free path (IMFP) λ in the photon energy range typically used (from few tens of eV for the He discharge lamp up to about 1.5 keV for the Al $K\alpha$ x-ray source). The IMFP, the average distance that electrons travel between inelastic collisions, is energy and material dependent, with a general trend that, for most of the materials, shows a broad minimum roughly between 20 and 200 eV with values at around 5 Å, which increases then with energy to about 20–30 Å at 1.5 keV.[2]

A practical estimation of the surface sensitivity in PES experiments is performed through measurements of the electron effective attenuation length (EAL) Λ, which describes the rate of change of a given signal intensity I_0 from a substrate for increasing thickness d of an overlayer as follows:

$$I_d = I_0 e^{-d/\Lambda}. \tag{1}$$

In practice, the EAL can depend on film thickness unless the emission depth distribution function is approximately exponential.[3] The EAL is identical to the IMFP only if elastic scattering effects are negligible. According to some experiments and calculations,[4] Λ should steeply increase at very low (<10 eV) electron energies E (where E is the electron energy measured with respect to the Fermi level; hence, it represents the electron kinetic energy inside the material, which is not corrected for the work function). This is justified by the fact that the cross section for electron-electron scattering strongly decreases at low energies.[5] The Seah–Dench (SD) formulas[4] describe the general trend for EAL for different compounds and energies and were derived as best fits to sets of experimental data available in 1979 with an imposed analytical dependence $\Lambda \propto E^{-2}$ at low electron energy as derived by Quinn.[6]

Recently, outstanding results were reported for laser excited ($h\nu \sim 7$ eV) photoemission experiments on several strongly correlated electron systems,[7] where one of the scientific issues was to overcome the problem posed by the different electronic properties at the surface and in the interior of the investigated materials. The claimed bulk sensitivity of the measurements was, however, not directly quantified, but was deduced from the fact that very similar spectra were obtained from *in situ* scraped surfaces and from samples without in-vacuum surface preparation,[8] or estimated from a very large EAL value according to Ref. 4. On the other hand, a direct demonstration of the bulk sensitivity of low-energy photoemission spectroscopy (LEPES) comes from photoemission electron microscopy experiments, where an EAL as large as ~160 Å was obtained for the magnetic signal in the Ag/Fe system after excitation with a Hg lamp ($h\nu < 5$ eV).[9]

In order to set a firm experimental basis for the surface and/or bulk sensitivity of LEPES, here we quantify the EAL in the low-energy PES regime by using the so-called overlayer method: the attenuation of the metallic Fermi-edge signal from a Ag(100) single crystal was measured for increasing thicknesses of a CoO overlayer. This system was chosen because CoO is known to grow in a layer-by-layer fashion on Ag(001),[10] which offers a good control of the sample thickness. Moreover, while much experimental work has been done on EAL determinations in pure elements, fewer data are available in literature for compounds.[4] The obtained values of Λ are compared with the results of the predictive formulas of Seah and Dench.[4]

The experiments were performed at the BaD ElPh beamline of the ELETTRA synchrotron radiation facility at Basovizza-Trieste (Italy). The angle of photon incidence was 45° from the sample surface normal and the estimated acceptance angles of the electron energy analyzer were about ±3.5° (horizontal) and ±0.5° (vertical). Photoelectron spectra were taken at normal emission with an overall (photon and electron analyzer) energy resolution of about

90 ± 10 meV, as estimated from the Fermi edge of clean Ag(001). The CoO film was prepared *ex situ* by reactive growth on the clean Ag(001) surface by evaporating Co in an oxygen pressure of 1×10^{-4} Pa.[11] Film thickness was estimated from the evaporation rate measured by a quartz microbalance before and after evaporation. Partial shadowing of the Ag substrate during CoO evaporation resulted in a staircaselike sample with 1 mm wide steps of thicknesses $d=0$ (as-introduced Ag in the following), 26, 52, 105, and 217 Å. After film growth, the sample was annealed at 620 K for half an hour. The low-energy electron diffraction pattern showed a (1×1) reconstruction, which indicates an epitaxial growth of CoO with the expected rocksalt structure with a (001) surface, for all thicknesses. The sample was then transferred through air into the BaD ElPh UHV chamber, where the experiments were performed at room temperature in a vacuum of about 1×10^{-8} Pa. Spectra were taken close to the Fermi level at different photon energies for different CoO thicknesses d and compared to the spectra from the $d=0$ as-introduced Ag surface and from a clean Ag surface.

Due to air exposure, we expect a contamination layer to be present on our surface. In order to characterize the contamination layer, we prepared a further CoO/Ag(001) sample by following the same procedure as previously described, with a uniform thickness of about 5 nm. Mg $K\alpha$ excited photoemission spectra were acquired at room temperature with 45° photon incidence and a normal emission geometry from both the as-grown sample and the same sample after about 40 min of air exposure (the sample used for the synchrotron radiation experiments was exposed to air for about the same time). In the air-exposed sample, the presence of carbon and oxygen indicates hydroxylation and/or carbonation phenomena.[12] In Fig. 1(a), we show the Co $2p$ core level spectra of the as-grown sample (open circles) and of the air-exposed sample (solid squares). Apart from a lower peak intensity in the air-exposed sample, the two spectra are identical, and are representative of CoO,[13] but not compatible with other cobalt oxide species.[14,15] The O $1s$ spectrum from the as-grown sample [Fig. 1(b)] shows a single component (cobalt-coordinated oxygen) at a binding energy of about 530.5 eV, while the air-exposed sample [Fig. 1(c)] has an additional prominent shoulder (oxygen in a different coordination from the contamination layer) at about 532.2 eV. In Figs. 1(b) and 1(c), the experimental spectra (open circles) were fitted with Voigt profiles (thin solid lines) plus an integral background (dashed lines). The thick solid lines are the results of the fit. The contamination was modeled by a layer of uniform thickness x, which attenuates the intensity of the cobalt-coordinated oxygen peak. The unknown parameter is the electron attenuation length Λ of this layer. Supposing Λ to be in the range of 10–30 Å,[16] we estimate the thickness of the contamination layer to be $x=5 \pm 3$ Å.

Figure 2 shows Fermi-edge spectra recorded by using 19 eV [Fig. 2(a)] and 8 eV [Fig. 2(b)] photons from the as-introduced Ag (squares) and from the clean Ag surface (circles). The spectra are normalized to the acquisition time and the incoming flux. Figure 2 shows that the intensity of the Ag Fermi edge is strongly suppressed on the as-introduced Ag surface. The effect is much more evident when using 19 eV photons (more than 15 times intensity decrease) rather than 8 eV photons (about a factor of 2 decrease).

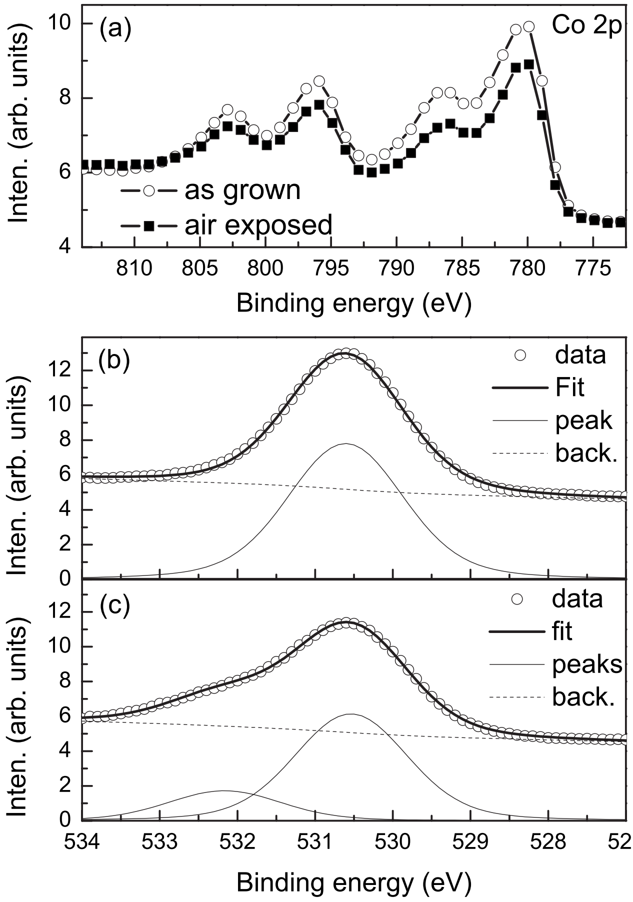

FIG. 1. (a) Mg $K\alpha$ excited Co $2p$ photoemission spectra from an as-grown and an air-exposed CoO/Ag(001) sample. (b) and (c) show the O $1s$ spectrum for the as-grown and the air-exposed surfaces, respectively.

As an example of the results obtained for the different photon energies, Fig. 3 shows the spectra taken at $h\nu=7$ eV of the as-introduced Ag and of the CoO/Ag system for various overlayer thicknesses, as indicated by the labels. The observed intensity at the Fermi level rapidly decreases upon increasing the CoO thickness and vanishes for films thicker than 105 Å, as evidenced by the inset in Fig. 3.

In order to quantify the attenuation of the emitted electrons upon increasing the CoO thickness, we integrated the intensity of each spectrum over the energy interval ± 0.2 eV with respect to the Fermi level and we fitted the result to Eq. (1), where I_d is the integrated intensity corresponding to the CoO thickness d and I_0 is the integrated intensity for the as-introduced Ag sample $(d=0)$. We verified that the experimental intensity, at a given energy, exponentially depends, indeed, on film thickness. The obtained values for the attenuation length are plotted as symbols versus the electron energy E in Fig. 4. The larger error bar for $E=5$ eV reflects a poorer fit with an exponential decay function. The values of Λ are given in angstrom as well as in monolayers (ML) by taking 2.13 Å as the thickness of 1 ML of CoO from the bulk lattice constant.[17] The dashed and full lines in Fig. 4 are the predicted EALs from two of the empirical formulas intro-

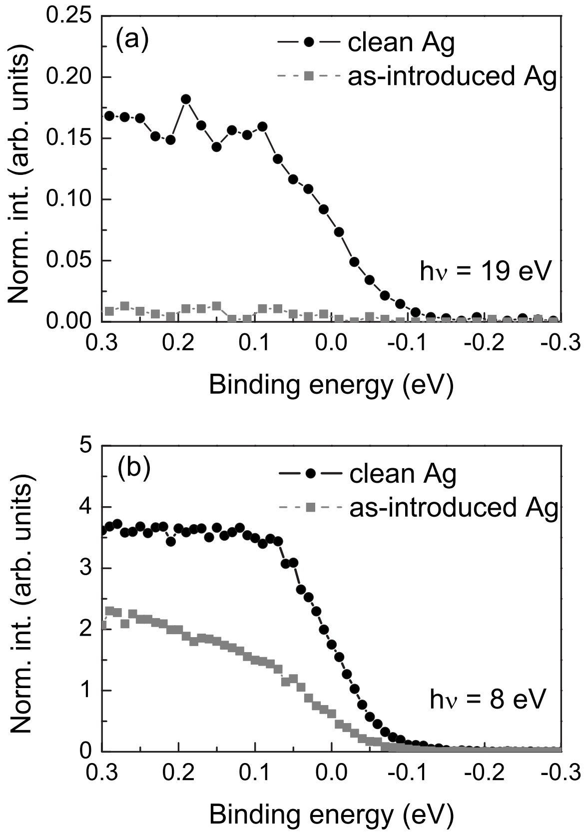

FIG. 2. (a) Spectra taken with $h\nu = 19$ eV from a clean Ag sample (circles) and from the as-introduced silver (squares). (b) Spectra from the same samples as in (a) with an excitation energy of $h\nu = 8$ eV.

duced by Seah and Dench to fit experimental data for elements (SD ELEMENTS) and inorganic compounds (SD COMPOUNDS), respectively. It is apparent that the Seah–Dench formulas give substantially higher values than we experimentally obtain, while the same trend, i.e., an increase in Λ upon a decrease in the electron energy, is observed.

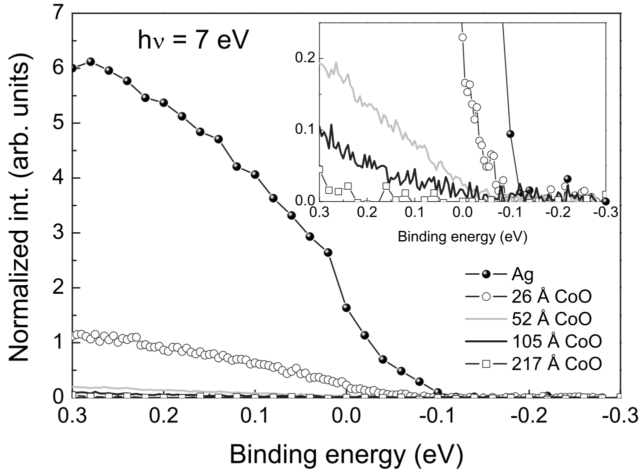

FIG. 3. Spectra taken close to the Fermi level for the as-introduced Ag and for different CoO thicknesses at $h\nu = 7$ eV. The inset shows that some intensities are observable also underneath the 52 and 105 Å CoO thicknesses.

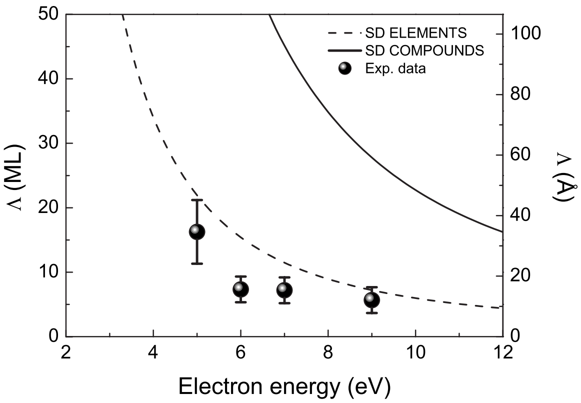

FIG. 4. Obtained values of electron effective attenuation length are plotted as solid symbols with error bars. The superimposed dashed and solid lines are the predictive formulas of Seah and Dench (Ref. 4) for elements and inorganic compounds, respectively.

It is actually not so surprising to have a poor agreement between our measured data and the given formula. The Seah–Dench formulas were derived from fits to data acquired prior to 1979, when the morphological and structural characterizations of the overlayer films were done with techniques less reliable than nowadays.[3] While the formulas, indeed, provide a useful guide, they cannot be used to obtain reliable quantitative results. This is probably even more true at low energy, where the expected variation of the EAL is much steeper than at higher energy and where the number of experimental data, in particular, for the case of compounds, is very limited.[4] Moreover, a pronounced material dependence of the EAL and the IMPF is to be expected[2] in the low-energy regime.[18,19] On the other hand, the results shown in Fig. 1 qualitatively demonstrate that the EAL is, indeed, increasing at lower energy: for an excitation energy of $h\nu = 19$ eV, the Fermi level from the as-introduced Ag is not visible [Fig. 2(a)], while it is prominent at $h\nu = 8$ eV [Fig. 2(b)]. The difference between the as-introduced and the clean Ag is attributed to the presence of the contamination layer on the sample surface due to air exposure, which attenuates the intensity according to the used photon energy, and, therefore, to the corresponding values of Λ.

According to Fig. 4, we conclude that, at least for the system under consideration, LEPES is much less bulk sensitive than expected, with a pronounced increase in the EAL only at very low energies, close to the material's work function, a result consistent with previous findings.[9] Actually, it has to be noted that our results are just slightly lower than the Seah–Dench curve for elements and not too dissimilar from the Λ experimental values for noble metals such as gold, silver,[20] and copper.[21] Those data indicate just a moderate increase in EAL at the low electron energies accessible in photoemission experiments. On the other hand, the experimental points of Fig. 4 are almost an order of magnitude less than the Seah–Dench curve for inorganic compounds that is often used to calculate the EAL of photoemission at low energies, but which was obtained from a very limited amount of experimental data.[4] A comparison with EAL values as obtained in high-energy photoemission spectroscopy,[22] estimated to be of the order of 40–60 Å at 5.7 keV electron energy for *ex situ* grown samples, suggests that the surface contribution is quite larger in the present LEPES case.

Our results suggest that for a practical use of LEPES as a bulk-sensitive technique, the real sample properties have to be taken into account. In this kind of analysis, care should be exerted since spectral changes versus photon energy may have origins different from a varied probing depth. The variation of the photoemission cross section in the low-energy regime, for instance, is not well known and often simply neglected. Moreover, as the adiabatic regime is approached, the interpretation of the measured intensity in terms of the spectral function becomes questionable,[23] although recent findings on strongly correlated materials would suggest that experiments performed at these energies can still be described within the frame of the sudden approximation.[24] Finally, one always has to consider that the terms *bulk* and *surface* have a loose meaning, with the surface region of a material having different properties from those in the interior and with a thickness that might vary from case to case. As an example, in the recent report by Yoshikawa *et al.*,[25] which showed synchrotron radiation ($h\nu=7$ eV) excited LEPES spectra for an Yb compound, while bulk sensitivity is assumed, a contribution of the subsurface region is still recognized by the authors even at the used energy. This means that either the surface is thicker than that assumed or that the EAL is less than that predicted by the Seah–Dench formulas.

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