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Abstract
Substrate-induced effects on the transport properties in thin KCl films on the Cu(100) surface
have been studied using K^+ 2p photoelectron, photoabsorption and resonant Auger spectra. The
measurements were performed at different KCl coverages ranging from a partial monolayer to a
thick bulk-like film.

The morphology and layer thickness were estimated from an analysis of the electron energy
loss structure of the K^+ 2p and Cl^- 2p photoelectron peaks, and from the variations in the
photoelectron peak fine structure.

The resonant Auger spectator decay spectra measured at the photoabsorption resonances
show that the significant differences between the spectra of the solid and of thin layers are
related to the charge delocalization from the K^+ 3d excited state into the metal substrate. The
core-hole-clock approach yields an estimate of 1.5 fs for the corresponding charge transfer time
at a single monolayer KCl coverage.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Ultrathin insulator films have been used when studying the
properties of insulators by photoelectron spectroscopy (PES),
because they offer a possibility to avoid the sample charging
problems characteristic of the photoelectron emission of bulk
insulating samples. Such films and their fabrication processes
have received attention related to their potential usefulness
in electronics: for example, CaF_2 films on semiconductor
surfaces [1, 2]. Recent progress in nanosciences has stimulated
considerable interest in alkali halide overlayers at near
monolayer coverages (see e.g. [3–11]).

Alkali halides represent model insulators, where the
inner-shell electronic processes can be described in a good

approximation on the basis of only a single ion located at a
regular crystal lattice site.

We have studied potassium chloride as an adsorbate on
a Cu(100) surface with a coverage range from a partial
monolayer (ML) to a thick film with the spectral characteristics
of bulk polycrystalline KCl. Our study focuses on the
substrate-induced effects in the creation and decay of $K^+2p \rightarrow$
3d core excitations in KCl films.

The resonant Auger (RA) and normal Auger (NA) spec-
tra of K^+ in solid KCl as well as of free potassium
atoms were reported and analyzed earlier [12–14]. Addi-
tionally, the NA spectra of free KCl molecules have been
reported [15]. Good references for us would be the cor-
responding processes in the free ion (K^+ in our case),

but currently no such spectra for the ionic potassium are available.

The K^+ 2p photoabsorption spectrum of the KCl crystal reveals strong differences compared to the spectrum of atomic potassium due to the lowered symmetry. In particular, the atomic 3d orbital to which the K^+ 2p electrons are excited is split in the crystal by the anisotropic crystal field into two components of different energies and spatial orientations. Therefore, the 2p absorption spectra of atomic potassium display two peaks and the respective absorption spectra of KCl films four major peaks. It has been shown that the appearance of this splitting in K^+ 2p photoabsorption can be used to characterize the adsorbates [16]. Nevertheless, the RA decay spectra of the 2p excitations of K^+ in solid KCl exhibit a basic similarity to the corresponding RA spectra of atomic potassium [14].

A simple ionic compound like KCl is particularly suitable for studying the effects induced by the solid environment, since the excited 3d electron is strongly influenced by the crystal field [17] and is coupled to the electrons of the potassium ion [18]. The 3d electrons thus reflect the effects of the crystal field in the otherwise atomic RA spectra.

A question that invariably rises in connection with resonant excitations in adsorbates concerns the probability of delocalization of the excited electron. In weakly bound physisorbed systems the delocalization has been shown to have a comparable timescale with the RA decay [19, 20], whereas in some chemisorbed systems the delocalization can be much faster [21–24]. Given the prominent role of the excited 3d electron in 2p photoexcitation of KCl, its delocalization will have a direct influence on the resonantly excited Auger decay spectra. Therefore, the behavior of the 3d electron serves also as a probe of the charge transfer dynamics (see e.g. reviews [25, 26]) and thus carries information about the creation of insulating properties in thin films.

Several other effects can be seen in the RA electron spectra. The energy of the resonant excitations relative to the K^+ $2p_{3/2,1/2}$ ionization thresholds can vary depending on the environment, changing the contribution from the normal Auger decay. The characteristics of the adsorbate build-up from a partly formed first monolayer up to the polycrystalline structure will be also reflected in the RA and NA spectra.

2. Experimental setup

The experiments were carried out at beamline D1011 of the MAX-II storage ring (Lund, Sweden). The beamline has a modified SX-700 plane grating monochromator and a Scienta SES-200 electron energy analyzer. The electron energy analyzer axis at the endstation is at 40° angle relative to the photon beam, in the polarization plane. The SX-700 monochromator was calibrated using the Au 4f photoelectron (PE) lines excited in the first and in the second order. The kinetic and binding energies, presented in this paper, are calibrated using the calibrated monochromator and the Cu $3p_{1/2}$ line at 75.13 eV binding energy [27] as additional reference. The Cu $3p_{1/2}$ line was measured as a reference to each electron spectrum, but is not usually shown in the

figures. The resolution of the SX-700 monochromator was set to 0.1 eV and the resolution of the electron energy analyzer was approximately 0.3 eV. A separate MCP detector at right angles to the beam and to the polarization was used to measure the total electron yield (photoabsorption) spectra. All the spectra are measured near normal (4°) incidence.

For the deposition of the films a separate growth chamber was attached to the preparation chamber of the beamline endstation. The base pressure in the growth chamber was 5×10^{-10} mbar. The pressure did not increase significantly during the evaporation. The mechanically and electrochemically polished Cu(100) single crystal surface (Metal Crystals Ltd) was used as a substrate onto which the films of KCl were evaporated from a tantalum crucible. To ensure stable deposition rate, the sample was moved into the deposition position only after the crucible was heated up and in a stable evaporation regime.

Resistive heating of the tantalum support wires allowed the copper crystal substrate to be rapidly heated to temperatures of up to 800 K. The Cu(100) surface was initially cleaned *in situ* by Ar^+ ion bombardment while annealing. Prior to the deposition of each thin film sample, three step cleaning of the Cu(100) substrate was performed: (i) Ar^+-ion sputtering for 15 min, (ii) Ar^+-ion sputtering together with annealing for 15 min and (iii) annealing for 15 min. The substrate was checked before the preparation of each sample and no contaminants were observed above the noise level of the electron spectra. In addition, the prepared samples were checked using PE spectra and no contamination was observed.

3. Results and discussion

3.1. Photoabsorption

The K^+ 2p photoabsorption spectra at different substrate coverages are presented in figure 1. The spectra were measured in the total electron yield (TEY) mode and normalized to the incident photon flux. The topmost spectrum in the figure is measured from a thick film of KCl on Cu substrate. This spectrum is in good agreement with the absorption spectra of a KCl single crystal [17] and of a polycrystalline film of approximately 200 Å thickness [12]. The spectrum contains four distinct major peaks (labeled A–D in figure 1), which arise from the K^+ 2p $\rightarrow$ 3d excitations in the presence of an octahedral (O_h) crystal field. In the one-electron approximation, peaks A and B correspond to the excitation from the K^+ $2p_{3/2}$ spin–orbit component to the 3d level, which in the O_h symmetry of the crystal field has split into the t_{2g} (peak A) and the e_g (peak B) components. Analogously, peak C arises from the K^+ $2p_{1/2} \rightarrow 3d(t_{2g})$ and peak D from the K^+ $2p_{1/2} \rightarrow 3d(e_g)$ excitation. The spin–orbit and the t_{2g}–e_g splittings for the thick film are found to be 2.73 and 0.95 eV, respectively.

At the surface, and for the films with thicknesses in the monolayer range, the symmetry of the crystal field can no longer be expected to be as high as O_h, but rather a maximum of C_{4v}, or even lower if the excitation site lies, e.g., at a film island edge. The lower symmetry of the crystal field
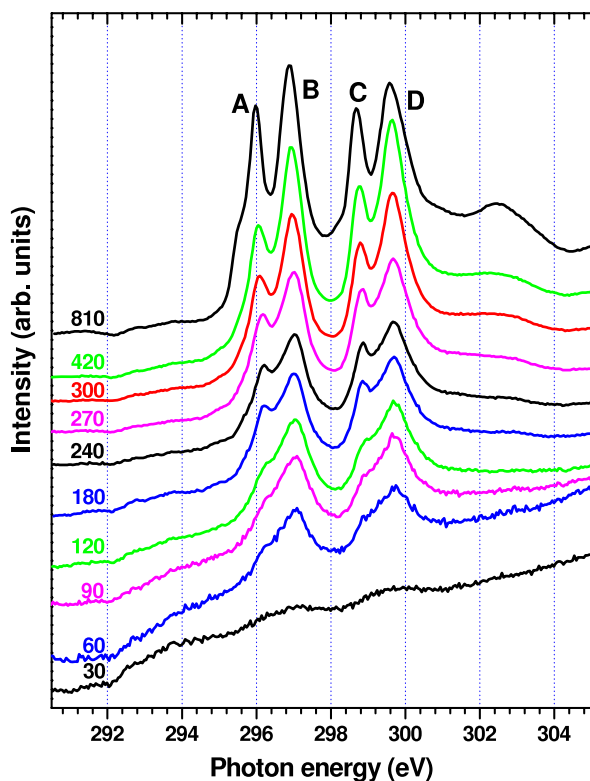
Figure 1. The x-ray photoabsorption (TEY) spectra of the KCl films of varied thickness on the Cu(100) surface near the K$^+$ 2p ionization threshold (film thickness is proportional to the deposition time in seconds, given next to each curve).

further reduces the degeneracy of the 3d final state (e.g. four inequivalent components under C$_{4v}$) and results in a greater number of more or less energetically distinct resonances and/or in the broadening of the main peaks.

One should keep in mind that in the presence of core-hole interaction the one-electron picture would not yield valid relative intensities even for the bulk film. Qualitatively, however, the single-particle approximation gives a guideline for rationalizing the main trends in the spectra when the coverage is varied.

The more realistic strong interaction model increases the number of inequivalent 2p → 3d transitions to seven for d^0 compounds in octahedral symmetry, though four of these transitions still generate the four main peaks while the remaining three give rise to pre-peaks and smaller features [13, 18]. When crystal field symmetry is lowered to C$_{4v}$, the number of inequivalent transitions increases to 22, with four resonances still significantly more intense than the others [16]. For example, a 'shoulder' at 295.5 eV visible below peak A for the '810 s' sample is caused by crystal field multiplet effects, discussed in detail in [18].

The photoabsorption spectra of the films of lower KCl coverage (namely the bottom spectra in figure 1) differ from the bulk film spectrum mainly by overall broadening of the peaks and a intensity distribution in the region between energies of the bulk O$_h$ crystal field split peaks. The slight changes in the locations and the intensity ratio of the crystal field split components can be attributed to the spectral

weight redistribution within the grown number of inequivalent transitions.

The spectra of the (sub)monolayer films can be compared to the photoabsorption spectra of the CO/K/Ni(100) coadsorption system [16], where the K$^+$ ion was found to be embedded at sites with C$_{4v}$ symmetry and where an intensity distribution similar to the (sub)monolayer KCl films was observed. The similarity of the spectra suggests that in ultrathin KCl films the K$^+$ ions are mainly embedded at sites with C$_{4v}$ symmetry. When the KCl coverage is increased, the main peaks in the K$^+$ 2p photoabsorption spectra become sharper and more pronounced, which reflects the gradual increase of absorption at bulk sites with O$_h$ symmetry and the corresponding decrease of absorption at interface and surface sites with C$_{4v}$ symmetry.

The crystal field splitting of the K$^+$ 2p photoabsorption peaks similar to the bulk KCl is seen already at very low coverages. Already the 0.3 ML sample (deposition time 60 s) indicates crystal field splitting, although not well resolved. This can be explained by the formation of relatively wide islands of KCl already at low coverages of the adsorbate. It has been shown that the initial growth of alkali halide films is seeded at surface irregularities, particularly at terrace edges [6, 7]. The growth then proceeds at the initial island edges, where the adsorbed species are readily transported due to the high thermal surface mobility [28].

3.2. Photoelectron lines and QUASES analysis

Figure 2 presents the K$^+$ 2p PE spectra measured from films of different thicknesses. The shape of the photolines changes significantly with the increase in film thickness. We are able to distinguish four components for both spin–orbit components of the K$^+$ 2p level: the submonolayer (i.e. partially filled first monolayer), interface, surface and bulk. It is demonstrated by Wertheim *et al* that in the case of alkali halides the surface component of the alkali ion is located at higher binding energy than the respective bulk component [29].

In order to characterize the KCl distribution on the surface and the film thickness, inelastic electron background analysis was used in the structure analysis. KCl layer thickness and morphology were determined by an analysis of the inelastic PE backgrounds (the QUASES analysis [30, 31]) of K$^+$ 2p and Cl$^-$ 2p transitions excited at higher photon energy ($h\nu$ = 700.0 eV). The spectrum obtained from the thick KCl film (deposition time 810 s) was characterized and no peaks originating in the copper substrate were observed. This spectrum was used as a reference for the analysis.

The QUASES-software package developed by Tougaard *et al* [32] was used. The empirically derived inelastic mean free path (IMFP) values of 25.6 Å for K$^+$ 2p (kinetic energy 404.8 eV) and 28.5 Å for Cl$^-$ 2p (kinetic energy 512 eV) were used [33]. The universal cross-section [34] was employed throughout the analysis. KCl monolayer thickness of 3.0 Å was used, estimated from the Seah and Dench formula [33].

A particularly good fit between the model and the experimental spectra was obtained for the K$^+$ 2p transition (see figure 3). The analysis of the Cl$^-$ 2p region yielded similar

Table 1. KCl layer thicknesses obtained from inelastic electron background (QUASES) analysis, and on the basis of PES. The accuracy of uniform thickness is estimated to be ±20%. '—' means that the very weak signal is disturbed by Cu 2p second order peaks and therefore it is not possible to perform the correct QUASES analysis.

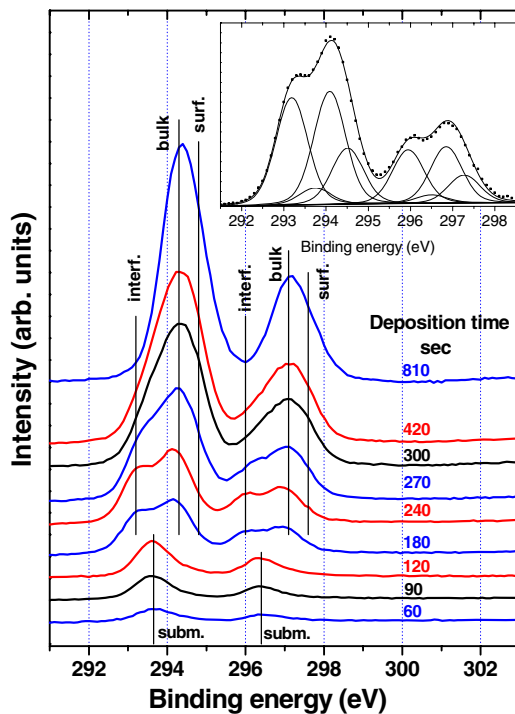| Sample (label)	Evap. time (s)	Thickness using K^+ 2p (uniform, ML)	Thickness using Cl^- 2p (uniform, ML)	PES estimate
0.3 ML	60	0.3	—	Partial ML
0.6 ML	90	0.6	—	
1 ML	120	1.0	1.0	Complete ML
1.5 ML	180	1.4	1.7	Full first ML + partial second ML
2 ML	240	1.8	2.2	
3.4 ML	270	3.3	3.5	Sample thickness more than 2 ML
5.4 ML	300	5.0	5.8	
7.3 ML	420	7.2	7.4	
Thick film	810	Bulk	Bulk	Thick polycrystalline film

Figure 2. K^+ 2p PES from the KCl films of different thicknesses (the deposition times in seconds are indicated in the figure). Incident photon energy was 401.3 eV. All the spectra have been normalized with respect to the ring current and the acquisition time. Locations of the submonolayer, interface, surface and bulk band maxima are marked with bars. The inset demonstrates the decomposition of the PE spectrum of an intermediate thickness sample (deposition time 240 s).

Figure 3. Inelastic electron background analysis (K^+ 2p) of the thickest KCl reference film (a) and experimental spectrum obtained after 120 s deposition (b). Insets demonstrate respective surface morphologies.

morphologies. Uniform film thicknesses, determined using the QUASES method, are given in table 1. The accuracy of uniform thickness is estimated to be ±20%.

We also present the thickness estimates made on the basis of significant variations in the photoelectron peak fine structure shown in figure 1. Respective arguments are discussed below and estimations are shown in the right column of table 1, alongside the QUASES results.

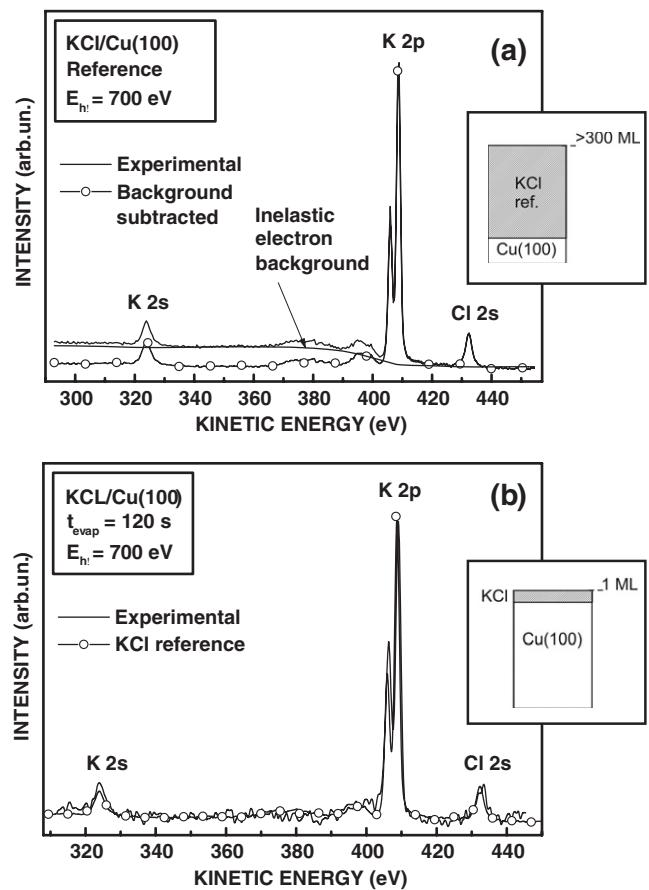The samples with deposition time up to '90 s' can be assigned as a partial first monolayer since the PE spectra contain only a submonolayer peak. The PE spectrum of the '120 s' sample also shows only a submonolayer peak, and this sample can be characterized as a completed first monolayer.

The PE spectra of the '180 s' and '240 s' samples contain two components with comparable intensities. We presume that these belong to the substrate–film interface and to the surface layer. Such behavior of the PE bands is in agreement with
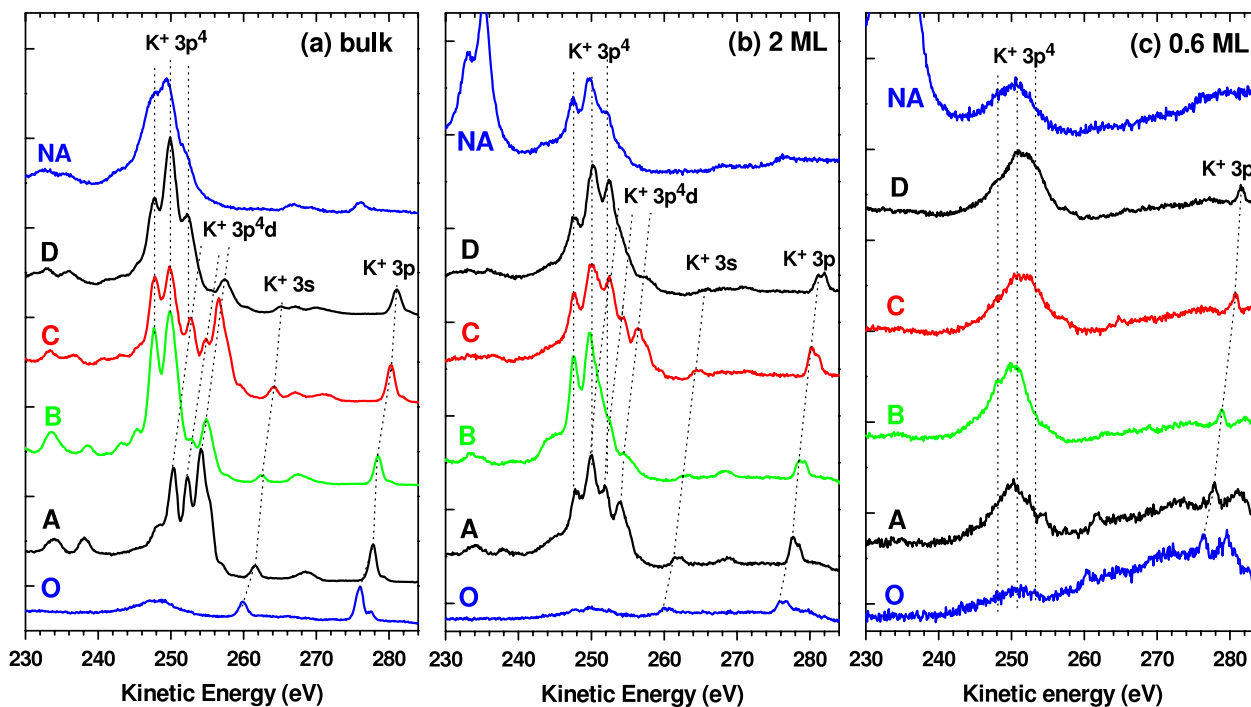
Figure 4. Resonant Auger spectra of KCl films with different thicknesses: (a) bulk, (b) 2 ML and (c) 0.6 ML. Labels A–D correspond to the resonances as indicated in figure 1, NA denotes the normal Auger spectrum, excited above resonance by photons with energy 310.5 eV, and O denotes the off-resonant Auger spectrum, excited below resonance, at 294.5 eV photon energy. The spectra are not normalized.

the QUASES results—the first monolayer is completed and the formation of the second monolayer has started.

When the evaporation time is increased to 270, 300 and 420 s, the core photoelectron spectra demonstrate two components—the interface and the bulk component. The relative intensity of the bulk component is increasing with the deposition time. A weak surface component is distinguishable beside the bulk component as well. The behavior of the PE bands is in agreement with the QUASES results—the first two monolayers are formed and the formation of the subsequent layers continues.

The PE spectrum of the '810 s' sample consists of a bulk component and a weak surface component. No substrate photoelectron lines are observable any longer.

3.3. Auger electron spectra

3.3.1. General overview. The Auger decay spectra following K^+ 2p photoabsorption in the KCl adsorbate are shown in figure 4: panel (a) corresponds to the thick film, panel (b) to the 2 ML sample and panel (c) to the 0.6 ML sample. The spectrum labels A–D denote the excitation resonances shown in figure 1. The NA spectrum is measured at $h\nu = 310.5$ eV, and the off-resonance spectrum (label 'O', $h\nu = 294.5$ eV) corresponds to the excitation energy below absorption resonance A. The spectra are not normalized.

Let us first consider the spectra of the thick film given in panel (a). The K^+ 3s PE lines on the high kinetic energy side in the spectra show linear energy dispersion with the incident photon energy. The Auger structure consists of two sets of lines: one set at constant kinetic energy and the other at constant binding energy. The strongest peak in spectrum A

at kinetic energy 254.1 eV and two additional peaks can be traced through spectra B–D, with the kinetic energy following the increase of the incident photon energy (see the eye-guide lines in figure 4(a)). This set of lines can be assigned to the $3p^43d$ final state. The Raman-like linear dispersion of these peaks is characteristic of the Auger decay of well localized excited states [12, 20].

In contrast, the low energy side of the Auger structure in spectra B–D (the peaks below 253 eV, which roughly coincide with the NA lines) remains at nearly constant kinetic energy independent of the excitation (see the eye-guide lines in figure 4(a)). These lines correspond to the doubly ionized $3p^4$ final state. It is important to note that the peaks at 250.3 eV and 252.2 eV kinetic energy are of different origin in spectrum A as compared to the spectra measured at higher lying resonances. The low kinetic energy side structure is stronger in spectra B–D, indicating that it results mainly from the decay of ionized states following the delocalization of the K^+ 3d spectator electron and/or direct core ionization [12].

Figure 4(c) shows the corresponding spectra from a KCl film with thickness 0.6 ML. For this sample only a broad emission band is observable and the structure is unresolved. As will be clarified below, the reason for this is the delocalization of the excited 3d electrons into the copper substrate.

Figure 4(b) shows the RA spectra from the 2 ML KCl film. The lines appear to be less resolved than in the spectra of the thick film. This relates to the delocalization effects of the 3d electron, to the energy shifts in electron emission from layers closest to the substrate and to the surface and to film non-uniformity. There is also a significant redistribution of intensity in all the spectra, compared to the thick film. The weakening of the highest energy Raman-like structure in the
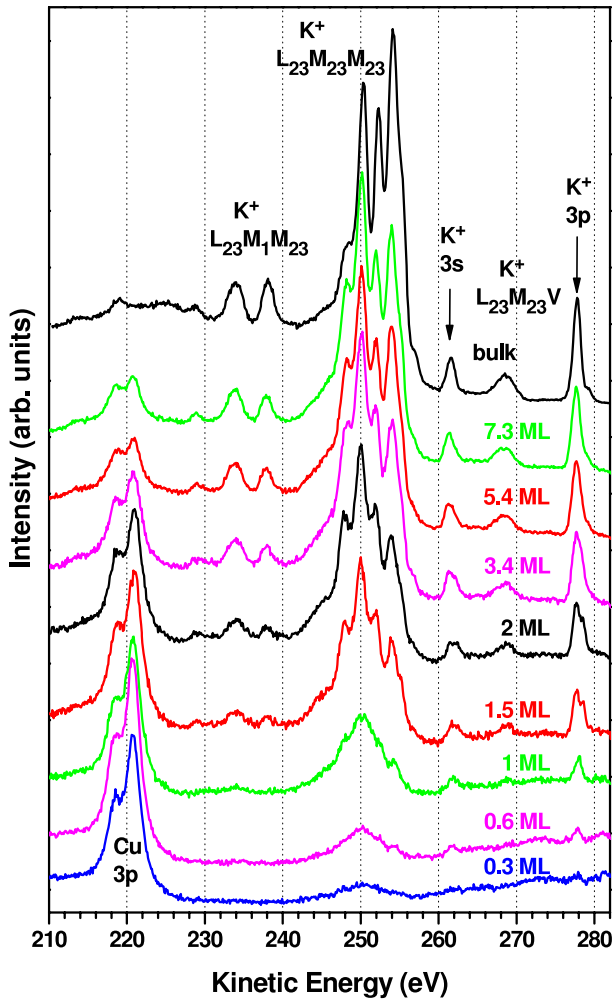
Figure 5. Resonant Auger spectra of KCl films with different thicknesses, excited at the maxima of the first photoabsorption resonances (marked with (A) in figure 1). Sample thicknesses are given next to each curve. The spectra are not normalized.

2 ML film (as compared to the thick film) is characteristic of the delocalization effects.

3.3.2. Auger spectra excited at resonance A. In order to compare changes related to sample thickness in further detail, the spectra measured at resonance A at varied coverage are presented in figure 5. Resonance A is dominated by excitations to the intermediate state $2p^6 \rightarrow 2p_{3/2}^{-1}3d(t_{2g})$, followed by the RA decay to the $3p^43d(t_{2g})$ final state [12, 13]. The RA electron spectrum of the thick film is very similar to the spectrum measured from a polycrystalline sample [12].

The positions of individual Auger peaks align well in all the spectra of figure 5, although the structure becomes unresolved for samples with thickness below 1.5 ML. A redistribution of the intensity occurs when the film thickness changes. In the thick film, the high kinetic energy peaks (located above 251.3 eV) are intense. With decreasing thickness, the intensity of these peaks decreases until, in thin films, only a broad structure at low kinetic energy is seen. The spectra of thin films excited at resonance A are very similar to
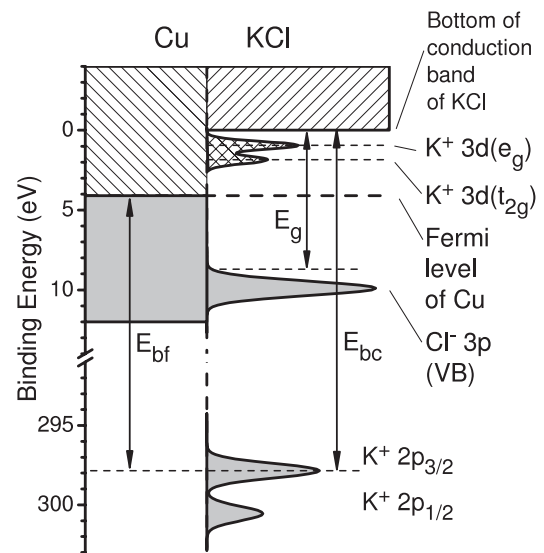

Figure 6. Schematic diagram of energy levels at the interface between Cu and KCl.

the NA spectra of thin films (see figure 4(c)). This leads us to the conclusion that the spectra of 'intermediate' thickness samples in figure 5 also contain a contribution from the decay of ionized $2p^{-1}$ states and they should be treated as a sum of two parts—NA and RA. To understand this, the peculiarities of photoionization near the threshold in crystals and thin films should be discussed. Note that under photoionization we understand here the removal of the electron from the inner level to the empty conduction states of the crystal/adsorbate (i.e. photoexcitation plus delocalization).

Figure 6 presents the scheme of the available energy levels at the KCl–Cu interface, obtained using the PES. In a bulk crystal the threshold for K^+ 2p core ionization is equal to the binding energy relative to the bottom of the conduction band (marked by E_{bc} in figure 6). This value can be obtained by adding the band gap $E_g = 8.7$ eV [35] to the energy difference between the inner $2p_{3/2}$ level and the top of the valence band 289.1 eV (present work, the thick film). Such a procedure [12] gives the value for E_{bc} of 297.8 eV for the L_3 level of the KCl crystal, which is 1.8 eV higher than the energy of the photoabsorption resonance A, 296.0 eV (this work, the thick film). Consequently, at resonance A the ionization of the inner levels should not be energetically possible and the photoabsorption leads to the creation of a well localized bound state of excitonic character, the decay of which would result in $3p^43d$ final states (the spectator decay). However, such an estimation procedure for E_{bc} is not very accurate (for example, see [36]), as we observed the appearance of the NA peaks already at excitations in the vicinity of the minimum between the absorption resonances A and B for the thick film sample (not shown in the figure). Nevertheless, for thick films, it is plausible to assume that at photoabsorption resonance A the photon energy is not sufficient to result in 2p core ionization.

The situation in thin films differs from bulk solid because the empty states of the metallic substrate become available. As the 3d states of the K^+ ion are energetically above the
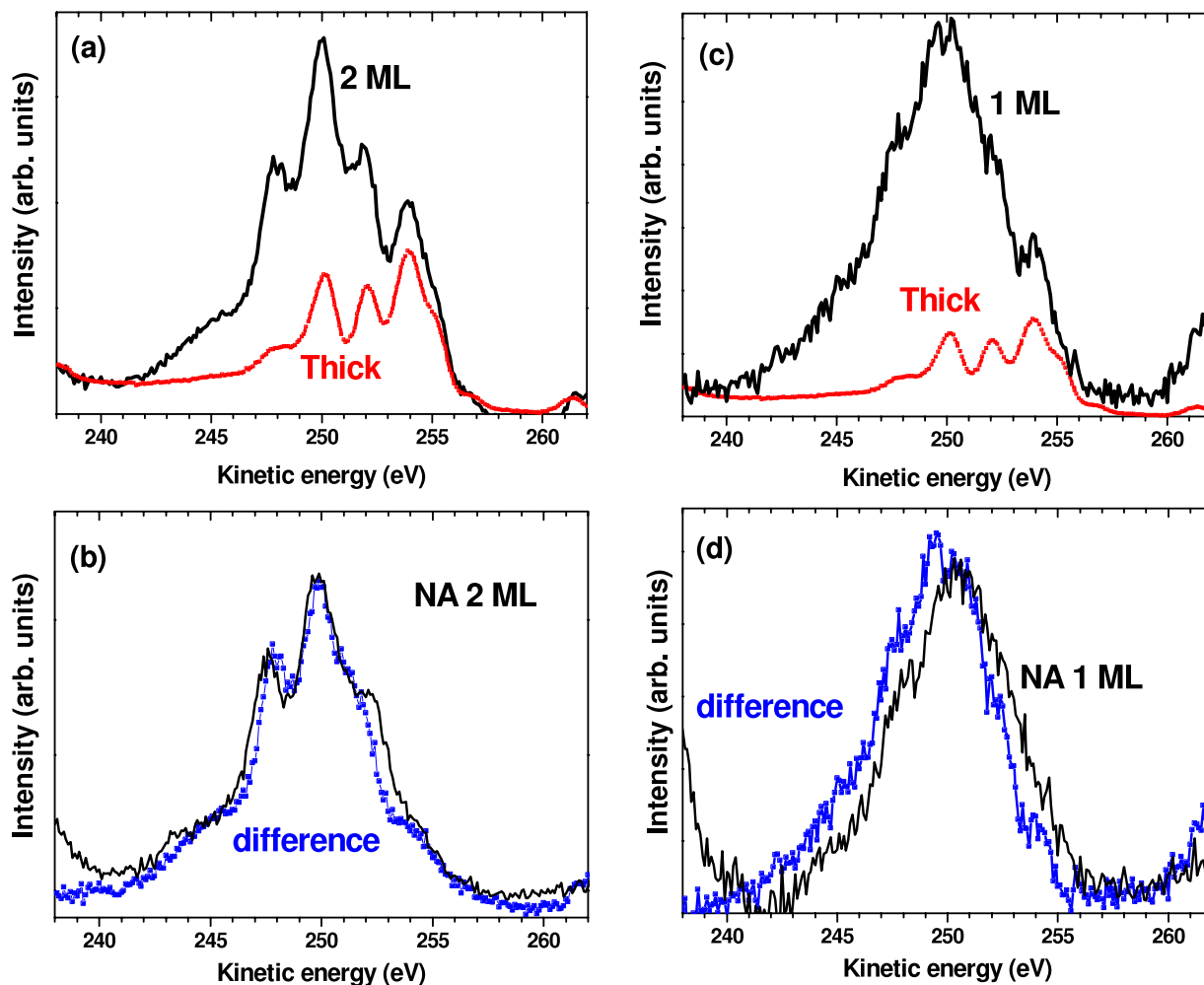
Figure 7. (a) The resonant Auger spectra of the 2 ML and the thick film samples, excited at resonance A. (b) The difference spectrum (dotted) of the latter, compared with the NA decay spectrum of the 2 ML sample (excitation energy 310.4 eV). (c) The RA spectra of 1 ML and the thick film of KCl, excited at resonance A. (d) The difference spectrum (dotted) and the NA spectrum of the 1 ML sample. A straight background is subtracted from all the spectra.

Fermi level of the metallic substrate, the fast delocalization path of the excited 3d electron into the unoccupied states of the copper substrate becomes available. The distribution of the unoccupied copper states in Cu above the Fermi level is discussed in [37]. In such a case the K^+ 2p ionization threshold is roughly equal to the binding energy of the inner level of the adsorbate relative to the Fermi level of the substrate (marked by E_{bf} in figure 6).

At 0.6 ML coverage of KCl on the Cu substrate, our PE spectra yield the values $E_{bf} = 293.8$ eV for the K^+ $2p_{3/2}$ level and 296.6 eV for the K^+ $2p_{1/2}$ level. It follows that for thin films at photon energies above 293.8 eV the excited electron will be able to delocalize from the K^+ $2p_{3/2}$ level (see figure 6), which would then result in intensity redistribution into the NA peaks in the decay spectra. In figure 4(c) the NA structures are really seen even at an excitation energy below photoabsorption resonance A, although these are rather weak.

In the case of 'intermediate' thickness samples the decay spectra contain both resonant and nonresonant features. To exemplify this we subtract spectrum A of the thick film from the corresponding spectrum of the 2 ML film. We assume

that the spectrum of the thick film only contains the RA component. Prior to subtraction the spectra were normalized at the spectator peak at 253.9 eV kinetic energy (see figure 7(a)). The difference spectrum is seen to be very similar to the NA spectrum of the 2 ML film (see figure 7(b)). We interpret this strong if not dominant presence of the core ionized (Auger) initial state as an indicator of partial charge transfer. A similar procedure giving similar results was performed for the 1 ML film as well (see figures 7(c) and (d)).

3.4. Discussion

From figure 5 is clearly seen the splitting of the K^+ 3p and 3s photoelectron lines, which is similar to the splitting discussed earlier in the case of the K^+ 2p photoelectron lines. At 1.0 ML coverage and below the K^+ 3p and 3s photoelectron spectra contain one component, and the RA component in the Auger decay (resonant de-excitation) spectra is very weak. For 1.5 ML and 2 ML spectra there is seen clear splitting of photoelectron lines, and in the de-excitation spectra appears the high kinetic energy structure, which is

due to decay of the localized core excited state. Therefore, when splitting of photoelectron lines appears, there appears also the decay of localized core excited states. Thus in these samples the second layer appears, for which the probability for delocalization of the excited 3d electron into the substrate is sufficiently reduced in comparison with the first layer. When the film thickness increases, the bulk component increases in photoelectron spectra and intensity corresponding to the decay of core excited state increases in de-excitation spectra.

Note that the intensity of the K^+ 3p photoelectron line is enhanced at the photoabsorption resonances, showing that the electron which is excited to the K^+ 3d level has a probability to decay in a 'participator' process. Figure 4(b) shows that the low kinetic energy branch of the photoelectron line is more intense when the incident photon energy is at resonances A and C. Such resonant enhancement appears in the samples with a localized excited state.

Weak spectator peaks are distinguishable in the spectra of the 0.6 ML and the 1 ML samples at resonance A (see figure 5). For the 0.3 ML sample the peak is not seen, but there is some intensity in the corresponding spectral region. We suggest that this indicates the probability that the Auger decay takes place prior to charge delocalization, even if the average charge transfer time becomes shorter than the Auger timescale.

In order to obtain a numerical estimate, we will now apply the core-hole-clock approach. According to the references [26, 38], the charge transfer time τ_{ct} can be estimated by the following equation: $\tau_{ct} = \tau_\Gamma * f/(1 - f)$, where τ_Γ is the natural lifetime of K^+ 2p level and $f = I_{sp}/I_t$ is the ratio of the total intensity of the spectator transitions I_{sp} and the total intensity of all Auger transitions I_t. The spectrum of the 1 ML film yields the value $f = 0.23$.

To the best of our knowledge, the natural lifetime of the 2p core hole in the ionic (argon-like) K^+ is not available in the literature. For the Ar atom, which is isoelectronic to the ionic K^+, the 2p core hole lifetime has been reported [39] to be 5.9 fs. An estimate of approximately 5 fs for the K^+ 2p core-hole lifetime can be therefore considered plausible. Using this value we obtain that the charge transfer time for a single KCl monolayer at a Cu(100) surface is about 1.5 fs.

Applying the same approach to the 2 ML film, we obtain for the charge transfer time the value of about 3 fs. Note that although this value is a superposition of the charge transfer times from the first and the second layer, it illustrates the fact that the charge transfer from the second layer of the overlayer is larger than for a single monolayer.

As K^+ is isoelectronic with Ar, it is reasonable to compare our estimate for the charge transfer times with argon at metal surfaces. Our estimation of charge transfer time for a KCl monolayer, 1.5 fs, is similar to the charge transfer time from the Ar 4s level in Ar monolayer metals. For example, for Ar on Ru metal the value of 1.5 fs has been obtained [26]. Such a similarity is somewhat surprising, as Ar on Ru is known as example of weak substrate–adsorbate coupling, but for KCl on Cu it can be assumed that there is a strong coupling between the KCl molecules and the copper substrate, which usually leads to short charge transfer times (similar to the case of CO on Ru, where charge transfer times below 1 fs

have been reported [23]). The reason for this may be the sufficiently small radius of the 3d wavefunction of the K^+ ion in comparison with argon, known as the collapse of the 3d wavefunction [40]. Collapse reduces the overlap with the copper states in comparison with the case of Ar on Ru.

4. Conclusions

The principal features of the K^+ 2p photoabsorption spectra of KCl are seen to remain at roughly the same energies throughout the sample thickness range from submonolayer films to a bulk polycrystalline sample, with variation in relative intensities and peak widths.

Crystal field splitting is obvious already at the lowest coverage of approximately 0.3 ML. We suggest that in the case of increase of the layer thickness, the photoabsorption spectra reflect the gradual increase of the absorption at bulk sites with O_h symmetry and the corresponding decrease of the absorption at interface and surface sites with C_{4v} (or lower) symmetry.

The shapes of the resonant Auger spectra of submonolayer (and complete monolayer) films are qualitatively different from the spectra of the films with thicknesses over 1 ML. In the case of thin films, the 3d level is strongly hybridized with the unoccupied states in the copper substrate. This opens a channel for fast (as compared to the core-hole decay) delocalization of the electron, which is excited to the K^+ 3d state. Therefore, for thin films the Auger decay spectra at all resonances reflect mainly the decay of the core ionized state ($3p^4$ final state). In contrast, in the thick film, the decay spectra show a well resolved structure typical of the decay of core excited states with $3p^4 3d$ final states. The decay spectra of the samples with 'intermediate' thicknesses include both the core ionized and the core excited components. By using the core-hole-clock approach we obtained for the charge transfer time from the first monolayer of KCl to the copper substrate the value 1.5 fs.

The probable scenario for the film formation is that the initial growth stage comprises a partly formed monolayer of KCl molecules. When the coverage increases, the first layer will be completed and the growth on the next monolayers starts. This differs from the case of NaCl on Al, where the formation of the second and the third layer starts before the first layer is completed [7]. To obtain more information about the KCl growth mode, additional systematic studies, e.g. using UHV AFM and LEED, are necessary.

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