# Observation of Metallization Transition of 2D Alkali Metal Films

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The deexcitation rate of metastable $^3S$ He$^*$ atoms was measured during the growth of Na, K, and Cs films on a Cu(100) surface. As a consequence of the reduced work function, which is caused by adsorption of small amounts of alkali metals, the He$^*$ deexcitation mainly takes place via Auger deexcitation. Since the incident He$^*$ atoms interact only with the vacuum side tails of the electronic states of the surface atoms, the deexcitation rate for this mechanism reflects the electronic surface density of states. At coverages of about 0.4 monolayer a dramatic increase in the deexcitation rate was obtained, which is attributed to the subsequent filling of the alkali metal valence band and thus the onset of metallization.

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The adsorption of alkali metal (AM) atoms on surfaces has been studied extensively since Langmuir discovered a large enhancement of electron emissivity for AM covered metal surfaces [1–4]. Although AM atoms are considered as prototypical chemisorption systems because of their electronic simplicity, they reveal a rather complex behavior. Because of their different electron affinity compared to metal substrates a significant fraction of the AM valence *s* electron is displaced towards the metal surface and creates a dipole moment. With increasing coverage these dipoles become depolarized and the AM atoms begin to form a metallic film. Since then this classical picture, originally proposed by Gurney [5], has been refined by realistic quantum theoretical calculations [4,6,7]. The metallic character of a complete AM monolayer on metal substrates is well established [2], whereas the metallization transition itself is difficult to observe experimentally.

The direct observation of occupied AM *s*-valence states by ultraviolet photoelectron spectroscopy, the standard tool to study the electronic structure of adsorbate systems, is hampered by the low density of states (DOS) of the *s* band which is superimposed on the high density of states of the substrate at the Fermi level and additionally by the small photoemission cross section of *s* states [8]. Woratschek *et al.* utilized the unique surface sensitivity of metastable deexcitation spectroscopy (MDS) [9] to overcome this difficulty and measured the occupation of the 4*s* level of K atoms adsorbed on Cu(110) [8,10]. However, their interpretation was questioned in a later MDS study by Hemmen and Conrad who demonstrated that the observed electron emission near the Fermi edge is mainly caused by an *autodetachment* process of the impinging metastable He$^*$ atoms [11].

Here we introduce a new approach by combining the high sensitivity of ground state He atom scattering (HAS) for measuring the AM coverage and the extreme surface sensitivity of the metastable atom deexcitation rate to detect modifications of the electronic surface structure. We report on measurements of the survival probability of He$^*$ atoms scattered from a Cu(100) surface as a function of the Na, K, and Cs coverage. At relative K and Cs coverages of $\theta = 0.13$ and $\theta = 0.11$, respectively, a drastic reduction of the He$^*$ survival probability with further coverage appears and is attributed to the filling of the AM *s* band and thus reflects the onset of metallization.

This experiment was carried out with a UHV atom scattering apparatus (base pressure $7 \times 10^{-11}$ mbar) which allows the angular and time-of-flight resolved detection of scattered ground state He and metastable He$^*$ atoms. It is described in detail elsewhere [12]. Essentially, an intense supersonic $2^3S_1$ He$^*$ beam of thermal kinetic energy ($E_i \approx 100$ meV) is produced by a cold discharge burning within the expansion zone [13]. The scattered He and He$^*$ atoms are simultaneously detected by a magnetic mass spectrometer and a channeltron, respectively, mounted at fixed angles of 90° and 60° relative to the incident beam. By rotating the sample angular distributions can be recorded. The Cu(100) sample was prepared in UHV by standard cleaning procedures involving sputtering and annealing cycles until the corresponding Auger electron spectra revealed no traces of contaminations and a sharp specular peak was obtained in the He atom angular distributions. The AM films were prepared *in situ* by evaporation of Na, K, and Cs from SAES Getters dispensers at a surface temperature of 120 K. Growth was monitored via HAS which reveals characteristic specular intensity oscillations with increasing coverages [see inset of Fig. 1(a)] [14]. The actual submonolayer coverage was determined through the deposition time relative to that for a monolayer as indicated by the first sharp oscillation maximum which is displayed in Fig. 1(a) for the growth of Cs. The corresponding relative monolayer (ML) coverages with respect to the substrate, $\theta_{\mathrm{ML}}$, depend upon the size of the AM atoms, and values of 0.50, 0.37, and 0.27 for Na, K, and Cs, respectively, have been determined by LEED (see, e.g., [15]).

Figure 1(b) displays the intensity of He$^*$ atoms scattered from the Cu(100) surface as a function of AM

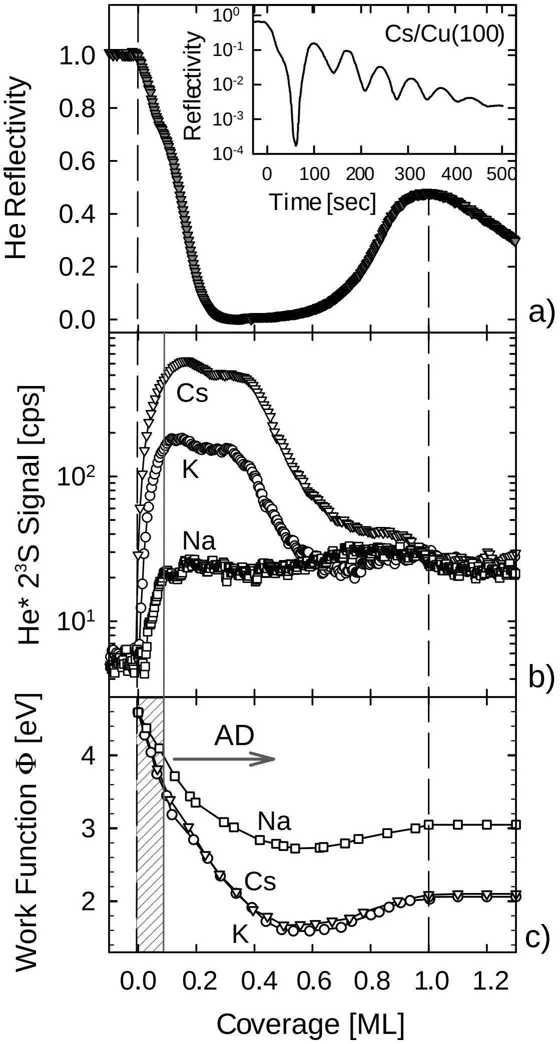

FIG. 1. (a) HAS reflectivity and (b) scattered He* signal recorded during evaporation of alkali metal atoms on Cu(100) at $T = 120$ K. Note that the He* signal is drawn in a logarithmic scale. The inset displays the typical oscillations of the specular He atom reflectivity (growth curve) during the growth of AM multilayers. (c) Corresponding work function as the function of the various AM coverages (see [15]).

coverage upon formation of the first monolayer of Na, K, and Cs. For all of the AMs initially a steep increase in the He* signal was obtained which reaches a maximum at about 0.15 ML. The value of the maximum depends upon the size of the AM atoms and is largest for Cs which is more than 2 orders of magnitude higher than for the clean Cu(100) surface. For K and Cs coverages of 0.35 ML ($\theta_K = 0.13$) and 0.40 ML ($\theta_{Cs} = 0.11$) the He* signal starts to decrease dramatically and reaches the same asymptotic monolayer value for all of the AMs. It is about 6 times larger than for the clean Cu(100) surface and remains constant for multilayer films. Very broad, cosine shaped angular distributions of the scattered He* atoms are observed with a FWHM of about 40° in agreement with previous measurements for clean and absorbate covered surfaces [12,16]. The total He* survival probability was determined by angular integration of the measured He* signal and is found to be proportional to the He* signal close to the specular condition [12]. Therefore the scattered He* intensity was recorded to monitor the He* survival probability during the growth of the AM films.

To gain further information on the electronic properties of the AM films from the measurements an understanding of the underlying He*-surface interaction and the resulting deexcitation processes is required. Whereas in general He* deexcitation can take place via different mechanisms, all of which have been identified previously by extensive MDS studies and by comparison of the resulting electron emission spectra with the corresponding UP spectra [9,11], some of them can be omitted in the present system. On clean metal surfaces the deexcitation of He* is dominated by the *resonance ionization* (RI) mechanism which is shown schematically in Fig. 2(a). In the first step the He* $|2s\rangle$ electron is resonantly transferred to an empty surface state $|\overline{k}\rangle$, leaving a He$^+$ ion behind, that is neutralized in the second step by an Auger type transfer involving filling of the $|\overline{1s}\rangle$ state and emission of a surface electron. Because this (resonant) process is very efficient, the resulting total He* surviving probability is only about $10^{-6}$ for Cu(100) [12]. If the work function, $\Phi$, of the surface becomes smaller than the effective ionization energy of the metastable atom $E^i_{\text{eff}}$, the RI process is suppressed, because no unoccupied resonant states exist for the $2s$ electron, and deexcitation takes place only via *Auger deexcitation* (AD). As depicted in Fig. 2(b) the empty He* $|\overline{1s}\rangle$ state is filled by a substrate surface electron and the He* $|2s\rangle$ electron is emitted simultanously in an Auger process, carrying the excess energy of the system. The most important feature of this process in terms of the present experiment is its dependence on the electron density of states at the surface. In a first order approximation the deexcitation rate for this process $\Gamma_{\text{AD}}$ is proportional to the overlap of the wave functions of the empty He $|\overline{1s}\rangle$ state and the filled surface state $|k\rangle$ [17]:

$$\Gamma_{\text{AD}} \propto |\langle \overline{1s}|k\rangle|^2. \tag{1}$$

The reduction of RI with decreasing work function therefore leads to an increase in the scattered He* signal that stops abruptly when the work function equals $E^i_{\text{eff}}$. This is apparent in the Na curve [see Fig. 1(b)], where exclusion of RI appears at a Na coverage of 0.1 ML.

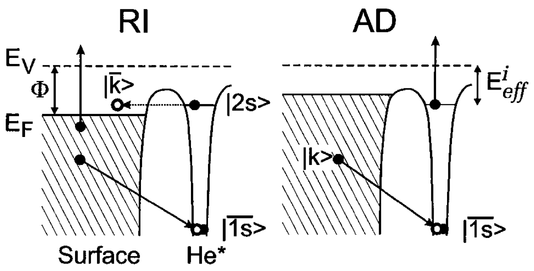

FIG. 2. Schematic potential diagrams for the resonance ionization (RI) and Auger deexcitation (AD).

Comparison with the corresponding work function which is shown in Fig. 1(c) gives an effective ionization energy of $E^i_{\mathrm{eff}} = 4.0$ eV. Hagstrum *et al.* demonstrated that the actual value of $E^i_{\mathrm{eff}}$ depends upon the closest distance of the He* atom from the surface. The image potential interaction leads to an upward shift of the occupied levels and a downward shift of the affinity levels. For $E^i_{\mathrm{eff}} = 4.0$ eV these calculations yield an interaction distance between He* and the surface imaging plane of about 4 Å [18].

For K and Cs the initial increase of the He* signal at low coverages is far greater than the increase that was found for Na. The AD deexcitation rate, which becomes the determining factor after exclusion of RI, must therefore be very much lower for the K or Cs covered surfaces in comparison to the Na covered surface. This can be understood in terms of a surface screening by the AM adatoms. At low coverages alkali atoms have a reduced electron density on their vacuum side [5–7], which lowers the deexcitation rate and reduces, with increasing adatom size, the interaction of the He* atom with the substrate surface. Therefore, the surviving He* intensity is highest for the largest investigated alkali metal, cesium. In addition, the dipole moments of the isolated AM atoms attract the incident He* atoms due to their high polarizability and thus reduce the effective visible copper surface area. From the relative coverage, corresponding to the largest He* intensity for K and Cs, an effective screening cross section of about 160 Å$^2$ per adatom can be calculated which is similar to the He atom cross section for isolated AM adatoms of about 120 Å$^2$ as deduced from the initial decrease of the HAS reflectivity [14].

As mentioned initially the interpretation of MD spectra at low work function is further complicated by the occurrence of *singlet-to-triplet conversion* and *autodetachment* deexcitation processes. These arise when the work function becomes smaller than the affinity level of the He* atom, whose empty $|\overline{2s}\rangle$ level can then be filled by a surface electron [11]. In the second step the electron with antiparallel spin relative to the $|1s\rangle$ electron is either emitted into the surface (singlet-to-triplet conversion) or into the empty He $|\overline{1s}\rangle$ state under synchronous emission of the second $|2s\rangle$ electron into the vacuum (autodetachment). While singlet-to-triplet conversion is excluded in the present experiment by using a pure triplet He* beam, the latter process might have a measurable influence on the He* survival measurements. However, the integrated electron emission corresponding to this deexcitation channel compared to the total MD spectrum is negligible. Even for the deexcitation of singlet He*, where autoionization is enhanced, it contributes less than 5% of the total spectrum intensity [19].

The Cs experiment has also been carried out for metastable Ne. Despite the small incident Ne* beam intensity, the relatively higher survival probability allowed a measurable signal. As displayed in Fig. 3(a) the shape of the recorded Ne* intensity versus coverage curve was identical to the one obtained for He*.

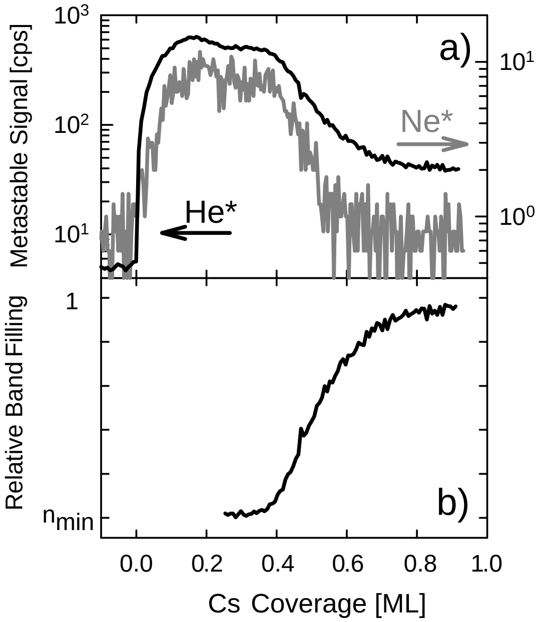

FIG. 3. (a) Comparison of the intensities of scattered He* atoms (black line, left axis) and Ne* atoms (grey line, right axis) from a Cu(100) surface during the growth of a monolayer of Cs. (b) Coverage dependent relative occupation of the surface electronic states upon completion of the Cs monolayer obtained from the decrease of the scattered He* signal.

In summary, the only significant deexcitation process for AM coverage above 0.15 ML in the present He* scattering experiment is the Auger deexcitation. Thus the observed decrease in the He* intensity ($\equiv$ increase in $\Gamma_{\mathrm{AD}}$) above 0.4 ML reflects the increase of the surface electronic DOS (SDOS) corresponding to the subsequent filling of the AM *s* band. The proportionality between the band filling $n$ and the deexcitation rate $\Gamma_{\mathrm{AD}}$ [Eq. (1)] makes it possible to convert the measured He* signal, $I_{\mathrm{He}^*}$, into a relative band filling. Because the deexcitation process is a first order reaction, an exponential decay law gives the number of the surviving metastables; hence $\Gamma_{\mathrm{AD}} \propto -\log(I_{\mathrm{He}^*})$. Substituting $|k\rangle$ in Eq. (1) by the SDOS $n$ yields the expression

$$n \propto -\log(I_{\mathrm{He}^*})\,. \tag{2}$$

As plotted in Fig. 3(b) for the Cs layer the relative band filling starts to increase at about 0.4 ML ($\theta = 0.11$) and is already almost saturated at about 0.7 ML.

In an accompanying spot profile analysis LEED study of the submonolayer structure of K and Cs on Cu(100), diffraction pattern with characteristic sharp isotropic diffraction rings have been observed for coverages below about 0.5 ML [20]. From the radius of the diffraction patterns, which arise from a *quasihexagonal* superstructure with appreciable azimuthal disorder but with a well defined nearest-neighbor spacing $d$, average adatom separations can be calculated [15] and values of $d_{\mathrm{K}} = 8.5$ Å and $d_{\mathrm{Cs}} = 7.6$ Å were found for the onset of metallization which correspond to 55% and 68% of the nearest-neighbor bulk distances of potassium and cesium, respectively. Furthermore, at slightly higher coverages of about $\theta = 0.17$, the formation of azimuthally regularly ordered hexagonal overlayers takes place. In contrast, sodium is found to order in commensurate superstructures on Cu(100) already at coverages of $\theta = 0.12$ [21]. The different behavior observed for sodium is in accordance with the significantly shorter bond length of Na with respect to the copper surface plane. This causes a very effective screening of the initial dipole moment and has also been found to affect the AM adatom vibrations [15]. Similar differences in the AM-substrate interaction were also reported in a previous *ab initio* study for K and Na on Al(111) [22].

To test our interpretation, the scattered $He^*$ signal was also measured during subsequent exposure of the various AM monolayer (at 120 K) to oxygen. This causes a continuous increase in the $He^*$ signal until after an exposure of 3 L $O_2$ the maximum values obtained at the initial AM coverages of 0.2 ML were again reached. Since the adsorption of oxygen on cesiated surfaces causes an additional lowering of the work function [8] and thus an increase in the $He^*$ deexcitation probability through autodetachment, the measured increase of the $He^*$ scattering signal corroborates further that this deexcitation channel is of no relevance for the present experiment. Instead it is attributed to the demetallization of the AM film due to the oxygen-cesium interaction. A similar effect has recently been reported for the coadsorption of CO and Cs on Ru(0001) [23].

In summary, we have demonstrated that recording of the intensity of scattered $He^*$ or $Ne^*$ atoms is a very sensitive tool for measuring metallization transitions on surfaces and thin films which have a sufficiently low work function to suppress RI. In contrast to HAS, $He^*$ scattering is not sensitive to geometrical disorder on surfaces and thus also provides a method to study electronic properties of polycrystalline surfaces. A quantitative analysis of the metallization based on the present data deserves detailed calculation of the deexcitation rate $\Gamma_{AD}$.

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