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ABSTRACT
The composition-dependent change in the work-function (WF) of binary silver–potassium nanoparticles has been studied experimentally by synchrotron-based x-ray photoelectron spectroscopy (PES) and theoretically using a microscopic jellium model of metals. The Ag–K particles with different K fractions were produced by letting a beam of preformed Ag particles pass through a volume with K vapor. The PES on a beam of individual non-supported Ag–K nanoparticles created in this way allowed a direct absolute measurement of their WF, avoiding several usual shortcomings of the method. Experimentally, the WF has been found to be very sensitive to K concentration: Already at low exposure, it decreased down to ≈2 eV—below the value of pure K. In the jellium modeling, considered for Ag–K nanoparticles, two principally different adsorption patterns were tested: without and with K diffusion. The experimental and calculation results together suggest that only efficient surface alloying of two metals, whose immiscibility was long-term textbook knowledge, could lead to the observed WF values.

I. INTRODUCTION

The work-function (WF) change due to alkali-atom adsorption has been occupying researchers for almost a century by now, and our understanding of this change has been progressing with each new theoretical and experimental advancement. In the 1930s, the WF decrease was first addressed by Langmuir. In his picture, which conceptually survived for almost half a century, the valence electrons of the adsorbed alkali atoms were “lost” to the substrate and the dipoles built by the alkali ions and their image charges produced a field lowering the potential at the substrate surface so that the WF decreased.

With the development of WF measuring techniques, in the 1960s, not only the decrease but also a WF minimum was observed at alkali sub-monolayer coverage on several tight-metal substrates—Mo, W, and Ni, actual for vacuum-tube electrodes, e.g., Refs. 2–4. This minimum was explained by the competition of two parallel changes taking place with the coverage: the adatom-number increase and the decrease in dipole moment per adatom.

It was not until the 1970s when the minimum was first adequately explained using a quantum-mechanics approach—the jellium model of metals. In that treatment, the tightness of the substrate metal (3.1–3.3 Å for Mo, W, and Ta lattice constants) was critical to rule out the alkali diffusion into the substrate. In the diffusion absence, two slabs of non-mixed metals could be used in the modeling. After the jellium-model success, the study of the alkali adsorbates went on involving more and more parameters and details in the experiments and theory: crystal orientation, adsorption sites, substrate temperature, and so on. The bonding type was vividly discussed: to what extent and at what coverage it was metallic, ionic, or covalent.

Density functional theory was employed disclosing the role of the alkali-island formation and of the substrate-surface rumpling. From the practical side, around the time when the jellium picture for the electron-tube relevant cases was developed, another application of alkali adsorbates matured: In catalysis, the alkali atoms covering such noble metals as Ag or Pt served as promoters of chemical reactions. Among the most peculiar WF-results obtained in the second part of the 1980s and in the 1990s were those for the alkalis on heavier coinage metals Ag and Au: depending on the conditions, the WF-vs-coverage curve was shown to have either...
a minimum, no extremum, or even a maximum.\textsuperscript{10,15,16,29} Theoretical treatment of such binary systems was complicated by the fact that alkalis, especially K, not only rumpled Ag upper layers\textsuperscript{13,22} but diffused into Ag bulk,\textsuperscript{26–32} which crystal is rather “loose” (bcc lattice constant = 4.1 Å). A strong diffusion of alkalis was observed\textsuperscript{33–37} in the 1990s for another metal with such a “loose” lattice—aluminum, in which the bcc constant is 4.0 Å. This observation was quite unexpected since historically alkalis were considered to have low solubility in Al.\textsuperscript{40} Contrary to this earlier image, Na, K, and Rb were detected at least four Al monolayers deep and at concentrations equal to that of the substrate atoms. Several experimental techniques led to such conclusions: photoelectron spectroscopy (PES), low energy electron diffraction (LEED), and extended x-ray absorption fine structure (EXAFS).

In these experiments\textsuperscript{41,42} as well as in the earlier mentioned ones, well-ordered metal surfaces were studied, while in real catalytic reactors the metals, also Ag, are typically used in the form of nanoparticles\textsuperscript{1}—with the surface far from ideal crystalline. Clearly, one would like to be able to describe the important nanoparticle case in the same simple but insightful way as the jellium approach once enabled for the alkalis adsorbed on the plane surface of “light” metals typical for the vacuum-tube electrodes.

Involving the jellium model for such a description has an additional motivation—it was this model which once brought a breakthrough in the understanding of the peculiar electronic structure of metal clusters/nanoparticles, especially their WF change with the particle size.\textsuperscript{37–40} Thus, with these two achievements on its account, the jellium model has been an approach worth trying for Ag particles with an alkali adsorbate.

Experimentally, however, preparing individual free nanoparticles with different alkali coverages and measuring their WF remained for a long time a project for the future due to the substantial technical complexity. Even for the macroscopic samples, the two typical techniques for the WF-measuring, photoelectron spectroscopy and a Kelvin-probe method, were with the time realized to have pitfalls\textsuperscript{41,42} (see the Appendix for the details of the two methods). In particular, the observed differences for K–Ag (e.g., Refs. 10 and 15) or K–Au systems (Refs. 16 and 29) may have been caused, at least to some extent, by the shortcomings of the techniques used. In the case of K–Ag systems, while at $T \approx 100$ K both studies\textsuperscript{10,15} showed a fast WF drop within the first 0.2 monolayer of K and a minimum at $\approx 0.5$ monolayer, there was a $\approx 30\%$ difference between Refs. 10 and 15 where the WF droppad within the first 0.2 monolayer of K and a minimum at $T \approx 100$ K both studies\textsuperscript{10,15} showed a fast WF drop within the first 0.2 monolayer of K and a minimum at $\approx 0.5$ monolayer, there was a $\approx 30\%$ difference between Refs. 10 and 15 in how much the WF dropped. In Ref. 15, where the WF was measured not only at the cryogenic $T$, but also at $T = 325–335$ K, at this latter temperature, no WF minimum was observed. Moreover, the saturation WF values at a monolayer coverage differed noticeably for the cryogenic and the elevated $T$ (see the text below). All these discrepancies remained unexplained.

In the present work, we have addressed the WF change in a joint experimental and theoretical study of free Ag nanoparticles doped with K. The particles were prepared in a beam and exposed to K vapor “on-the-fly” —as the beam of Ag particles passed through the K vapor created in an oven (Fig. 1). The WF of these particles in a beam was determined by synchrotron-based photoelectron spectroscopy. Using the jellium modeling, the nanoparticle energy levels were calculated for two different scenarios: without and with diffusion. The combined experimental and theoretical studies on the nanoscale objects under investigation provided an insight into the nature of the WF change and component distribution realized as the result of K adsorption on Ag.

II. EXPERIMENT

An experiment on free nanoparticles in a beam is in many senses an advantageous way of studying WF and the influence of adsorption on it, with the results relevant not only for nanoscale but also for the macroscopic case. Such an approach allows overcoming the weak points of the conventional PES as a method for measuring the WFs. These weak points are especially pronounced when alkali metals are involved and are as follows: the relatively long exposure of a reactive sample to the rest-gas, the necessity of the bias voltage in PES, and the dependence on the poorly known transmission of an electron spectrometer in the low-kinetic energy range (see the Appendix for details). In the PES measurements on a particle beam, the absolute binding energy calibration of the particle energy levels can be done using the spectral lines of the inert carrier-gas.\textsuperscript{43} Such calibration allows obtaining the Fermi-level energy, and thus the WF, directly from the spectrum since it is calibrated relative to the vacuum level.\textsuperscript{43,44} It is the onset of the valence band, which defines the WF. Additionally, this value allows estimating the dimensions of the parent Ag nanoparticles using the so-called conducting-sphere approximation valid for metallic particles (see the Appendix for details). According to this approximation, the difference between the particle WF and the corresponding macroscopic solid is equal to $\frac{1}{2}e/R$, where $e$ is the electron charge in Gaussian units and $R$ is the particle radius in angstroms. We used this approach to estimate the particle dimensions in our experiments.

A. Nanoparticle fabrication and spectroscopy

Free Ag nanoparticles were created using an in-house built apparatus\textsuperscript{45}—a nanoparticle source. The primary atomic-Ag vapor was detected by the spectrometer.

FIG. 1. Experimental setup for the production and PES studies of free K-doped Ag nanoparticles propagating in a beam and ionized “on-the-fly” by x rays: (1) nanoparticle source, (2) magnetron inside a crystal (3), (4) XYZ-manipulator, (5) turbo-pump. The source is attached to the ionization chamber (6). The latter has a vertically mounted electron Scienta R4000 spectrometer (not shown) on port (7). The nanoparticle beam (8) passes through K vapor created in a heated crucible (9). The x-ray photon beam (10) crosses the nanoparticle beam at $90\^\circ$. The photoelectrons (11) emitted in a narrow solid angle along the vertical direction are detected by the spectrometer.
was produced by a magnetron-sputtering gun placed inside a liquid-nitrogen-cooled cryostat. This vapor aggregated into nanoparticles within a continuous flow of the cooled argon and helium gases (Fig. 1). Our nanoparticle source was earlier shown to produce free metal particles with the dimensions of few, below or around 10 nm,\(^{43}\) determined using the conducting-sphere approximation and confirmed by electron-microscopy imaging after the deposition. In the present work, the apparatus was attached to a port on the ionization chamber (Fig. 1) of the I411 beamline at the National Swedish synchrotron radiation facility Max-Lab. Potassium vapor was created by inductive heating of a crucible containing solid potassium. The crucible was mounted inside the ionization chamber along the axis of the water-cooled induction coil (not shown in Fig. 1). The temperature could be varied by changing the power of the RF-generator feeding the induction coil. Crucible temperatures in the range from \(\approx 100\) to \(\approx 155\) °C created K-vapor pressures in the \(10^{-4} - 10^{-5}\) Torr interval\(^\text{(51)}\) within the oven volume. The achieved difference between the lowest and the highest vapor concentrations was of \(\approx 40\) times.

The crucible had a shape of a cylinder with two coaxial holes for the Ag-particle beam entrance and exit. On their passage through the crucible, the free Ag nanoparticles picked up K atoms (Fig. 1 and more details in the Appendix). Such a pickup arrangement showed its functionality in our earlier work on multicomponent nanoparticles (see, e.g., Refs. 47–49). After passing through the K vapor, the resulting beam was crossed by the x-ray radiation of the beamline (Fig. 1) and the species in the beam were photoionized. The ejected photoelectrons were collected by a Scienta R4000 electron spectrometer mounted on the ionization chamber perpendicular to both the photon and the nanoparticle beam (Fig. 1). The photon energy of the beamline was set to 40 eV, which is close to the maximum of the ionization cross section for Ag 4\(d\) and K 3\(p\) levels.\(^{50}\) The experimental settings for the beamline monochromator and for the electron spectrometer were chosen to provide sufficient photoelectron-signal intensity over a short (a few minutes) acquisition time. The best spectral resolution possible to achieve in this case was of \(\approx 0.06\) eV. The photoelectron spectra of the species in the beam were recorded in the region from 0 to \(\approx 30\) eV absolute binding energy (relative to the vacuum level). This interval included the region where Ag 5s and Ag 4\(d\) bands of the pure-Ag nanoparticles were earlier detected by us,\(^{43}\) as well as the K 3\(p\) signal from free K nanoparticles and K-vapor atoms.\(^{47,52}\) In addition, the Ar 3\(p\) signal from the co-present in the beam argon gas is within this interval. The Ar 3\(p\) response was used for the binding energy calibration. Figure 2 presents an overview spectrum recorded with around two times larger (than described above) spectrometer collection efficiency and a twice wider monochromator slit, both changes leading to lower resolution (\(\leq 0.2\) eV). For this spectrum also, the strongest possible heating of the crucible was used. The effusive K-atom beam from the oven also reaches the ionization point (along with the nanoparticle beam), so the K 3\(p\) atomic signal is seen at \(\approx 25\) eV. The Ar 3\(p\) feature is just below 16 eV, as expected.\(^{53}\) The spectra recorded with 0.06 eV resolution for a set of K-vapor concentrations are shown in Fig. 3.

![FIG. 2. Overview-spectrum in the binding energy region from silver valence up to the potassium 3\(p\) level. The case corresponds to the strongest doping of Ag particles by K. Apart from the Ag 4\(d\) and Ag 5s bands, there is an atomic Ar 3\(p\) signal (doublet not resolved) between 15 and 16 eV and atomic K (multiplet not resolved) between 24 and 25 eV. The “bump” between 20 and 21 eV is likely to be from potassium adsorbed on the nanoparticles.](image)

![FIG. 3. Series of valence-region spectra recorded at different K-vapor pressures in the crucible. The spectra are calibrated relative to the vacuum level using the Ar 3\(p\) signal (Ar 3\(p_{3/2}\) is at 15.76 eV) observed due to the Ar atoms’ presence in the nanoparticle beam. The K-vapor pressure increases from (b) to (e) spectra.](image)
III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 4 presents the enlarged Ag 5s region for the spectra in Fig. 3. For the pure-Ag particles [Fig. 4(a), no K exposure], the onset of the Ag 5s band, which defines the WF, is at ≈4.5 ± 0.2 eV [Fig. 4(a)]. This is within the range of WF values found in the literature for macroscopic silver,10,35,34,57 meaning that the particles are metallic. Various studies58–60 on free Ag clusters/nanoparticles showed that the macroscopic polycrystalline silver WF is likely to be 4.25 eV. Using this value, the conducting sphere approximation, and the 4.5 eV for our bare nanoparticles, one obtains their diameter of ≈5 ± 1 nm.

With the increase in exposure to potassium, the onset of the Ag 5s band decreases in the absolute binding energy (Fig. 4). The highest potassium exposure gave the lowest value of the WF of ≈2.0 ± 0.2 eV [Fig. 4(e)]. The WF decrease is interpreted by us as a direct evidence of K atoms agglomerating with the Ag particles. While being generally expected, such a conclusion is supported by the comparison to another PES work,10 which contains a series of photoelectron spectra for macroscopic silver exposed to potassium at coverages from 0.15 to 10 monolayers. It is from these spectra that the WFs for different K coverages were extracted in work.10 There, the same photon energy as in our experiments (40 eV) was used which means that the ratio of Ag to K ionization cross section and the photoelectron escape depth were the same as in our experiments. The similarity between our spectra and extracted from them WFs and those from Ref. 10 is an argument for the similar conditions realized. In Ref. 10, the main WF change took place in the range of coverages lower than one monolayer. A close situation must have realized in the present study. Another work that reported a set of WF values for the same range of coverages is Ref. 15. There, the WF was measured using the LEED electron optics, allowing performing some sort of threshold electron spectroscopy. A peculiar feature of this latter work15 was that it included measurements at an elevated temperature of up to 335 K. In Fig. 5, the WFs obtained in studies10,15 are summarized to facilitate the comparison that is crucial for the conclusions of the present work. The comparison of our WFs for each case in Fig. 4 with the WFs of the Ag–K systems with different K fractions from Refs. 10 and 15 (Fig. 5) makes possible the judgements on the amount of K in our bimetallic nanoparticles. As shown in Fig. 5, the results of Refs. 10 and 15 differ somewhat in absolute numbers, so in certain aspects, the judgements would depend on what work is chosen to compare. One should also mention here that also the coverage is understood differently in these two works. In Ref. 15, it is defined as a ratio of the surface density of K atoms to that of Ag surface atoms, so one monolayer is reached when there is equal amount of K and Ag atoms at the surface: (K/Ag)surf = 1. In Ref. 10, one K monolayer is complete when a typical closed-packed K structure is finished at the surface, with a surface-layer atom ratio (K/Ag)surf of ≈0.33.

If one uses Ref. 10 in which the WFs were extracted from the photoelectron spectra similar to ours, it can be deduced that ≈0.1 monolayer of K decreases the WF from the pure Ag value of ≈4.7 eV down to ≈3 eV, and at ≈0.2 monolayer, the WF falls further to ≈2 eV (Fig. 5). To compare, for our bimetallic particles, the WF of ≈3 eV is observed in case (d) of Fig. 4, and in case (e), it is ≈2 eV. In the measurements performed in Ref. 15 at elevated T ≈335 K, no WF minimum was observed (Fig. 5): The WF value of 2 eV reached at the ≈0.3 monolayer practically did not change further with the coverage. Similarly to the latter result of Ref. 15, no obvious minimum was observed in our measurements. This can be due to the particle temperature being well above the cryogenic region: Due to the
collisions with the hot K vapor, the initially cold \((T \approx 100 \text{ K})\) particles should be warmed up.

The \(WF \approx 2 \text{ eV}\) staying constant above one monolayer in work\(^{33,34}\) can mean, in principle, that also in our case we reach more than a monolayer or higher coverage, at least in case (e). However, there are two experimental observations speaking against a multilayer of potassium at the nanoparticle surface: (a) the insignificant change in the spectral shapes of Ag 4d and Ag 5s bands and (b) no signal from the adsorbed potassium until the highest K exposure \((\text{Fig. 2})\). Indeed, while in Ref. 10, the PES signal from the first completed K layer is comparable in intensity with that of the Ag 4d band, in our case, the adsorbed-K signal, expected to appear in the \(20–22 \text{ eV}\) region,\(^{62}\) is barely seen even at the highest K concentration \((\text{Fig. 2})\).

In this case of the highest K exposure, there are two other peculiarities in the Ag 4d spectrum \([\text{Fig. 3(e)}]\): (a) a decrease in the separation between the two maxima in the Ag 4d band and (b) a change in the shape and relative intensity of the lower-binding-energy maximum at \(\approx 7 \text{ eV}\) in \([\text{Fig. 3(e)}]\) in the band. This latter maximum is usually assigned to the electrons emitted mainly from the surface part of the sample, while the higher-energy maximum at \(\approx 8.2 \text{ eV}\) in \([\text{Fig. 3(e)}]\) is attributed to the electrons emitted mainly from the bulk.\(^{33}\) The relative decrease in the lower-binding-energy maximum is consistent with noticeably more K at/within the surface than at lower exposures. As for the separation of the maxi- mum, while in a typical pure-Ag nanoparticle spectrum, they are more than \(2 \text{ eV}\) apart from each other \([\text{Fig. 3(a)}]\), the splitting between them decreases to \(\approx 1.6 \text{ eV}\) in the strongest binary case \([\text{Fig. 3(e)}]\). It is known that in Ag alloys the splitting between the Ag 4d maxima is smaller than in pure Ag.\(^{63}\) For the bimetallic particles, the splitting decrease is likely an indication of K diffusing into/alloying with Ag. As mentioned in the Introduction, K diffusion was suspected to be a multi-layer of potassium on the nanoparticle surface: (a) the insignificant change in the spectral shapes of Ag 4d and Ag 5s bands and (b) no signal from the adsorbed potassium until the highest K exposure \((\text{Fig. 2})\). Indeed, while in Ref. 10, the PES signal from the first completed K layer is comparable in intensity with that of the Ag 4d band, in our case, the adsorbed-K signal, expected to appear in the \(20–22 \text{ eV}\) region,\(^{62}\) is barely seen even at the highest K concentration \((\text{Fig. 2})\).

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Having established the calculation procedure for the single-component particles, we could approach the modeling of the bimetallic ones. One should note that the results of the jellium-model application in the present case should be seen more as a phenomenological approach showing the trend rather than giving the exact numerical answer. The two limit cases of the component distribution—no mixing at all and a uniform mixing—could be modeled easier than the more complex and possibly closer to the reality case with a gradient in K concentration inside the silver parent particles. Nevertheless, as it will be shown below, the results for the limit cases occurred to be so different that the choice of the closer to the experiment model composition could be done with a large degree of confidence.

A. Modeling of potassium adsorption—no diffusion

As discussed above in Sec. III, from our experimental results and the literature, we concluded that diffusion/alloying took place in the K–Ag particles under investigation. Nevertheless, in the modelizing, we first considered a build-up of a potassium “peel” on top of an Ag core—without K diffusion (Fig. 6, top). As discussed in the Introduction, this type of component distribution was the case studied in the pioneering work,\textsuperscript{5} which introduced the jellium approach to alkali adsorbates. For the “infinite” plane layers, the absence of diffusion leads to a step-wise jellium potential. In the present work, such a potential was constructed for the nanoparticles, whose geometry was approximated by a sphere of radius \(R_o\). At \(r < R_o\)—inside the Ag core—\(V_{\infty}\) and \(r_1\) of silver were used as parameters in the jellium potential, and at \(r > R_o\)—in the peel—\(V_{\infty}^p\) and \(r_1^p\) of K were used. The jellium potential \(V(r)\) for such a particle would be as follows:

\[
V(r) = \frac{V_0 - V_0^p}{1 + \exp\left(\frac{r - R_o}{a_o}\right)} - \frac{V_0^p}{1 + \exp\left(\frac{r - (R_o + D)}{a_o}\right)}
\]

The parameters with an apostrophe refer to the “peel” potential, with \(D^p\) being the thickness of the K peel. The depth of the peel potential, \(V_{\infty}^p\), was defined by requiring that the integral over the peel potential would be equal to the integral over a potential created by the same amount of atoms without the core. \(V_0^p\) is then

\[
V_0^p = \frac{R_{op}^3V_{op}}{R_{op}^3 + 3R_{op}R_{oc}(R_{op} + R_{oc})},
\]

where \(R_{op}\) and \(R_{oc}\) are the radii of the particle peel and core.

Several different Ag-core radii of the model particles were considered in the calculations, with the largest being 2.0 nm. As discussed above, the particle radii defined the total number of Ag atoms. For different amounts of K atoms on an Ag core, a characteristic of the model composition would be the ratio of the total numbers of atoms: \((K/Ag)_{total}\). At the same time, in the experimental works, the \((K/Ag)_{surf}\) ratio was used, referring to the relative surface densities of atoms in the K ad-layer and in the Ag surface layer of an infinite microscopic sample. The connection between these two ratios will be discussed further down.

In Fig. 7, the calculated \(WF\) is presented as a function of \((K/Ag)_{total}\). The decrease in the \(WF\) in such particles proceeds rather slowly; for the largest model Ag-core \((R_o = 2\) nm), \(WF = 2\) eV would be reached when \((K/Ag)_{total} \approx 4\), which is not likely to be realized at our experimental conditions. For the smallest model Ag-core \((R_o = 0.5\) nm), the \(WF\) changes in a zigzag manner (similarly to the pure Ag particles of this radius), with the drops caused by a transition to a new size-specific electronic shell.\textsuperscript{38–40}

To find the connection between \((K/Ag)_{total}\) and \((K/Ag)_{surf}\) for the core–shell nanoparticles, one can calculate the number of atoms in each complete spherical K-monolayer built on top of the Ag core of a given radius—using the spherical-layer concept and the \(4\pi r^2/3\) volume of a single atom. Figure 8 illustrates such conversion. There, the calculated \(WF\) of the core–shell particles is presented as a function of the number of adsorbed K atoms divided by the number of atoms in one complete K-monolayer. For the core–shell particles such a fraction of a complete monolayer can be seen as a K-coverage characteristic analogous to the “infinite” plane case.\textsuperscript{38} One complete monolayer over the Ag core of 2-nm radius corresponds to \(WF \approx 3.8\) eV (Fig. 8), while such coverage should have given \(WF \approx 2\) eV—according to Ref. 10.

If the coverage is characterized like in Ref. 15—by the ratio of K atoms to the number of Ag atoms in the surface layer of the Ag substrate, a monolayer means \((K/Ag)_{surf} = 1\). For a nanoparticle, a complete spherical layer of K gives \((K/Ag)_{surf} < 1\) because

FIG. 6. Schematic presentation of the two cases in modeling for an approximately equal amount of silver and potassium atoms. Top—Ag core of 2 nm radius with three layers of K. Bottom—a uniform mixture of the same amount of Ag and K atoms.
“high” \((K/Ag)_{\text{surf}}\) value is reached, while the calculated \(WF\) of the core–shell particle decreases only down to \(\approx 3.8\) eV by that point. Thus, the core–shell model contradicts with the experiment also if the coverage is defined as in Ref. 15.

If the build-up of the peel continues, two complete monolayers over the 2-nm-radius Ag-core would be reached when \((K/Ag)_{\text{total}} \approx 0.64\), and three monolayers would be reached when \((K/Ag)_{\text{total}} \approx 1.2\). It is the latter case that is schematically illustrated in Fig. 6. The corresponding calculated \(WF\) is equal to \(\approx 3\) eV—for the Ag cores with the radii from 1.0 to 2.0 nm (Fig. 7). Experimentally, already at three-monolayer coverage, the flux of the photoelectrons from the Ag core would be substantially attenuated because of the electron escape depth being close to the interatomic distance. Then, the K \((3p)\) to Ag \((4d)\) signal ratio would be strongly in the favor of K, which is not the case in our experiment.

All-in-all, from the considerations above, it follows that the model in which adsorption of K occurs without diffusion is not consistent with the experimental observations.

### B. Modeling of potassium adsorption with diffusion/alloying

Clearly, the modeling of the situation with K atoms diffused into an Ag particle is more challenging than that with no diffusion. Several additional assumptions should be made and tested. The first question to be answered is about the distribution of K atoms in a bimetallic particle. As discussed above, in the calculations, the largest used Ag-particle radius before exposure to K was 2 nm. This is just few times larger than the Ag lattice constant of \(\approx 0.4\) nm. In Refs. 33 and 34, the diffusion depth of four monolayers for alkalis deposited on an Al substrate was shown to be not unusual—with the diffused-alkali concentration reaching that of Al. As discussed above, in free nanoparticles, the diffusion can be additionally facilitated. These considerations—together with the results \cite{33,34}—allow assuming that the diffused K distribution can be not far from the uniform one. The next question, strongly connected to the distribution, is how to define the Wigner–Seitz radius in the mixed case. For the uniform distribution, one way to do it is to take \(r_1\) and \(a_o\) to be \(n\)-weighted averages of Ag and K values. Then, one can use the jellium potential in the form of Eq. (1). The uniformly mixed composition also means that the relative total concentration \((K/Ag)_{\text{total}}\) in the bulk is the same as the concentration in the surface layer, the latter being analogous to \((K/Ag)_{\text{surf}}\), as it is defined in Refs. 10 and 15. The next critical question is what macroscopic \(WF_{\infty}\) value to take as a parameter in the jellium potential. As discussed above, for the “infinite” plane samples \cite{10,15} starting from as low as \((K/Ag)_{\text{surf}} \approx 0.2\), the work-function is already at \(\approx 2\) eV and stays very close to this value for the larger coverage, so from \((K/Ag)_{\text{total}} = (K/Ag)_{\text{surf}} \approx 0.2\) and above, the macroscopic work-function \(WF_{\infty}\) in Eq. (2) can be taken equal to \(2\) eV.

With the jellium potential defined, the modeling of the mixed-composition particles was done in the following way: We started with an amount of Ag atoms corresponding to the largest radius of the pure Ag particles—2 nm—the size most closely approaching the experimental dimensions. Then, in steps, a certain number of K atoms was uniformly mixed into such Ag particles: The weighted Wigner–Seitz radius \(r_1\), the corresponding new particle-radius \(R_0\), and the new jellium potential \(V(r)\) were calculated. The \(WFs\) (more
exactly, the top-orbital energies) were calculated as the eigenvalues of the corresponding Schrödinger equation. For the initial size of the pure-Ag particle with $R_0 = 2$ nm ($\approx 1.7 \times 10^3$ atoms), the calculated WFS are presented vs $(K/Ag)_{total}$ ratio in Fig. 9. One peculiarity caused by the particle spherical geometry is a considerably smaller than in the plane case absolute amount of diffusing atoms, necessary to create the high K concentration in the bulk. From Fig. 9, one notices that the range of the computed WFS matches that observed by us experimentally at larger exposures. The model WF values close to 2 eV are reached at rather low $(K/Ag)_{total} = (K/Ag)_{total}$ fractions of K— as expected from the experiment, when we just started seeing the adsorbed K.

V. CONCLUSIONS
The phenomenon of WF lowering due to the alkali metal adsorption has been known for a century and explored intensively; however, the studies of the WFS for individual binary nanoparticles containing an alkali metal have remained challenging. Our PES measurements on an in-vacuum beam of in situ produced K–Ag particles have provided the information on their inherent electronic properties, such as the WF and the valence-band shape. For several K-doping concentrations within the range of almost two orders of magnitude, the WF was observed to gradually decrease from $\approx 4.0$ eV at the lowest K exposure down to $\approx 2.0 \pm 0.2$ eV at the highest one. The observed changes in the Ag 4d-band spectral shape were consistent with the presence of K in the particle “bulk,” which would mean K diffusion into Ag.

Our modeling approach, on the one hand, followed the steps of the pioneering work where the jellium representation was first successfully used to describe the experimentally observed WF behavior of adsorbates; on the other hand, it introduced the nanoscale dimension to the jellium modeling of adsorption results—treating the sample as an agglomerate of an exact finite number of atoms, even when this number was several thousands of atoms. Such modeling represents a relatively simple and transparent alternative to the first-principles theory and calculations, which would demand state-of-the-art computational facilities and which would definitely deserve a separate publication.

In comparison to PES measurements of WFS for supported bimetallic samples, the experiment on a beam provided several advantages: The WF of the electron spectrometer was excluded from the energy balance equation, the reliance on the secondary electrons’ cutoff was avoided, and no bias voltage on the sample was necessary. The measurements were direct and relied only on one value: the absolute binding energy of the valence band onset. In this sense, the measurements were also absolute.

The experimental and calculation results considered together support the hypothesis of K adsorption resulting in diffusion/alloying in/with Ag within several monolayers under the surface, while their immiscibility was considered handbook knowledge.

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APPENDIX: PRELIMINARILY CONSIDERATIONS AND DETAILS FOR THE EXPERIMENT AND MODELING

1. Relevant details of WF experimental determination
For macroscopic samples, the experimental determination of the WF is made practically only by two methods. One approach is based on photoelectron spectroscopy (PES), which allows detecting, in this or the other way, the appearance threshold of the photoelectron signal—corresponding to a certain electron binding energy. In metals, the threshold energy is the WF. In the numerous works on alkali adsorbates, where PES was used, most often, the WF was extracted using a fixed VUV (vacuum ultraviolet) photon energy of a He lamp ($\approx 21$ eV), recording the whole valence photoelectron spectrum down to zero kinetic energy (see, e.g., Refs. 10 and 25). There are, however, several “pitfalls” in a typical vacuum-ultraviolet PES (UPS) experiment. Most problematic is the absence of an accurate “zero-energy” point on the energy scale in a spectrum. This forces involving the so-called cutoff of the signal produced by the secondary electrons. The cut off energy-point in a spectrum should correspond to the zero kinetic energy of the photoelectrons. However, in practice, most of the typical electron energy analyzers have problems operating close to zero kinetic energy. A more reliable detection of the cut off point can be done by holding the sample at a bias potential (from a few to few tens of volts)—in order to shift the cut off point up in energy, thus away from the problematic for the spectrometer kinetic energy region. Nevertheless, since the transmission function (sensitivity) of typical analyzers remains non-uniform and not well known even at a few eV kinetic energies, a shift due to the bias may not solve the problem. Additionally, the
bias-voltage imposes extra demands on the experimental geometry, which, if not designed properly, may result in errors in the measured \(WF\).\(^{42}\)

The second widely used method of the \(WF\) measurement is a relative one—the so-called Kelvin-probe method, in which the sample should be in contact with a reference electrode relative to which the contact potential is measured. This method has been used since the early days for monitoring the \(WF\) changes with the alkali coverage.\(^{75,76}\) However, while for the bulk, inert metals, the method works well, for an experiment when alkali-metal atoms are dosed onto the substrate or removed from it by thermal desorption in a sub-monolayer regime, one can expect some uncertainties. There has been experimental evidence for the PES to be a better choice for a reactive substance.\(^{43}\)

2. Details of the present experiment

The nanoparticle source comprised a dedicated vacuum chamber pumped with a 500-l/s turbo-pump and an XYZ manipulator with 400 mm \(Z\)-travel. The cryostat was mounted inside the chamber on the rod of the manipulator (Fig. 1). The 2\(\text{''}\)-diameter magnetron sputtering gun was placed inside the cryostat in \(\approx\)20 cm from the output orifice. Argon and helium were let into the cryostat at the pressures of \(\approx\)5 to \(\approx\)10 mbar. The flow of sputtering gas Ar, injected in the vicinity of the target via a homemade gas-burner-type way, was measured to be 10–12 SCCM at the input. On the exit from the cryostat, the beam of nanoparticles was collimated by a 30-mm long cylindrical copper nozzle mounted at the cryostat tip. The diameter of the nozzle channel was \(\approx\)1.5 mm. The volumes of the nanoparticle apparatus and the experimental chamber of the beamline were connected via a 2-mm orifice in a conical skimmer, what allowed maintaining the ionization volume at high vacuum. The skimmer shaped the nanoparticle beam additionally before it entered the experimental chamber. The oven with potassium was placed inside the experimental chamber right after the skimmer. The coaxial input and output orifices of the oven were aligned along the nanoparticle beam axis. The spread of the effusive K-atom beam from the oven was limited by a special protecting tubular arrangement (not shown in Fig. 1).

The x rays crossed the resulting beam containing the nanoparticles, Ar and He gases, and K atoms inside the protecting tube, which had holes for the incoming light and toward the spectrometer—for the electrons. The photoelectrons ejected from the beam were detected by the Scienta R4000 spectrometer within a narrow solid angle of \(\approx\)10\(^{-2}\). In the experiments in question, the axis of such a solid angle—the detection-direction axis—was perpendicular to the horizontal polarization plane of the radiation. The exact calibration of the photoelectron spectra was performed during the analysis, using the spectral lines from argon and helium present in the spectra of the nanoparticles.

As mentioned in the experimental part, the dimensions of the parent silver nanoparticles were estimated using the conducting-sphere approximation\(^{19}\) in the runs when the K oven was turned off. According to this approximation, the work-function \(WF_p\) of the particles can be calculated: \(WF_p \approx WF_m + \frac{1}{2}(or\ 3/8)\ e/R(\AA)\), where \(WF_m\) is the work-function of the corresponding macroscopic solid. The difference in the coefficients (1/2 or 3/8) was argued for almost two decades since the first derivation of the free-particle \(WF_p\)\(^{46}\) was presented. With the time, it has been realized that the formula connecting \(WF_p\) and \(WF_m\) should take into account the electron density spillout \(\sigma\) for the metal in question (\(R + \sigma\) replaces \(R\)) and that the coefficient in front of the radius-dependent term should include a quantum correction varying with the metal type. Thus, the earlier argued universal coefficient was shown to be an approximation.

Knowing \(WF_m\) allows estimating the nanoparticle radius. It should also be noted that in the size range in question, a noticeable change in the number of atoms \(n\) per nanoparticle does not significantly change \(WF_p\). In simple terms, this can be shown using the formula above and the formula connecting the radius \(R\) with the Wigner–Seitz radius \(r_s\): \(R = r_s h^{1/2}\). For \(R = 2.5\ nm\), the difference in \(WF_p\) relative to the case with \(R = 2\ nm\) is \(\approx 0.07\ eV\). At the same time, the number of atoms \(n\) per particle increases from \(\approx 1700\) to \(\approx 3900\). \(R = 5\ nm\) would mean just \(\approx 0.1\ eV\ larger\) \(WF_p\) than the macroscopic solid \(WF_m\).

This \(WF_p(n)\) behavior derived from the formula above and supported also by our jellium calculations allows ruling out the explanation of the observed large changes in \(WF_p\) upon the alkali-atom exposure as due to the change of the number of atoms in the parent Ag particle. In the hypothetical case of the Ag atoms’ ejection from the particles due to the K atom “bombardment,” \(WF_p\) would increase, not decrease. In addition, this loss would be seen only if a significant fraction of Ag atoms were ejected from the particles, what seems to be not very likely. In its turn, this consideration gives the grounds to make the estimate of the size of the binary Ag–K particles in an assumption that the number of Ag atoms in them is practically the same as in the corresponding parent particles.

The parent Ag particle experimental range of dimensions defined the choice of that in the modeling: The studied model particle diameter was from 1 nm, at which \(WF_p\) is definitely well above the macroscopic solid value \(WF_m\) (Fig. 10), to 7 nm, at which \(WF_p\) is long stabilized in the close vicinity to \(WF_m\). The value of 4 nm diameter (2 nm radius) is also in the range of the stabilized \(WF_p\) and is thus representative for the range of dimensions in question. Its choice as a starting point for the modeling of the K–Ag binary particles was defined by the considerations of a compromise: Being close to the experimental dimensions, it is still relatively small to be used in the feasible jellium calculations. As discussed above, the number of atoms grows as \(R^3\) and the jellium model has to take all these atoms into account.

3. Modeling results for the monometallic particles

As just mentioned above, the jellium calculations for pure Ag and pure K nanoparticles were performed for the particle radius \(R_o\) range between 0.5 nm and 3.5 nm and the absolute values of the energy of their top-most populated orbitals, taken as the \(WF\), are presented in Fig. 10. For neutral metal particles, the \(WF\) is known to change from the values close to the parent-atom ionization energy to those approaching \(WF_{\infty}\). Our calculations are in accord with that behavior (Fig. 10). When the number of atoms is relatively low (\(R_o \leq 1\ nm\)), the \(WF\) changes in a zig-zag way (Fig. 10), dropping each time when the next particle-specific electronic shell is completed.\(^{37,40}\) At larger dimensions, the changes in the energy become...
smoother. For the pure-Ag nanoparticles with $R_a > 1$ nm, the calculated WF is indeed close to the Ag macroscopic $WF_{\infty}$ of 4.25 eV. In other words, the particles of such dimensions can be considered nanoscale pieces of solid silver. A similar situation is observed for potassium, which has $WF_{\infty} \approx 2.3$ eV.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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