

Growth and electronic structure of alkali-metal adlayers on icosahedral $\text{Al}_{70.5}\text{Pd}_{21}\text{Mn}_{8.5}$

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We report x-ray photoelectron spectroscopy (XPS) study of Na and K adlayers on icosahedral $\text{Al}_{70.5}\text{Pd}_{21}\text{Mn}_{8.5}$ (*i*-Al-Pd-Mn) quasicrystal. The Na $1s$ core-level exhibits a continuous linear shift of 0.8 eV towards lower binding energies (BE) with increasing coverage up to one monolayer (ML) saturation coverage. In the case of K/*i*-Al-Pd-Mn, a similar linear shift in the K $2p$ spectra towards lower BE is observed. In both cases, the plasmon related loss features are observed only above 1 ML. The substrate core-level peaks, such as Al $2p$, do not exhibit any shift with the adlayer deposition up to the highest coverage. Based on these experimental observations and previous studies of alkali metal growth on metals, we conclude that below 1 ML, both Na and K form a dispersed phase on *i*-Al-Pd-Mn and there is hardly any charge transfer to the substrate. The variation of the adlayer and substrate core-level intensities with coverage indicates layer by layer growth.

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I. INTRODUCTION

Adsorption of alkali metals on metal surfaces has been a topic of active research because of the interesting modifications in the electronic properties, for example, a decrease in the work function of the substrate, a change in reactivity of surfaces, etc.^{1,2} Quantum well states and collective excitation in alkali metal adlayers on metals have been extensively studied.³⁻⁵

Icosahedral Al-Pd-Mn (*i*-Al-Pd-Mn) is a complex ternary alloy quasicrystal exhibiting unusual properties such as high resistivity, high frictional constant, and a low sticking coefficient.^{6,7} Scanning tunneling microscopy (STM) experiments have shown that the surface corrugation of quasicrystalline surfaces is quite different from that of metals.⁸⁻¹⁰ Recently, some groups have reported pseudomorphic growth of elemental quasicrystalline films such as Cu, Sb, and Bi on *i*-Al-Pd-Mn.^{11,12}

From a fundamental physics viewpoint, alkali metals form the simplest adsorbate system, where one *s* electron is expected to participate in the bonding with the substrate. Wehner *et al.* performed a thermal desorption spectroscopy study of K adsorption on *i*-Al-Pd-Mn and Al(111). They found that K binds weakly to *i*-Al-Pd-Mn and the density of the first layer is lower than K/Al(111).¹³ However, so far no photoemission study of alkali metal adsorption on the quasicrystals has been reported in literature. If the alkali metals when deposited on *i*-Al-Pd-Mn were to transfer the *s* electron to the substrate, this could be clearly indicated by change in the core-level binding energy (BE). In fact, the nature of bonding of the adsorbate alkali metal to the substrate has been explained by charge transfer.¹⁴ On the other hand, there is a large body of literature which suggests that there is almost no

charge transfer from the alkali metal adsorbate to the metal substrate and the change in work function results from a dipole moment associated with the polarized adsorbate atom itself.¹⁵⁻¹⁸ Different studies on metal substrates have shown that alkali metals grow as a dispersed phase or as condensed islands for the first monolayer (ML).^{15,19-25}

In this paper, we report on the growth and electronic structure of alkali metal adlayers on the fivefold surface of an *i*-Al-Pd-Mn quasicrystal using x-ray photoelectron spectroscopy (XPS), since the core-level BE shift and line shape depend sensitively on the local surroundings and charge transfer. We find a decrease in the BE of the alkali metal core levels and an absence of any plasmon related loss feature until 1 ML saturation coverage. These show that alkali metals grow on the *i*-Al-Pd-Mn surface as a dispersed phase. We do not find any evidence of charge transfer from Na or K to *i*-Al-Pd-Mn, which supports the covalent picture of alkali metal adsorption on metals. These results are compared with alkali metal adsorption on other metals, and Al in particular, since the top layer of *i*-Al-Pd-Mn is Al rich.²⁶ The variation of adlayer and substrate core-level intensities with coverage indicates layer by layer growth.

II. EXPERIMENTAL

Single grain *i*-Al-Pd-Mn quasicrystal with composition $\text{Al}_{70.5}\text{Pd}_{21}\text{Mn}_{8.5}$ was grown by the Czochralski method.²⁷ The base pressure of the experimental ultrahigh vacuum chamber was 6×10^{-11} mbar. A commercial electron energy analyzer (Phoibos 100 from Specs GmbH, Berlin, Germany) and a nonmonochromatic MgK α x-ray source have been used for the XPS measurements. A pass energy of 20 eV was used in the medium magnification mode resulting in an overall in-

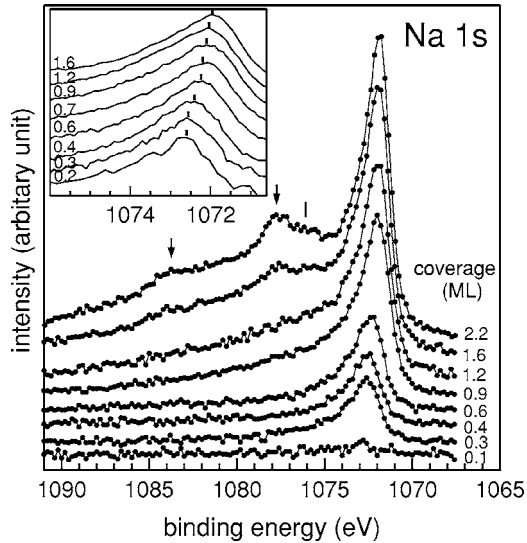


FIG. 1. Na $1s$ core-level spectra for Na/*i*-Al-Pd-Mn as a function of coverage at 125 K. The spectra have been staggered for clarity of presentation. The inset shows the shift in BE of the Na $1s$ core-level peak in an expanded scale.

strumental resolution of 0.9 eV. The polished *i*-Al-Pd-Mn surface was cleaned by repeated cycles of Ar⁺ sputtering and annealing up to 875 K. The surface composition and cleanliness were checked by recording Al $2p$, Pd $3d$, Mn $2p$, and O KLL Auger signal. Na and K were deposited on *i*-Al-Pd-Mn at 125 K by using well-degassed commercial SAES getter sources for different deposition times. During depositions, the chamber pressure rose to 9×10^{-11} mbar. The thickness of the adlayers has been calculated from the area under alkali metal (Na $1s$, K $2p$) and substrate related (Al $2p$) core-levels after an x-ray satellite and Tougaard background subtraction. These spectra are recorded under similar conditions, for example, analyzer settings, x-ray source intensity, sample position, etc. The intensity of the substrate signal depends on the inelastic mean free path of photoelectrons and the thickness of the adlayer. For layer by layer growth, the substrate core-level intensity decays exponentially due to adlayer coverage. The details of the equations used for the coverage calculation considering both integral and fractional monolayer coverage are given in Ref. 28. One ML refers to the saturation coverage.

III. RESULTS AND DISCUSSION

The coverage dependence of the Na $1s$ core-level spectra for Na/*i*-Al-Pd-Mn is shown in Fig. 1. For the lowest 0.1 ML coverage, the Na $1s$ peak appears at 1072.8 eV BE. With increasing coverage, the Na $1s$ intensity increases accompanied by a monotonic decrease in BE until 1 ML saturation coverage (see the inset in Fig. 1). Below 1 ML, satellite loss features are not observed. On the other hand, for higher coverages a clear feature is observed at 1077.8 eV with a weak feature at 1083.8 eV, as indicated by arrows for the 2.2 ML spectrum. Compared to the main peak at 1072 eV, these features are at 5.8 and 11.8 eV higher BE, respectively and

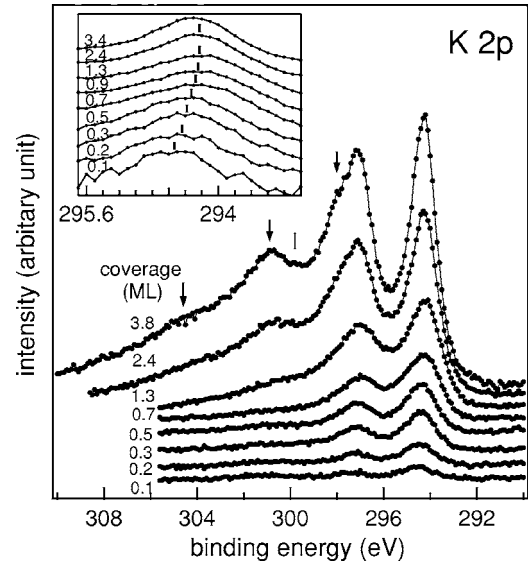


FIG. 2. K $2p$ core-level spectra for K/*i*-Al-Pd-Mn as a function of coverage at 125 K. The inset shows the shift in BE of the K $2p_{3/2}$ core-level peak in an expanded scale.

correspond to the loss features related to one bulk plasmon ($1\omega_p$) and two bulk plasmon ($2\omega_p$) excitations, respectively. A surface plasmon related feature is also observed at 4.1 eV loss energy with respect to the main peak, as shown by a tick mark. The energies of the bulk and surface plasmon features are in good agreement with the literature.^{4,29} We find that the plasmon loss energies do not change significantly with coverage above 1 ML.

In Fig. 2, we find that for 0.1 ML, the K $2p_{3/2}$ peak appears at 294.5 eV BE. A monotonic shift of the BE for sub-monolayer coverages is clearly observed (as shown in the inset). Above 1 ML coverage, the loss features corresponding to the $2p_{1/2}$ peak (297.2 eV) appear at 300.9 and 304.6 eV BE (as marked by the arrows in Fig. 2). These are related to $1\omega_p$ and $2\omega_p$ excitations and the corresponding loss energies are 3.7 and 7.4 eV, respectively, as reported in the literature for K.^{4,30} A shoulder at 297.9 eV is visible in the 3.8 ML spectrum (arrow) because of the $1\omega_p$ loss feature related to the $2p_{3/2}$ peak. A surface plasmon feature corresponding to the $2p_{1/2}$ peak is also observed at 2.6 eV loss energy which is shown by a tick mark.

The variation of BE with coverage is shown in Fig. 3 for both Na and K. Since the BE variation is clearly different below and above 1 ML, we have fitted the data with different straight lines for these two regimes. A reasonably good fit within the experimental error indicates that the BE shift is indeed linear. Between 0.1 and 1 ML, the BE changes by 0.8 eV for Na $1s$. On the other hand, between 1 and 2.2 ML, the shift is quite small (0.1 eV). For K/*i*-Al-Pd-Mn, the overall BE shift is 0.33 eV between the lowest and 1 ML coverage. However, by normalizing the spectra to the same height, we find that there is hardly any change in the line shape or full width at half maximum for neither Na $1s$ nor K $2p$ with coverage. Thus, the overall behavior of Na and K alkali metal core-levels grown on *i*-Al-Pd-Mn is quite similar.

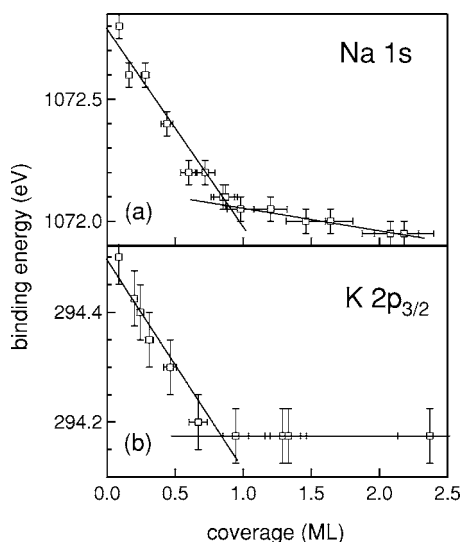


FIG. 3. Variation in the BE as a function of coverage for (a) Na $1s$ and (b) K $2p$ for alkali metals grown on i -Al-Pd-Mn at 125 K substrate temperature.

The i -Al-Pd-Mn surface consists of a topmost dense Al-rich layer followed by a layer with 50% Al and 50% Pd, and the lateral density of these two layers together is similar to that of Al(111).²⁶ The adsorption of Na, K, Rb, and Cs on the Al(111) surface at 100 K has been investigated by high resolution core-level spectroscopy by Andersen *et al.*²² It was found that initially the alkali atoms adsorb at surface defect sites. At higher coverages up to about one third of the maximum submonolayer coverage, the adsorbed alkali metal atoms exist as a dispersed phase. At higher coverages, a condensed island formation occurs in most cases.²² Formation of islands on the Al(111) for such coverages at 140 K is supported by the change in work function and observation of plasmon loss features at submonolayer coverages.^{19,25} Based on density functional theory calculations, Neugebauer and Scheffler showed that below 0.1 ML, the Na atoms on Al(111) are homogeneously dispersed, and the adsorbate-substrate interaction dominates.²⁴ On the other hand, above 0.1 ML, condensation occurs and attractive adsorbate-adsorbate interaction dominates.

In contrast to this, island growth has not been reported for Al(100), rather a continuous increase in adsorbate density corresponding to a dispersed phase is observed.²⁵ In fact, a similar dispersed phase has also been observed in other systems like K/Ag(001),²⁰ alkali metals on Ru(001),²¹ and W(110),¹⁵ Na on Cu(111) and Ni(111),²³ etc. For Na/Cu(111) and Na/Ni(111), a monotonic shift of 0.93 and 1.1 eV, respectively, towards lower BE is observed for the first monolayer.²³ Shi *et al.* related the BE shift to the change in electrostatic potential at the Na atom. They calculated the electrostatic potential and found that it decreases with increasing coverage, which results from the change in the valence charge distribution in Na and supports the covalent picture rather than the charge transfer. Another possible reason for the BE shift is related to more efficient screening of the Na core-hole in the photoemission final state with increasing coverage. Modesti *et al.* observed a dispersed phase

of K/Ag(001) at 90 K, while at 220 K they observed a condensed island formation.²⁰ In fact, the criterion for existence of the dispersed phase as against the condensed island phase is that the total energy gain by formation of alkali metal bonds does not compensate for the energy cost of repulsion due to the formation of a strong dipole moment and overcoming of the surface corrugation potential. Since the adsorbate dipole moment decreases with increasing coverage, the surface corrugation potential primarily dictates the formation of the dispersed phase.²²

The XPS data (Figs. 1–3) indicate that the formation of a dispersed phase occurs for alkali metals on i -Al-Pd-Mn below 1 ML. The linear shift in BE for the first monolayer supports this proposition. Furthermore, features related to plasmon excitations are observed below 1 ML coverage when a condensed island phase is formed.²⁵ So, in the present case, the absence of plasmons below 1 ML indicates that indeed the formation of a dispersed phase occurs. Although the atomic density of the i -Al-Pd-Mn surface is similar to Al(111), where condensed phase formation is reported,²² the formation of a dispersed phase for i -Al-Pd-Mn might be related to the characteristic quasicrystalline surface morphology. It has been reported that the i -Al-Pd-Mn surface is characterized by terraces of two types; void-rich and void-free. The voids are surrounded by S-type steps of height 2.4 Å.⁸ STM studies have shown different motifs on the surface resembling up and down white flowers. The down flower patterns have a hollow center which could be the nucleation center for the alkali metal atoms.⁹ Relatively rough steps exhibiting local facets have also been reported.¹⁰ Our results indicate that the alkali metal atoms are adsorbed on i -Al-Pd-Mn at sites that are homogeneously dispersed. From the present work, it can thus be inferred that the i -Al-Pd-Mn surface has a large surface corrugation potential that makes the formation of the condensed island phase energetically unfavorable. Indeed, a surface corrugation potential as large as 50 meV has been calculated for Xe on the decagonal quasicrystal, Al-Ni-Co.³¹ On the other hand, jellium based theoretical calculations show that the corrugation potential felt by alkali metals on Al(111) is quite small (<1 meV) and this explains the formation of the condensed phase on Al(111).³²

We have recorded Al $2p$ core-levels from i -Al-Pd-Mn for the different Na coverages (Fig. 4). For i -Al-Pd-Mn, the Al $2p$ BE turns out to be 73.1 eV, which is in good agreement with the literature.³³ The bulk (arrow) and surface (tick) plasmon related features are observed at 16 and 10.4 eV loss energies, respectively. The plasmon energies are in agreement with the electron energy loss spectroscopy data.³⁴ The bulk plasmon energy in i -Al-Pd-Mn is higher than Al ($\omega_p = 15.4$ eV) because of higher electron density due to Pd. Interestingly, a weak surface plasmon appears at the same energy as Al because the topmost surface layer resembles Al(111), as mentioned earlier. A comparison of the Al $2p$ core-level main peak for different Na coverages shows that there is hardly any shift in the peak position. The comparison of the line shape of the Al $2p$ peak normalized to the same height between the clean and 3.0 ML Na deposited surface in the inset shows that both the BE and line shape remain similar. The Mn $2p$ and Pd $3d$ core-level peaks also remain un-

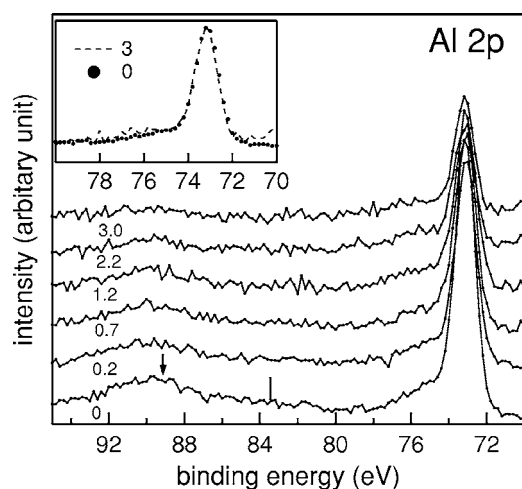


FIG. 4. Al $2p$ core-level spectrum of i -Al-Pd-Mn as a function of Na coverage in ML. The inset shows the comparison of Al $2p$ peak normalized to same height for clean (0 ML) and 3 ML Na coverage.

changed with the alkali metal deposition, as in Al $2p$. The behavior of the substrate core-levels is similar for K/ i -Al-Pd-Mn.

A decrease of the substrate core-level BE is expected if there is a transfer of charge from the alkali metal to the substrate. In fact, in many different metallic substrates, it has been reported that the physically appealing picture of charge transfer from the electropositive alkali metal to the metallic substrate does not hold.^{15–18,20–25} Riffe *et al.* showed that there is almost no shift between the clean and 1 ML alkali metal covered substrate core-level peak for W(110). The authors argued that if the induced dipole moment is due to charge transfer, the shift would be higher for lower coverages. However, no such shift has been observed indicating that there is hardly any charge transfer from the adsorbate to the substrate. If there is a charge transfer, the alkali metal core-level BE should shift to higher values. On the contrary, we find a shift to lower BE (Figs. 1–3). Moreover, the linear decrease in BE also does not support the charge transfer model, but rather indicates a covalent nature of alkali metal bonding as suggested by different theoretical calculations.^{16–18,23}

To ascertain the nature of adlayer growth beyond 1 ML, we have plotted the area under the adlayer Na $1s$ and K $2p$ and the substrate Al $2p$ peaks as a function of the coverage (Fig. 5). The data are fitted with standard exponential expressions.²⁸ In both cases, the fitting is quite good over the studied coverage range. Moreover, the alkali metal to substrate core-level intensity ratio shows a monotonic increase until the highest coverage studied. These observations indeed indicate the occurrence of layer by layer growth for both Na and K on i -Al-Pd-Mn.

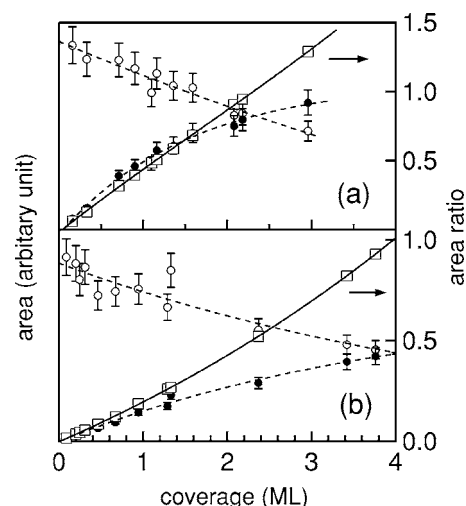


FIG. 5. Area under (a) Na $1s$ and (b) K $2p$ (filled circles) core-level peaks compared with area under Al $2p$ (unfilled circles) core-level peak for alkali metal/ i -Al-Pd-Mn as a function of coverage. The data are fitted with exponential curves (dashed lines). The ratio of adlayer to substrate signal (unfilled squares) and the ratio of the two exponential curves (solid line) are also shown.

IV. CONCLUSIONS

The linear shift of the adlayer Na $1s$ and K $2p$ core-level peaks towards lower BE and the absence of any plasmon related loss feature until 1 ML saturation coverage show that alkali metals grow on the i -Al-Pd-Mn surface as a dispersed phase at 125 K. While the atomic density of the i -Al-Pd-Mn surface is similar to Al(111), where condensed phase formation is reported,²² the formation of a dispersed phase for i -Al-Pd-Mn is probably related to the characteristic quasicrystalline surface morphology and the large corrugation potential of the quasicrystal surface compared to Al(111). There is almost no shift in the core-level BE of the substrate i -Al-Pd-Mn, which indicates the absence of charge transfer from the alkali metal adlayer to the i -Al-Pd-Mn substrate. The variation of adlayer and substrate core-level intensities with coverage indicates layer-by-layer growth up to the highest coverage studied. It would be interesting to perform STM and related experiments to study whether the alkali metal layers exhibit pseudomorphic growth on i -Al-Pd-Mn.

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