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Quantum size effects in Pb islands on Cu(111): Electronic structure calculations

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The appearance of ''magic'' heights of Pb islands grown on Cu(111) is studied by self-consistent electronic structure calculations. The Cu(111) substrate is modeled with a one-dimensional pseudopotential reproducing the essential features, i.e., the band gap and the work function, of the Cu band structure in the [111] direction. Pb islands are presented as stabilized jellium overlayers. The experimental eigenenergies of the quantum-well states confined in the Pb overlayer are well reproduced. The total energy oscillates as a continuous function of the overlayer thickness reflecting the electronic shell structure. The energies for completed Pb monolayers show a modulated oscillatory pattern reminiscent of the supershell structure of clusters and nanowires. The energy minima correlate remarkably well with the measured most probable heights of Pb islands. The proper modeling of the substrate is crucial to set the quantitative agreement.

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The confinement of valence electron states in low-dimensional systems has a strong influence on the size distributions of nanostructures produced in experiments. In clusters of alkali-metal atoms the confinement occurs in three dimensions and the structures corresponding to closed electronic shells are the most stable and the most abundant ones.[1] Alkali-metal nanowires[2] and metallic overlayers on solid surfaces[3–5] exhibit two- and one-dimensional (1D) confinement, respectively. In these systems the sinking of the bottom of a new subband below the Fermi level is accompanied with an increase in the total energy destabilizing the system. The detailed understanding of the mechanisms controlling the growth of nano-objects is of vital importance when producing highly organized atomic-scale structures in nanodevices.

In this work we focus on the 1D confinement in Pb islands on the Cu(111) surface. The growing of Pb occurs in the [111] direction. Hinch and Toennies[3] studied the island height distribution of Pb using the He atom scattering (HAS). Brown and Toennies[6] determined by HAS the apparent height of the Pb coverage as a function of the number of Pb monolayers (ML's) and found a double ML periodicity. Recently, Otero *et al.*[5] have determined the height distribution of Pb islands using the scanning tunneling microscope (STM) up to heights over 20 Pb ML's. The lateral dimension of the islands is large, of the order of 500 Å, justifying the 1D modeling of their energetics. The vertical confinement in the Pb overlayer is due to the potential barrier between Pb and the vacuum and the energy gap in the projection of the Cu bulk bands in the [111] direction. A closed shell occurs periodically when the thickness D of the Pb layer satisfies $D=n\lambda_F/2$, where λ_F is the Fermi wavelength of Pb and n is an integer. The effect of this shell structure on the physical properties was recognized already in early jellium slab calculations[7] and the stability as a function of the thickness was discussed on the basis of density-functional-theory (DFT) calculations already two decades ago.[8] Later jellium and pseudopotential calculations[9–13] have dealt with quantum size effects in unsupported metallic slabs. For example, the pseudopotential-slab calculation by Materzanini *et al.*[12] enlightened the origin of the double ML periodicity in apparent heights, and they discussed also the importance of the strain induced by the Cu substrate. However, the effects of the substrate have not been explicitly considered in the calculations thus far.

We model the whole system consisting of the Pb overlayer and the Cu(111) substrate by using the stabilized jellium (SJ) model[14] for the overlayer and a 1D pseudopotential for the substrate and obtain results with a quantitative predictive power. We calculate electronic structures using the local-density approximation (LDA) of the DFT. The free-electron character of Pb at the Fermi level justifies the use of the SJ model with $r_s=2.3a_0$ to describe the overlayer. The SJ model gives the work function of 4.1 eV, which is close to the experimental value of 4.0 eV for Pb.[15] The relevant feature giving physical insight is that the SJ model allows us to simulate overlayers of any thickness. For the Cu(111) surface we have constructed a 1D pseudopotential. We start from the 1D model potential by Chulkov *et al.*,[16] cosinelike bulk part of which reproduces correctly the experimental energy gap of Cu in the (111) direction. The position of the Fermi level with respect to the model potential determines the electron density. We subtract then the interactions between valence electrons from the model potential within the LDA and obtain an unscreened local 1D pseudopotential. The pseudopotential is constructed to give the experimental Cu(111) work function of 4.94 eV.[16] The self-consistent screening of this 1D pseudopotential within the LDA accounts correctly for the energy gap in the (111) projection, both in width and in position with respect to the Fermi level. The details of the construction are described in a forthcoming paper.[17]

In numerical calculations a semi-infinite crystal is simulated by the slab geometry in which 25 layers of Cu are covered on both sides by Pb-SJ with the desired thickness. In Fig. 1 we show the effective potential in the case of 3 ML of Pb; 1 ML corresponds to the thickness $d=5.41a_0$. In Cu, the

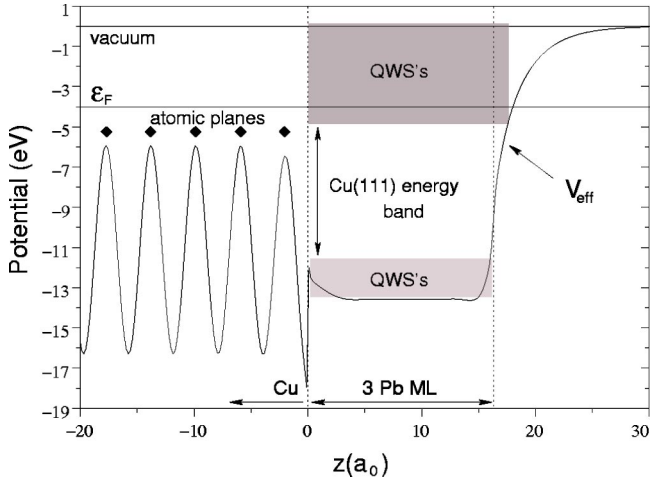

FIG. 1. Effective potential as a function of the distance to the Cu/Pb interface. The vertical dotted lines give the limits of the 3 ML Pb slab. The dark gray area corresponds to the Cu(111) energy gap and the light gray to the potential well at Pb due to its deeper effective potential compared with the average of Cu(111) potential.

potential maxima due to the 1D-pseudopotential mimics the orthogonalization of the valence states to core states. The Pb jellium edge begins, as is usual in jellium calculations, $0.5d$ above the outermost ''Cu-atom layer.'' At the Pb/Cu interface the potential is affected by the alignment of the Fermi levels of the substrate and the overlayer accompanied by the charge transfer from Pb to Cu. The dark gray region denotes the energy gap induced by the Cu potential and the light gray region gives the energy range between the potential in Pb and the bottom of the Cu bulk band. These two regions will accommodate the quantum-well states (QWS's) localized perpendicular to the surface and mainly in the Pb overlayer. QWS's in the Cu band gap determine the energy shell structure.

The QWS eigenenergies (bottoms of two-dimensional bands) are shown in Fig. 2 as a function of the number of Pb ML's completed. They are compared with the results measured by STM.[18] The agreement is good for coverages thicker than 6 ML. In particular, both the theory and the experiment give a QWS at ≈ 0.65 eV for every even number of ML's (no experimental data are available for 14, 18, 20, and 22 ML). For coverages less than 6 ML the correspondence is worse. This disagreement may be due to the fact that we omit the compression of the surface atom layers (self-compression effect) and the expansion in perpendicular direction due to parallel intraplane compression of the Pb layers at the interface (strain due to the Cu substrate).[9,12] The discrepancy between the experimental and calculated eigenenergies can also be due to the omission of the interaction of the Cu $3d$ electrons with the delocalized Pb electrons in our model. Because of the very localized character of $3d$ electrons this interaction takes place mostly at the Cu-Pb interface and disappears at distances of a few Pb ML's due to the screening by Pb electrons. The overall agreement between the theoretical and measured eigenenergies for thick overlayers gives confidence to our model when studying the behavior of the total energy.

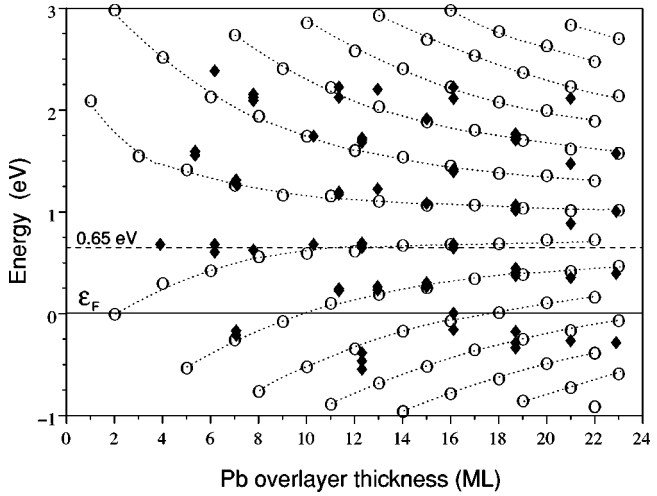

FIG. 2. Eigenenergies of the QWS's as a function of the Pb layer thickness. Open circles and filled diamonds show the calculated and measured (Ref. 18) values, respectively. The dotted lines are plotted as a guide to the eye. The energies are given with respect to the Fermi level of Pb/Cu(111) system.

The total energy of the Pb/Cu(111) system can be written as the sum $E_{\mathrm{Cu}}+E_{\mathrm{Pb}}+E_{\mathrm{Cu-Pb}}+E_{\mathrm{Pb-vac}}$, where E_{Cu} and E_{Pb} are contributions calculated by using the bulk energies corresponding to the 1D-Cu(111) pseudopotential and the Pb-SJ, respectively. The sum of the energies due to the Cu-Pb and Pb-vacuum interfaces, $E_{\mathrm{Cu-Pb}}+E_{\mathrm{Pb-vac}}$, contains the oscillating part σ of the total energy. In order to see the oscillations clearly also at high coverages σ is multiplied in Fig. 3 by the thickness of the Pb layer. As a continuous function of the thickness the oscillations are regular and their wavelength is half of the Fermi wavelength, $\lambda_F/2=3.77a_0$, for the Pb jellium.

The solid line in Fig. 3 links the points corresponding to completed Pb ML's. Because the interlayer spacing d

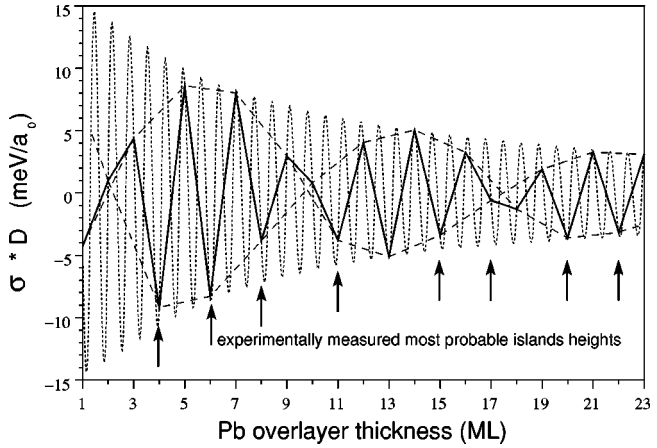

FIG. 3. Oscillating part of the total-energy per surface area of Pb/Cu(111) system (σ) multiplied by the Pb slab thickness D. The dotted line is a function of the continuous Pb-SJ thickness. The solid line connects the values corresponding to completed ML's. The dashed lines guide the eye in order to show the supershell structure. The arrows denote the measured thicknesses of the most abundant island heights (Ref. 5).

$\simeq \frac{3}{2}\lambda_F/2$, an even-odd staggering of the energy as function of the ML's is obtained. However, the above relation is not exact and therefore the staggering amplitude diminishes regularly and the phase of the staggering changes at the beats from that corresponding to minima at an even number of ML's to minima at an odd number of ML's or vice versa. The pattern resembles that of the supershell structures for atomic clusters[19] and metallic nanowires.[20]

The arrows pointing upward in Fig. 3 denote the most abundant island heights measured by Otero *et al.*[5] with the STM. Actually, the measurements give the percentage of area covered with islands of a given height and the highlighted heights correspond to maxima in this distribution. The correlation with the energy minima of our solid curve is remarkable. Even the even-odd phase changes (supershell structure) agree. The agreement means that the minima of the total energy determine the most abundant island heights at the growing temperature which is around the room temperature. According to Fig. 3 the energy differences between adjacent systems with even and odd ML's of Pb are of the order of 0.05 eV per surface atom, i.e., higher than the thermal energy. Menzel *et al.*[21] estimated the evolution of a seven-layer island from a five-layer island on Si(111) to occur through a barrier of 0.32 eV. They concluded that the thermodynamics determines the most abundant island heights but the kinetics is important in determining the height distribution.

However, there is some mismatch between the theory and the experiment in Fig. 3. In experiments, islands of 13 ML's of Pb are not especially abundant. The experimental situation in which the substrate is not flat but contains steps or terraces may affect the height distribution at this point.[22] At the second beat our model predicts similar energies for the island heights of 17 and 18 ML whereas according to experiments the 17 ML island should be more abundant. The ordering in the beat region is very sensitive, e.g., to the small variations in the layer thicknesses. We note that the Pb overlayer expansion of ~ 0.03–0.04 ML, estimated by taking into account the self-compression and strain effects (Materzanini *et al.*[12] and references therein), would still improve the agreement.

Hinch and Toennies[3] have measured the shell and supershell structure of the Pb island heights with the HAS technique. During the Pb deposition, a high intensity of the reflected He beam indicates smooth surfaces of islands of completed ML's. The heights of these islands are obtained indirectly from the deposition rate and the exposition time. The experiment shows the even-odd staggering which has an opposite phase in the comparison with the STM results by Otero *et al.*[5] and our calculations. The beat positions by Hinch and Toennies are located at coverages of 10–11 and 20–22 ML, which are slightly larger than those by Otero *et al.* and our predictions. Thus, it seems evident that the indirect measurement overestimates the Pb overlayer thickness.

We have calculated the total energy of free-standing Pb-SJ slabs. The results show oscillations with the same wavelength and a similar amplitude as the dashed curve in Fig. 3. But the $\lambda_F/2$ oscillating pattern is now shifted $\sim 1/7$ Pb ML forward. This changes the shell and supershell structure so that energy minima are shifted and the beat positions occur at 6–7 and 14–15 ML's, i.e., in a clear disagreement with the measurements. We have compared our unsupported Pb-SJ results with those obtained for Pb slabs in pseudopotential calculations.[12,13] These more sophisticated evaluations give a similar wrong position of the first beat as our unsupported Pb-SJ slabs. The damping of the energy oscillations makes the second beat hardly recognizable in these calculations. Thus, the energy oscillations are very sensitive to the correct determination of the potential barriers and it is crucial to take the Cu(111) substrate into account.

The shell structure of simple metal overlayers is a result of the periodic sinking of new QWS's below the Fermi level when the thickness of the overlayer increases. New QWS's increase the density of states at the Fermi level giving the oscillations in the energy with the wavelength of $\lambda_F/2$. Neglecting the damping we can write the oscillating part of the total energy as a function of the overlayer thickness D as $E_{\mathrm{osc}}(z)=\cos(2\pi\nu D+\theta)$, where $\nu=2/\lambda_F$ and θ is a phase that shifts the energy to the correct position depending on both the Pb-vacuum and the Cu-Pb interface properties. The energy values corresponding to N completed ML's are obtained from

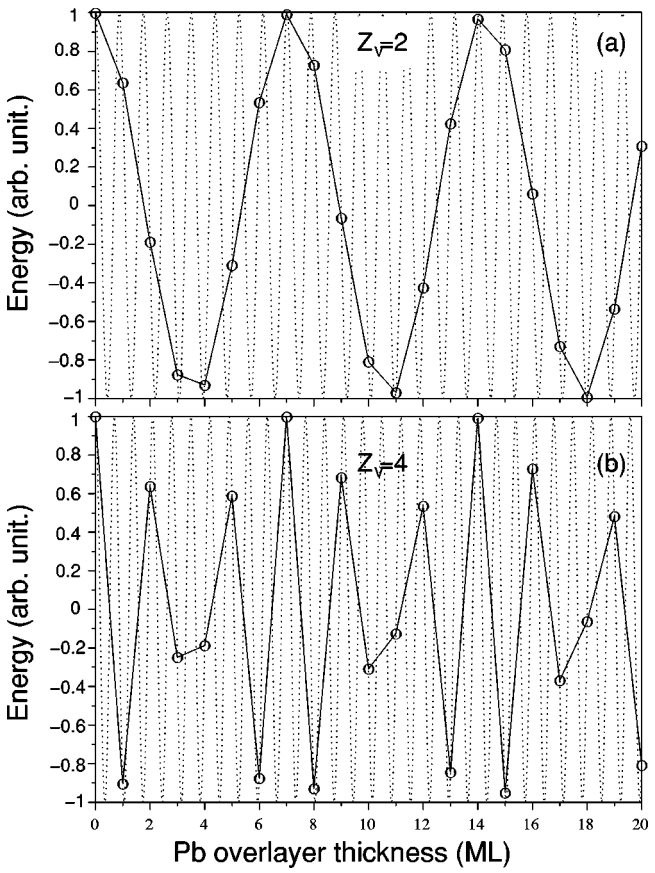

FIG. 4. Oscillating part of the total energy calculated using Eqs. (1) and (2) for fcc metals grown in the (111) direction. (a) and (b) correspond to two and four valence electrons per atom, respectively. The dotted lines are the energies as continuous functions of the slab thickness and the solid lines connect the energies corresponding to completed ML's.

$$E_{\mathrm{osc}}(N)=\cos(2\pi\nu dN+\theta). \quad (1)$$

For a fcc metal grown in the (111) direction the interlayer spacing $d=a/\sqrt{3}$, where a is the lattice parameter. The Fermi wavelength $\lambda_F=(2\pi/Z_v)^{1/3}a$, where Z_v is the number of valence electrons. These relations give

$$\nu d=\frac{1}{\sqrt{3}}\left(\frac{12Z_v}{\pi}\right)^{1/3}\approx 0.903Z_v^{1/3}, \quad (2)$$

and substituting this into Eq. (1) gives a general formula for E_{osc} of a fcc metal grown in the (111) direction.

Using Eqs. (1) and (2) and setting $\theta=0$ we have plotted in Fig. 4 the oscillating part of the energy as a function of the number of ML's for $Z_v=2$ and 4. The experimental counterparts are the abundance spectra of island heights. For monovalent and divalent overlayer metals the model predicts strong peaks occurring regularly after a certain number of ML's. However, this pattern may be suppressed in the real experiments, because the energy differences between neighboring completed ML's are small and the growing of a metastable island from the previous one requires several new ML's. For trivalent and tetravalent metals the energy oscillates more rapidly. For $Z_v=4$, νd is close to a half integer and the supershell structure with beats is clear. Note that the increase of the electron density as a function of Z_v decreases the wavelength of $E_{\mathrm{osc}}(z)$ as shown by the dashed curves. This makes the determination of the stable island heights very sensitive to the variations of parameters such as the interplane distances determining the overlayer thickness or the penetration of the QWS wave functions into vacuum or/and into the Cu substrate.

In summary, we have analyzed the electronic structures and the stability of Pb islands grown on the Cu(111) surface as a function of the island height. The Cu(111) substrate is described by a 1D pseudopotential and the Pb overlayer by the stabilized jellium model. As a function of Pb completed ML's our model gives quantum-well states in a good agreement with measurements.[18] The total energy shows modulated odd-even oscillations resembling the supershell structure of simple-metal atomic clusters and nanowires. The pattern correlates well with the height abundance spectrum measured by Otero *et al.*[5] We demonstrate that a proper modeling of the Cu(111) substrate plays a crucial role in predicting the beat positions of the abundance spectra.

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[1] W.D. Knight, K. Clemenger, W.A. de Heer, W.A. Saunders, M.Y. Chou, and M.L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).
[2] A.I. Yanson, I.K. Yanson, and J.M. van Ruitenbeek, Nature (London) **400**, 144 (1999).
[3] B.J. Hinch and J.P. Toennies, Europhys. Lett. **10**, 341 (1989).
[4] M.F. Crommie, C.P. Lutz, and D.M. Eigler, Science **262**, 218 (1993).
[5] R. Otero, A.L. Vázquez de Parga, and R. Miranda, Phys. Rev. B **66**, 115401 (2002).
[6] J. Braun and J.P. Toennies, Surf. Sci. **384**, L858 (1997).
[7] F.K. Schulte, Surf. Sci. **55**, 427 (1976).
[8] P.J. Feibelman, Phys. Rev. B **27**, 1991 (1983).
[9] I. Sarría, C. Henriques, C. Fiolhais, and J.M. Pitarke, Phys. Rev. B **62**, 1699 (2000).
[10] A. Kiejna, J. Peisert, and P. Scharoch, Surf. Sci. **432**, 54 (1999).
[11] P. Saalfrank, Surf. Sci. **274**, 449 (1992).
[12] G. Materzanini, P. Saalfrank, and P.J.D. Lindan, Phys. Rev. B **63**, 235405 (2001).
[13] C.M. Wei and M.Y. Chou, Phys. Rev. B **66**, 233408 (2002).
[14] J.P. Perdew, H.Q. Tran, and E.D. Smith, Phys. Rev. B **42**, 11 627 (1990).
[15] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Hold-Saunders International Editions, New York, 1981).
[16] E.V. Chulkov, V.M. Silkin, and P.M. Echenique, Surf. Sci. **437**, 330 (1999).
[17] E. Ogando, N. Zabala, E. V. Chulkov, and M. J. Puska (unpublished).
[18] R. Otero, A.L. Vázquez de Parga, and R. Miranda, Surf. Sci. **447**, 143 (2000).
[19] W.A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
[20] A.I. Yanson, I.K. Yanson, and J.M. van Ruitenbeek, Phys. Rev. Lett. **84**, 5832 (2000).
[21] A. Menzel, M. Kammler, E.H. Conrad, V. Yeh, M. Hupalo, and M.C. Tringides, Phys. Rev. B **67**, 165314 (2003).
[22] R. Miranda and A. L. Vázquez de Parga (private communication).