

Strong Quantum Size Effects in Pb(111) Thin Films Mediated by Anomalous Friedel Oscillations

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Using first-principles calculations within density functional theory, we study Friedel oscillations (FOs) in the electron density at different metal surfaces and their influence on the lattice relaxation and stability of ultrathin metal films. We show that the FOs at the Pb(111) surface decay as $1/x$ with the distance x from the surface, different from the conventional $1/x^2$ power law at other metal surfaces. The underlying physical reason for this striking difference is tied to the strong nesting of the two different Fermi sheets along the Pb(111) direction. The interference of the strong FOs emanating from the two surfaces of a Pb(111) film, in turn, not only results in superoscillatory interlayer relaxations around the center of the film, but also determines its stability in the quantum regime. As a simple and generic picture, the present findings also explain why quantum size effects are exceptionally robust in Pb(111) films.

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In recent fundamental and applied studies of thin film growth and low-dimensional phenomena, an especially active line of research is the exploration of the role of quantum size effects (QSE) in the formation and properties of metallic nanostructures. Briefly, the formation energy of thin metal films acquires a distinctive thickness dependence; this thickness-dependent energy or quantum stability, in turn, can be exploited to gain precise control of the film morphology down to the atomic layer scale [1–3]. Because the quantum stability of the films is directly tied to the overall electron density of states around the Fermi level, many of the physical and chemical properties of the films can also exhibit strong thickness dependence, thereby offering unprecedented opportunities for precise tuning of these properties in the quantum regime [4–17].

In this emerging area of electronic growth and QSE of metallic nanostructures, the growth of Pb(111) films has attracted particular interest. Not only can the thickness of the lead films or nanoscale lead islands or voids be tuned precisely [4–10], but also such tailored structures exhibit strong thickness-dependent oscillations in the interlayer lattice relaxation [11], superconductivity [12,13], atomic or molecular rate processes [14], and Kondo physics [15]. Such oscillations have typically been attributed to QSE associated with the confined motion of the conduction electrons along the growth direction [4–10,16–20]. In the particle-in-a-box model, such QSE are expected to vanish beyond about 10 monolayers (ML) at typical physical conditions [2,18]. However, extensive studies have shown that strong QSE still persist in Pb(111) films over 30 ML thick, whereas they are no longer discernible in other fcc(111) metal films of similar thicknesses [4–10]. The

underlying physical reason for this striking difference has been a long-standing puzzle.

In this Letter, we use first-principles density functional theory to carry out systematic and comparative studies of the Friedel oscillations (FOs) in electron density at different metal surfaces and the FOs' influence on the stability and other properties of ultrathin metal films. We show that the FOs at the Pb(111) surface decay with the distance x from the surface as $\sim 1/x$, distinctly different from the conventional $1/x^2$ decay at other metal surfaces. The underlying physical reason for this striking difference is tied to the strong nesting of the two sheets of Fermi surfaces along the Pb(111) direction. Furthermore, the interference of the strong FOs emanating from the two surfaces of a Pb(111) film results in superoscillatory interlayer relaxations around the center of the film, influencing the quantum stability of the film. Those findings explain why QSE are exceptionally robust along the Pb(111) direction, and also establish a simple and generic picture for understanding QSE in ultrathin metal films.

Geometric and electronic structure of freestanding representative metal films are carried out using the Vienna *ab initio* simulation package (VASP) with an ultrasoft pseudopotential plane-wave basis set [21,22]. Exchange and correlation effects are treated by the generalized gradient approximation [23]. The metal films are simulated using 1×1 supercells with a vacuum region of 20 atomic layers and a $21 \times 21 \times 1$ \mathbf{k} -point mesh to ensure total-energy convergence. Other numerical details can be found in Ref. [17].

We first consider the electron density oscillations of a semi-infinite solid surface, which acts as a giant defect, inducing a quasi-one-dimensional charge-density wave

into the film with decaying amplitudes [24,25]. In our calculations, the 1×1 supercells for the unrelaxed Pb(111), Al(111), Pb(100), and Pb(110) films containing 80, 80, 100, and 100 layers of atoms, respectively, plus 20 vacuum “layers” are used to simulate the semi-infinite solid surfaces. These large supercells ensure that the two sets of FOs emanating from the two bounding surfaces do not interfere with each other as they normally would in much thinner films. Likewise, the influence of QSE should be negligible for such thick films.

The planar-averaged charge-density variations in these films are calculated as $\Delta\rho(x) = \iint \rho(x, y, z) dy dz - \iint \rho_0(x, y, z) dy dz$, where $\rho_0(x, y, z)$ is the bulk value. The results are plotted in Fig. 1 for the four systems. This comparative study reveals that the FOs along the Pb(111) direction are quite exceptional, decaying much more slowly than those at the other three surfaces. Typically, Friedel oscillations due to a surface decay as $1/x^2$ [24]. In such cases, the FOs fade rapidly and become negligible about 10 ML away from the surface, as seen in Figs. 1(b)–1(d) for Al(111), Pb(110), and Pb(100), respectively. However, the FOs of Pb(111) persist into the bulk well beneath the first 20 ML below the surface. Qualitatively, the FOs at Pb(111) closely obey a $1/x$ power law rather than the conventional $1/x^2$ law, as indicated by the dashed and dotted lines in Fig. 1(a), respectively. Furthermore, a Fourier transformation of the FOs at Pb(111) has two well-defined peaks (i.e., two Fermi wave vectors), in contrast to only one well-defined peak for Al(111) and Pb(110) and no obvious peak(s) for Pb(100), as indicated by the insets in Figs. 1(a)–1(d).

To elucidate the physical origin of the exceptional Friedel oscillations at the Pb(111) surface, in particular, the slow $\sim 1/x$ decay, we plot the band structure of bulk Pb

along the $\Gamma LL'\Gamma'$ lines in the Brillouin zone, along with the full Fermi surface as shown in Fig. 2(a). We see that two bands cross the Fermi level along the [111] direction, corresponding to two different sheets of the Fermi surfaces. The corresponding Fermi wave vectors are very close to the two peaked values shown in the inset of Fig. 1(a) after proper conversion, and electrons from both Fermi sheets contribute to the Friedel oscillations along the [111] direction. To illustrate why the FOs of Pb(111) decay differently from the other cases, we plot in Figs. 2(b)–2(d) the Fermi surface contours perpendicular to the Pb[111], Al[111], Cu[111], and Pb[100] directions, respectively. As shown in Fig. 2(b), the two different Fermi surface sheets of Pb perpendicular to the [111] direction are very flat: this nesting of the Fermi surface, in turn, significantly enhances the charge-density oscillations characteristic of a quasi-one-dimensional electron system with $\sim 1/x$ decay. In contrast, the Fermi surfaces along the [111] direction of Al and Cu and the [100] direction of Pb are more curved, as shown in Figs. 2(c) and 2(d); the corresponding FOs therefore decay much faster.

The strong FOs in electron density at the bulk Pb(111) surface may have various important manifestations. To demonstrate the intricate connection between the FOs and interlayer lattice relaxations at the Pb(111) surface, we have discretized the charge density in Fig. 1(a) as a function of the layer number in Fig. 3(a). The interlayer lattice relaxations of this very thick Pb(111) film are further computed by fully relaxing the lattice. The lattice relaxation is defined by $\delta d_{i,i+1} = d_{i,i+1} - d_0$, where $d_{i,i+1}$ is the interlayer spacing between the i th and $(i+1)$ th layers and d_0 is the bulk layer spacing along

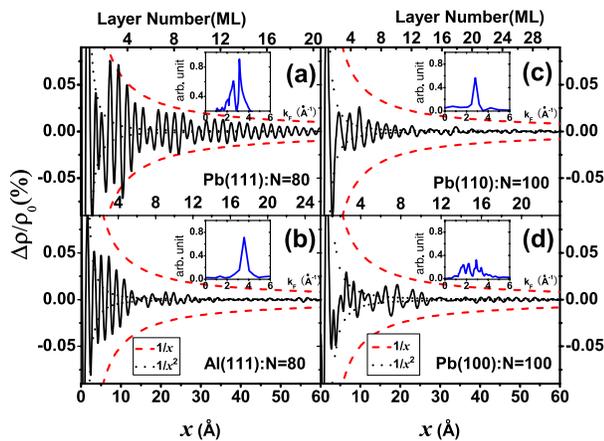


FIG. 1 (color online). (a) Changes of the electronic charge density relative to the bulk values as a function of distance from the surface in (a) Pb(111), (b) Al(111), (c) Pb(110), and (d) Pb(100) films, calculated with a total film thickness of 80, 80, 100, and 100 ML, respectively. The corresponding Fourier transformation for the Pb(111) films is also plotted in the inset of (a) with the unit $2\pi/a$, where a is the lattice constant.

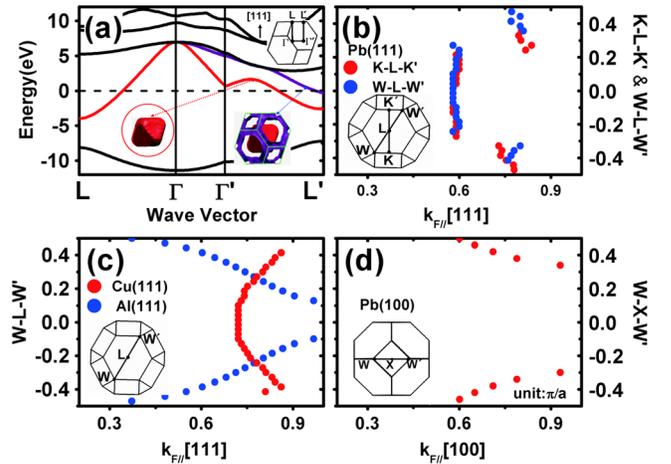


FIG. 2 (color online). (a) Calculated band structure of Pb along the $\Gamma LL'\Gamma'$ lines in the Brillouin zone; the Fermi surface is also plotted in the inset. (b) The projected value of the Fermi wave vector in the [111] direction of Pb along K-L-K' and W-L-W' lines of the Fermi surface. (c) The projected value of Fermi wave vector in the [111] direction of Al and Cu along the W-L-W' line of the Fermi surface. (d) The projected value of Fermi wave vector in the [100] direction of Pb along the W-X-W' line of the Fermi surface. The unit is $2\pi/a$.

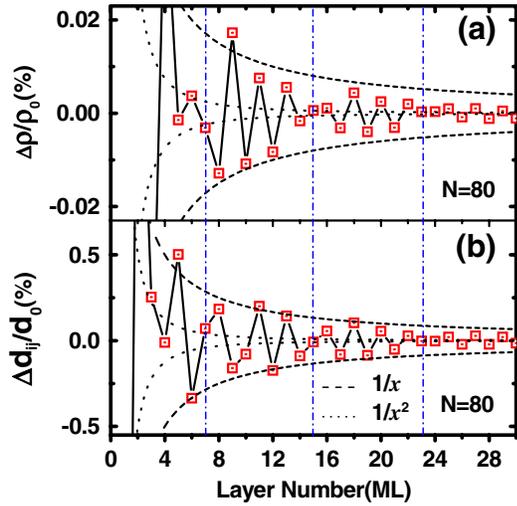


FIG. 3 (color online). (a) Changes of electronic charge density relative to the bulk value as a function of the layer number for a Pb(111) film 80 ML thick; (b) the interlayer lattice relaxations for this system. The vertical straight lines are guides to the eye.

the [111] direction. The results are plotted in Fig. 3(b) for comparison. Both sets of the data oscillate with the film thickness. These oscillations are interrupted by even-odd crossovers with a period of 9 ML, and again can be fitted much better with a $\sim 1/x$ decay envelope rather than a $1/x^2$ law. The close resemblance between the two plots also strongly suggests that the interlayer relaxations are driven by the surface FOs [26], even though the resemblance is not very good near the surface.

With this understanding of the FOs at the surface of bulk Pb(111), we now investigate interference effects of the FOs in thin Pb(111) films having two surfaces. We have calculated the interlayer lattice relaxations for Pb(111) films up to 40 ML, with part of the results illustrated in Fig. 4(a). For an ultrathin film of N MLs, we have excluded the relaxations for the four outmost layers, $\delta d_{1,2}$, $\delta d_{2,3}$ and $\delta d_{N-2,N-1}$, $\delta d_{N-1,N}$, because these values have already been discussed both experimentally [11] and theoretically [17], and their much larger magnitudes contain nonasymptotic corrections that may potentially obscure the simple behavior we aim to reveal here.

We found that the Pb(111) films reflect hitherto unnoticed frustrated interlayer relaxations manifested as superoscillations. Three distinctive features of the relaxations are shown in Fig. 4(a). First, the interlayer lattice relaxation exhibits oscillations with the atomic layer number for a given total film thickness N , corresponding to alternating contraction and expansion of the lattice spacing. Second, when N is even, the interlayer relaxations in the middle of Pb(111) films are larger than the relaxations near the surfaces, which is surprising because interlayer relaxation usually decreases for atom layers farther from the surface. Third, there exists another intriguing type of oscillation in the overall lattice relaxation pattern, which is termed *superoscillatory relaxation*: The magnitudes of the

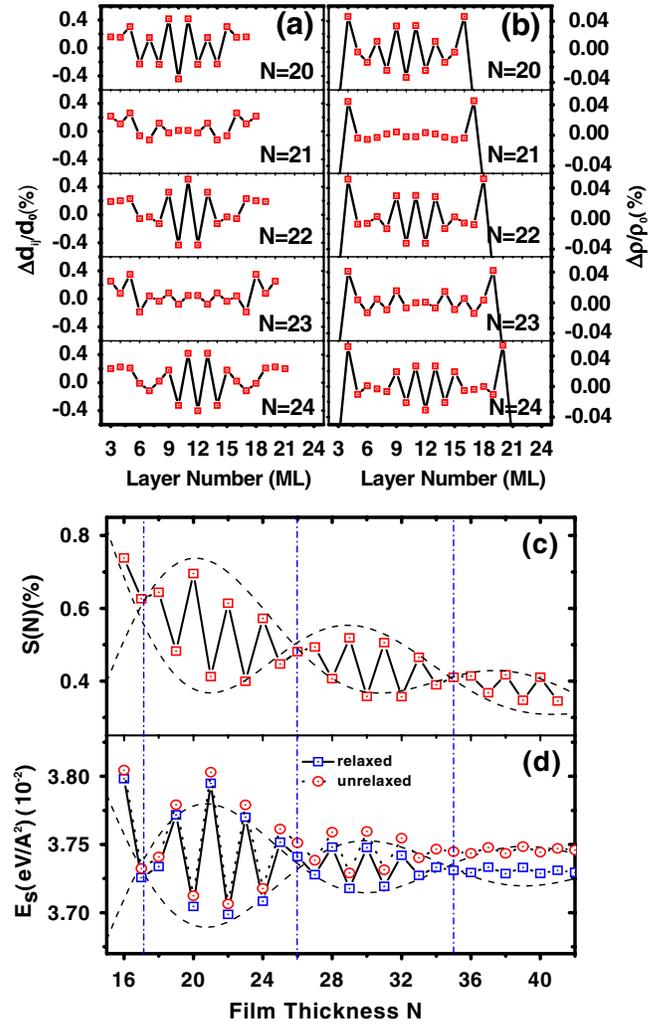


FIG. 4 (color online). (a) Interlayer relaxations of Pb(111) films as a function of the layer number for different film thickness N . (b) Change of electronic charge density of unrelaxed Pb films relative to the bulk value. (c) Standard deviations of the interlayer lattice relaxation as a function of the film thickness. (d) The surface energies for both the relaxed and unrelaxed cases.

oscillations of the interlayer lattice relaxation oscillate with the thickness of the films, much stronger for $N = 20, 22$, and 24 ML than those for $N = 21$ and 23 ML.

To check the expectation that interlayer relaxations for those thin films are driven by the changes of electron density, we computed the changes in electron density inside each layer in the freestanding Pb(111) films by freezing the lattice spacing at its bulk value. As shown in Fig. 4(b), the pattern is very similar to that of the lattice relaxations shown in Fig. 4(a), confirming that fluctuations in the charge density drive the overall lattice relaxations [25].

This superoscillatory trend can further be quantified by the standard deviation of the interlayer spacing from the bulk value, $S(N) = \sqrt{\sum_3^{N-2} (\delta d_{i,i+1})^2 / (N-5)}$. The results

are plotted in Fig. 4(c). We see that $S(N)$ oscillates systematically in an even-odd fashion that is interrupted by crossovers at 17, 26, and 35 ML. Thus, the period of the crossovers is 9 ML.

To study the relation between interlayer relaxation and film stability, we calculated the surface energy of Pb(111) films in both the relaxed and unrelaxed cases [17]. The results are plotted in Fig. 4(d), exhibiting essentially identical oscillatory patterns as that of $S(N)$, suggesting that both properties are driven by the FOs.

Taken together, these new findings show that the robust stability and the frustrated interlayer relaxations of Pb(111) films are due to the interference of the strong FOs in charge density rather than the mere presence of metallic quantum well states. In a freestanding Pt(111) film, Friedel oscillations propagate from one surface towards the other, interfering quantum mechanically in the middle of the film. If these two sets of FOs are in phase, the interference is constructive, yielding a stronger electronic charge-density wave, which in turn produces larger oscillations in the interlayer relaxation. Consequently, with full relaxation the Pb(111) films have lower total energies, becoming more stable. Likewise, if the two propagating density oscillations are out of phase, the films have weaker oscillations in the lattice relaxation and a higher total energy, making them unstable. Because the ratio between the lattice spacing d_0 and the period of the FOs is roughly 3:4 [see Figs. 1(a) and 3(a)], addition of one monatomic layer shifts the relative phase of the two sets of FOs by π . Therefore, the interference alternates between constructive and destructive as the film thickness increases layer by layer, resulting in the superoscillatory relaxations. However, the small deviation from the exact 3:4 ratio causes a small shift in the relative phase, accumulating to yield an interruption in the even-odd oscillations every 9 ML. We emphasize that the obviously frustrated relaxations in Pb(111) only occur when the FOs decay according to the $1/x$ law, disappearing if obeying the $1/x^2$ law.

Finally, we stress that the present FO interference picture explains successfully why QSE are so much stronger for Pb(111) films than for other metal films, as exemplified here by Pb(110), Pb(100), and Al(111). Because of the slow $1/x$ decay, the FOs in Pb(111) are still quite strong even at a depth of 20 ML, and can therefore produce pronounced quantum-mechanical interference in the interior of Pb(111) films as thick as 40 ML. In addition to the $1/x$ decay of lattice relaxations and surface energy explored here, our study also strongly suggests that other physical properties of Pb(111) films may also exhibit the $1/x$ behavior, such as the superconducting transition temperature reported recently [13,27], as well as various kinetic and chemical processes on the quantum films [14,28,29]. Such intricate relationships between the properties and the film thickness remain to be fully explored in future studies. Besides the prototype model system of Pb(111), other related systems exhibiting quasi-one-

dimensional electron behavior due to extreme anisotropy should also display similar intriguing physical properties [27,30,31].

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