Mass enhancement parameter in free-standing ultrathin Pb(111) films: The effect of spin-orbit coupling

I. Yu. Sklyadneva,^{1,2,3,4} R. Heid,¹ K.-P. Bohnen,¹ P. M. Echenique,^{2,5,6} and E. V. Chulkov^{2,5,6}¹Karlsruher Institut für Technologie, Institut für Festkörperphysik, D-76021 Karlsruhe, Germany²Donostia International Physics Center (DIPC), 20018 San Sebastián/Donostia, Basque Country, Spain³Tomsk State University, 6340501, Tomsk, Russian Federation⁴Institute of Strength Physics and Materials Science, pr. Akademicheskii 2/1, 634021, Tomsk, Russian Federation⁵Departamento de Física de Materiales, Facultad de Ciencias Químicas, UPV/EHU, Apdo. 1072, 20080 San Sebastián/Donostia, Basque Country, Spain⁶Centro de Física de Materiales CFM - Materials Physics Center MPC, Centro Mixto CSIC-UPV/EHU, 20018 San Sebastian/Donostia, Spain
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The influence of spin-orbit interaction on the electron-phonon coupling strength at the Fermi level of thin lead films is investigated using first-principles calculations in the density functional perturbation formalism. The calculations both scalar relativistic and including spin-orbit coupling (SOC) have been carried out for free-standing Pb(111) films consisting of four to ten atomic layers. It is shown that the spin-orbit interaction produces a large enhancement of the electron-phonon coupling strength regardless of the film thickness. This partly reflects a strong SOC-induced softening of the film phonon spectra, and partly a SOC-mediated increase in electron-phonon coupling matrix elements. For thin films, quantum size effects result in pronounced oscillations of the average coupling constant with the number of layers, which become damped for thicker films.

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I. INTRODUCTION

The superconductivity of supported lead films with a thickness of a few monolayers^{1–5} and even of a single Pb layer on silicon⁶ has stimulated an active scientific interest in thin Pb films.^{7–21} The experimental findings inspired a great amount of theoretical work focused on the thin film properties such as the critical temperature of superconductivity,^{5,12,13} the electron-phonon coupling,^{5,19,20} film surface vibrations,^{17–20} electronic characteristics^{14,15,22–24} as well as on the impact of quantum size effect on the physical properties.

The electron-phonon coupling strength in thin Pb(111) films was estimated for the highest occupied quantum-well states (QWS) from the temperature-dependent QWS peak widths in the photoemission spectra of uniform Pb(111) films on Si(111) using angle-resolved photoemission spectroscopy measurements.^{1,9} As for the momentum averaged strength of electron-phonon interaction at the Fermi level (the mass enhancement parameter), it has been studied only in free-standing Pb(111) films using *ab initio* calculations and without taking into account the spin-orbit interaction of electrons.^{5,19,20} However, the spin-orbit coupling (SOC) has been shown to have a profound impact on lattice vibrations^{25–27} in bulk Pb and on the electron-phonon (*e*-ph) interaction both at the Fermi surface of bulk lead²⁷ and beyond the Fermi energy.²⁸ This suggests that SOC is also very important for a proper quantitative description of the *e*-ph interaction in thin Pb films.

Here, we present an *ab initio* study of the effect of spin-orbit interaction on the electron-phonon coupling strength at the Fermi level of free-standing Pb(111) films. To this end, first-principles calculations were carried out for the Pb(111) films consisting of four to ten monolayers (ML). To assess the importance of SOC, we performed both scalar relativistic calculations (without SOC) and calculations including SOC self-consistently.

The paper is organized as follows. Section II contains a short outline of the calculational method and structural characteristics of Pb films. Then we focus on the effect of spin-orbit interaction on the electron-phonon coupling. Finally, we summarize in Sec. III.

II. CALCULATION RESULTS AND DISCUSSION

A. Calculation details

All the calculation were carried out within the density-functional formalism and the local density approximation²⁹ using a mixed-basis pseudopotential approach.^{30–32} The scheme employs a combination of local functions and plane waves to represent valence states.^{30,31} To calculate dynamical properties of films, the linear response technique^{33,34} is used. As in the case of bulk Pb and Pb(111) surface,^{27,35} the calculations both scalar relativistic and including spin-orbit effects were performed using fully separable, norm-conserving pseudopotentials³⁶ with *5d* semicore states included. Details of the spin-orbit coupling implementation within the mixed-basis pseudopotential method can be found in Ref. 27.

At each atomic site of Pb, *d*-type local functions were employed to accelerate the convergence with respect to the plane-wave basis set. For the latter, a kinetic energy cutoff of 20 Ry was sufficient. Brillouin zone integrations were performed by sampling a uniform 48×48×1 *k*-point mesh corresponding to 217 special points in the irreducible part of two-dimensional Brillouin zone (IBZ) and a Gaussian energy smearing scheme with a width of 0.2 eV.³⁷

B. Structural parameters

Since the dynamical properties of a material are closely related to its structure, we first present the structural information. Free-standing Pb(111) films are modeled by a supercell

FIG. 1. (Color online) Interlayer relaxations for the distances between the first (top) and second layers (Δd_{12}) and the second and third layers (Δd_{23}) as a function of film thickness. The changes are given in percents of the bulk value: $\Delta d_{ij} = (d_{ij} - d_{\text{bulk}})/d_{\text{bulk}}$. The values obtained both without (open circles) and with spin-orbit coupling (full, red circles) are presented. Also shown are the results of scalar relativistic pseudopotential calculations using gradient-corrected density functional theory: Ref. 38 (grey circles) and Ref. 17 (open squares). Black diamonds show Δd_{12} and Δd_{23} for ultrathin Pb films on Si(111) determined with low-energy electron diffraction.⁸

geometry: N -layer ($N = 4, \dots, 10$) Pb(111) films separated by a vacuum gap of 22 Å corresponding to 7.5 atomic layers. The in-plane lattice constant is fixed at the theoretical bulk lattice parameter obtained by total-energy minimization:²⁷ $a = 9.20$ a.u. (without SOC) and $a = 9.22$ a.u. (with SOC). The optimized bulk lattice constants are smaller by 1.4–1.6% compared to the experimental data,³⁹ $a_{\text{exp}} = 9.35$ a.u. Along the stacking direction, the Pb(111) layers are allowed to relax until the forces become smaller than 1 mRy a.u.⁻¹. Figure 1 shows the relaxation of the first two interlayer spacings, d_{12} and d_{23} , as a function of film thickness.

It is a common feature for metal surfaces that the topmost interlayer spacing contracts relative to the bulk value, a well-known surface effect,^{40,41} while d_{23} is somewhat widened, regardless of the film thickness. We also find that the magnitude of interlayer contraction or expansion shows oscillations with film thickness, indicative of a quantum size effect. The variation of Δd_{12} lies in the range from -4.4% to -5.6%, while Δd_{23} changes from +0.2% to +3%. With the film thickness the amplitude of oscillations gradually decreases. Hereinafter, the values obtained with spin-orbit coupling included are given. With increasing film

thickness the calculated average compression of d_{12} and expansion of d_{23} approaches 4.5–5.0% and ~2%, respectively. These values are consistent with the experimental low-energy electron diffraction (LEED) data⁴⁰ for the Pb(111) surface, $\Delta d_{12} = -3.5 \pm 1.0\%$ and $\Delta d_{23} = +0.5 \pm 1.4\%$, considering that the largest film thickness in our calculation is still different from a semi-infinite surface. Similar thickness-dependent relaxations of free-standing Pb(111) films were also found in the *ab initio* scalar relativistic pseudopotential calculations^{17,38} (see Fig. 1), which employ the generalized gradient approximation for exchange-correlation functional.⁴² Available experimental information relates to thin Pb(111) films grown on a substrate.^{8,43,44} The LEED results⁸ reported for ultrathin Pb films on Si(111) are shown in Fig. 1 for comparison. The experimental data, $\Delta d_{12} = -2.8 \pm 0.5\%$ and $\Delta d_{23} = +1.0 \pm 0.6\%$ being qualitatively consistent with the *ab initio* results are smaller in magnitude especially the contraction of the topmost interlayer spacing.

We note that while the inclusion of spin-orbit coupling does not modify significantly the bulk Pb lattice constant, which increases by less than 1% as compared to the scalar relativistic case²⁷ the SOC-induced modifications in the relaxation of thin Pb(111) films are considerable especially with decreasing film thickness. For instance, for a four-layer film, the relativistic corrections to the contraction of the topmost interlayer distance amount to ~20%.

C. Electron-phonon coupling

We have evaluated the strength of the e -ph interaction at the Fermi level (E_F) of free-standing Pb(111) films with thicknesses ranging from four to ten layers. The momentum averaged e -ph coupling strength (mass enhancement parameter) is defined as⁴⁵

$$\lambda(E_F) = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (1)$$

Here, $\alpha^2 F(\omega)$ is the Eliashberg spectral function, which measures the contribution of phonons with frequency ω to the e -ph coupling.⁴⁶ It can be expressed in terms of e -ph matrix elements $g^{n,n'}(\mathbf{k}, \mathbf{q}, \nu)$ as

$$\alpha^2 F(\omega) = \frac{1}{\hbar N(E_F)} \sum_{\mathbf{q}, \nu} \delta(\omega - \omega_{\mathbf{q}, \nu}) \sum_{\mathbf{k}, n, n'} \delta(\epsilon_{\mathbf{k}, n} - E_F) \times |g^{n,n'}(\mathbf{k}, \mathbf{q}, \nu)|^2 \delta(\epsilon_{\mathbf{k}+\mathbf{q}, n'} - E_F), \quad (2)$$

where $\epsilon_{\mathbf{k}, n}$ and $\epsilon_{\mathbf{k}+\mathbf{q}, n'}$ are electronic energies, and $N(E_F)$ is the density of electronic states at E_F . The summation is carried out over (i) all combinations of electronic states $\mathbf{k}, n$ and $\mathbf{k} + \mathbf{q}, n'$ at the Fermi level and (ii) phonon modes $(\mathbf{q}, \nu)$. The dynamical and e -ph matrix elements were calculated on a $(12 \times 12 \times 1)$ grid of wave vectors in the irreducible part of two-dimensional BZ. To average the mass enhancement parameter over electron momentum, 217 special points ($48 \times 48 \times 1$) in the IBZ were used.

The thickness-dependent $\lambda(E_F)$ calculated with spin-orbit effects is shown in Fig. 2 (the upper panel) by full circles. The mass enhancement parameter of free-standing Pb(111) films

FIG. 2. (Color online) Mass enhancement parameter $\lambda(E_F)$ (top) and the density of electronic states at the Fermi level $N(E_F)$ (middle) as a function of film thickness. The full and open circles correspond to the calculations with and without SOC, respectively. The values of $\lambda^{\text{bulk}}(E_F)$ and $N^{\text{bulk}}(E_F)$ shown by full (open) triangles were reported in Ref. 27. (Bottom) Electronic band structure of a five-layer free-standing Pb(111) film along high-symmetry directions of the film IBZ. The dashed lines denote the dispersion curves obtained in the semirelativistic calculation while the solid lines represent the calculation including spin-orbit interaction.

tends gradually to the calculated bulk value,²⁷ $\lambda^{\text{bulk}}(E_F) = 1.56$. Besides an oscillation between films with even and odd number of layers is clearly seen, similarly to the even-odd oscillation of the superconducting transition temperature.^{1,2} The oscillation in the electron-phonon coupling strength decreases with film thickness and at ten layers, its amplitude is reduced to about 1%. For odd-layer films, the mass enhancement parameter moves gradually down to the bulk value while, for even-layer films, $\lambda(E_F)$ increases with the number of layers.

Figure 2 (the upper panel) also shows $\lambda(E_F)$ calculated without SOC. A common feature of both calculations (with and without SOC) is that the mass enhancement parameter of free-standing Pb(111) films is higher than the corresponding bulk value regardless of the film thickness considered except for four-layer films. This is in contrast to the findings of another *ab initio* scalar relativistic calculation of the electron-phonon coupling in free-standing Pb(111) films.²⁰ While the reported

values of $\lambda(E_F)$ for five- and six-layer films, 1.37 and 1.38, respectively, do agree reasonably with our scalar relativistic results, $\lambda(E_F) = 1.32$ for five layers and $\lambda(E_F) = 1.22$ for six layers, their value for the bulk $\lambda^{\text{bulk}}(E_F) = 1.41$ is significantly larger than our scalar relativistic value of $\lambda^{\text{bulk}}(E_F) = 1.08$.

For all film thicknesses, the influence of relativistic corrections on the *e*-ph coupling is found to be crucial because in the scalar relativistic calculation the strength of electron-phonon interaction is strongly underestimated. Like the bulk case,²⁷ where the inclusion of SOC results in a large enhancement (44%) of the coupling strength thereby improving the agreement with experiment⁴⁷ [$\lambda^{\text{bulk}}(E_F) = 1.55$], the relativistic corrections increase the mass enhancement parameter in the free-standing Pb(111) films by 26–38%. In addition, the even-odd $\lambda(E_F)$ quantum oscillations appear pronounced. In the following, we will address the effect of spin-orbit interaction on two major factors, which determine the mass enhancement parameter: the density of electronic states at the Fermi level and the *e*-ph spectral function.

1. Electronic structure

The mass enhancement parameter is approximately proportional to the number of electronic states at the Fermi level available for scattering processes (phase space). Figure 2 (the middle panel) shows the electronic density of states, $N(E_F)$, as a function of film thickness. When the relativistic corrections are included, the variations of $\lambda(E_F)$ and $N(E_F)$ with thickness show a nice correspondence, which suggests that the mass enhancement parameter is essentially dominated by variations in the phase space. Like $\lambda(E_F)$, the density of electronic states exhibits damped oscillations with a higher $N(E_F)$ for the odd-layer films. An unusually high density of states at a thickness of five monolayers is caused by a quantum well state that lies very close to E_F (see Fig. 2, bottom) and is a flat curve in the vicinity of the BZ center. In general, the oscillation of $N(E_F)$ with thickness in thin Pb films was found^{1,9,12,13} to be correlated with the formation of quantum well states that affect strongly the electronic distribution near the Fermi level. With increasing film thickness, the density of states in free-standing Pb(111) films approaches the bulk value of $N^{\text{bulk}}(E_F) = 0.259$ states/eV/atom/spin. An analysis of electronic states participating in the phonon-mediated scattering revealed that the largest contribution to the *e*-ph coupling at E_F comes from electronic states of p_z symmetry (the highest occupied QWS, for example) for all thicknesses studied.

Around E_F , the effect of spin-orbit interaction on the phase space is not profound. On the one hand, the SOC-induced qualitative modification of electronic bands near E_F (see Fig. 2, the lower panel) is not enough to have an appreciable influence on phonon-mediated electronic transitions and, thereby, affect the *e*-ph matrix elements. Like in bulk Pb,^{27,28,48} significant differences due to the spin-orbit coupling are found only for bands above or below E_F where the SOC-induced splitting of electronic bands leads to changes of more than 20% in the electronic density of states. On the other hand, the SOC-induced changes of the density of electronic states at the Fermi level are not large (Fig. 2, middle). $N(E_F)$ usually increases by 2–6% like in the bulk where a 6% increase of $N(E_F)$ due to SOC was found.²⁷ Only at a thickness of five-layers, the

increase comes to 9% due to the quantum well state that crosses the Fermi level upon the relativistic corrections (Fig. 2, bottom). The SOC-produced increase in $N(E_F)$ is in general significantly smaller than the corresponding enhancement of $\lambda(E_F)$. For six- and eight-layer films, the rise of $N(E_F)$ does not exceed 2%, while the increase in $\lambda(E_F)$ comes to $\sim 30\%$. Moreover, in ten-layer films, though $N(E_F)$ becomes smaller, the strength of e -ph interaction increases. The absence of a proportionality between the SOC-induced modifications of $\lambda(E_F)$ and those of $N(E_F)$ shows that the main influence of SOC on $\lambda(E_F)$ comes through other factors, which we discuss in the following.

2. Lattice dynamics and spectral functions

Another factor that controls the variations of $\lambda(E_F)$ are the frequencies of the lattice vibrations. In general, the inclusion of spin-orbit interaction results in a shift of the phonon spectra of free-standing Pb(111) films towards lower frequencies that promotes an increase of $\lambda(E_F)$. The SOC-induced softening of practically all phonon branches is sizeable regardless the

FIG. 3. (Color online) (Top) phonon dispersion curves for a four-layer free-standing Pb(111) film calculated both with (solid lines) and without (dashed lines) spin-orbit coupling. The highest optical phonon branches are indicated as ε_1 and ε_2 . The mode labels are taken from Ref. 18. (Bottom) Phonon frequencies of optical modes ε_1 (circles) and ε_2 (triangles) at the BZ origin ($\bar{\Gamma}$) as a function of film thickness calculated with (full symbols) and without (open symbol) spin-orbit coupling. The experimental data (grey symbols) are taken from Ref. 18 for Pb(111) films on Cu(111). The maximum bulk phonon frequency⁴⁹ of 9.04 meV is shown by arrows.

FIG. 4. (Color online) (Top) Phonon density of states $F(\omega)$ of a four- and ten-layer free-standing Pb(111) films. (Bottom) Eliashberg spectral functions $\alpha^2 F(\omega)$, calculated at the Fermi energy of a four- and ten-layer free-standing Pb(111) films. The data obtained both with (solid lines) and without (dashed lines) spin-orbit coupling are presented.

film thickness. As an example, Fig. 3 (top) shows phonon dispersion curves of a four-layer free-standing Pb(111) film calculated with and without spin-orbit coupling. The SOC-produced softening can be also seen in phonon densities of states, $F(\omega)$, for a four- and ten-layer free-standing Pb(111) films shown in the upper panel of Fig. 4.

The SOC-induced difference in phonon energies at the BZ boundary is about 8–12% and amounts to 24% for shear-horizontal modes (the two lowest phonons in the vicinity of $\bar{M}$ point). To give an illustration of the SOC influence, the phonon frequencies of optical modes ε_1 and ε_2 (at the BZ origin) calculated both with and without spin-orbit coupling as a function of film thickness are shown in Fig. 3 (bottom) together with the experimental data taken from Ref. 18 for thin Pb(111) films on a Cu(111) substrate. At the $\bar{\Gamma}$ point, these optical modes are characterized by stretch vibrations of atoms in the surface and subsurface layers with shear-vertical polarization (along the stacking direction of films). With increasing film thickness they acquire step-by-step a surface character. The existence of such localized phonons above the bulk continuum was also revealed in first-principles scalar relativistic calculations of the zone-center phonons for Pb(111) films.¹⁷ Both present results and those reported in Ref. 17 exhibit a clear oscillation with film thickness. The optical modes split off above the bulk-like phonon spectrum appear even at a film thickness of two layers²⁰ and are most probably present in the phonon spectrum of Pb(111) surface as well.^{18,35} This feature reflects a stiffening of the interlayer force constant

between the surface and subsurface layers of Pb(111) films due to a large contraction of the outermost interlayer spacing.^{17,18,35} The contribution of the optical modes to the e -ph spectral function $\alpha^2 F(\omega)$ is clearly seen in Fig. 4 (bottom) as a separate peak at high frequencies. However, these phonons do not contribute much (from 8% to 2% with increasing film thickness) to the strength of electron-phonon interaction due to the weighting of $\alpha^2 F(\omega)$ by $1/\omega$ in the definition of λ [see Eq. (1)].

The effect of spin-orbit coupling on the e -ph spectral function is shown in Fig. 4. Since the phonon spectrum of Pb(111) films softens, a sizable shift of the $F(\omega)$ and $\alpha^2 F(\omega)$ peak structures related to both transverse and longitudinal lattice vibrations to lower frequencies is observed. In addition, the weights of the spectral function peaks are significantly enhanced. Both processes promote an increase of $\lambda(E_F)$.

3. Estimates for T_c

Available experimental information relates to the superconducting transition temperature, T_c , in ultrathin Pb(111) films grown on a Si(111) substrate.^{1–5} Any experimental data on the mass enhancement parameter in supported lead films were not reported. Unfortunately, T_c cannot be reliably calculated. To get an accurate T_c value, we need to know two input parameters, $\alpha^2 F(\omega)$ and μ^* , an effective Coulomb repulsion. Our calculations provide the spectral functions but it is not at all clear which value of μ^* should be used. In bulk Pb,^{50,51} the effective Coulomb interaction parameter, μ^* , is assumed to be in the range of 0.1–0.12. The value of μ^* suitable for ultrathin lead films is unknown. Furthermore, it should depend on film thickness. In spite of these uncertainties we have estimated T_c in order to demonstrate the effect of spin-orbit interaction on this quantity.

In the two-dimensional limit the electronic screening would be evidently reduced compared to the bulk. But in the case of lead, a comparison of the three-dimensional Thomas-Fermi screening length and the interlayer spacing in lead films showed that even a one-layer free-standing Pb(111) film should exhibit three-dimensional screening.¹¹ So, we have used typical bulk values^{50,51} of μ^* and the same effective Coulomb interaction parameter for all film thicknesses considered. Since μ^* depends also on the value of some reference frequency ω_c , in the calculations we took always $\omega_c = 5$ meV, which is close to the logarithmic averaged phonon frequency.⁵²

We have calculated the critical temperature T_c by solving the linearized gap equation of the Eliashberg theory.^{46,53} The thickness dependent T_c s estimated both with and without spin-orbit coupling are shown in Fig. 5. The results obtained without relativistic corrections were already published.⁵ Under the effect of spin-orbit interaction, the critical temperature considerably rises so that it becomes near to the experimental bulk $T_c = 7.2$ K. The values are higher than T_c obtained from the measured gaps in Pb(111) films grown on a Si(111) substrate.^{1–5} It is obvious that for such small thicknesses the influence of a substrate should be very important^{13,54} that is not included in the calculations done for freestanding films. The calculated layer-dependent transition temperatures show quantum oscillations down to the thinnest film considered (four layers) without any suppression. However, starting from

FIG. 5. (Color online) Superconducting transition temperature as a function of film thickness. The full and open symbols correspond to the calculations with and without SOC, respectively. The data obtained both with $\mu^* = 0.1$ (squares) and $\mu^* = 0.11$ (circles) are presented. The experimental⁴⁶ bulk $T_c = 7.2$ K is shown by an arrow.

eight-layer films, the T_c estimated with SOC are found to be in the range of 6.3–7.3 K with increasing film thickness. The T_c even-odd oscillations correlate with the oscillations of two main factors that determine superconductivity transitions: the density of electronic states and the electron-phonon coupling at E_F . Thus the magnitude and the thickness dependence of the superconducting transition temperature are both strongly affected by the spin-orbit interaction. That makes it crucial for a proper quantitative description of both the electron-phonon coupling and the superconducting transition temperature in thin Pb(111) films to take into account the relativistic corrections.

III. SUMMARY

We have studied the effect of spin-orbit interaction on the electron-phonon coupling strength at the Fermi level of free-standing Pb(111) films using first-principles calculations in the density functional perturbation formalism. For thin films, the mass enhancement parameter exhibits an even-odd oscillatory behavior with the number of layers. It correlates with the variation of the density of states at E_F , and thus manifests a quantum size effect. The oscillations are largely reduced already for films thicker than eight layers.

We find that the mass enhancement parameter is strongly underestimated in scalar relativistic calculations regardless of the film thickness. Both a sizable SOC-induced softening of the film phonon spectra and the SOC-mediated increase in the electron-phonon coupling matrix elements account for a large enhancement of the electron-phonon coupling strength, while changes in the optimized geometry and the available phase space for scattering processes at E_F play only a minor role. The SOC-induced large modification of the mass enhancement parameter indicates that the spin-orbit interaction must be taken into account for a proper quantitative determination of the superconducting transition temperature in Pb(111) films.

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