First-principles calculation of the electron-phonon coupling in ultrathin Pb superconductors: Suppression of the transition temperature by surface phonons

Jesse Noffsinger and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720, USA
and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
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We present a first-principles calculation of the electron-phonon coupling for thin layered lead systems. Using our Wannier-Fourier approach we show that the superconductivity in these systems is accounted for by traditional isotropic Migdal-Eliasberg theory through phonon-induced electron pairing. It is found that the transition temperature of Pb is suppressed by the presence of surface phonons which have been stiffened by an increased electronic spring constant. Superconductivity persists in ultrathin layered Pb despite the suppression from a decreased electronic density of states and weakened coupling to surface phonons.

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The possible existence of true two-dimensional superconductivity has been the subject of study for many decades.[1–5] Recent measurements have brought renewed interest to this field, as superconductivity has been confirmed in thin-film samples of lead down to a single monolayer (ML).[6,7] In ultrathin Pb samples, the electronic wave functions are confined along the out-of-plane axis to a length scale of only a few nanometers. For Pb, which is free-electron-like in the bulk, significant modifications of the electronic states are expected to arise from quantum-size effects. In fact, many of these effects have been observed.[8–12]

Past experimental work has suggested that the superconducting state in Pb films should not persist once the film thickness drops below a few monolayers,[4] while the Mermin-Wagner theorem indicates that fluctuations should destroy a two-dimensional superconducting state at finite temperatures for any finite-ranged attractive interaction.[13] However, recent experiments demonstrating the presence of superconductivity in films of all thickness[6,7] are an exciting contradiction to previous suggestions. Since Pb is the prototypical strong-coupling electron-phonon superconductor with a myriad of wide-ranging studies in the literature, and now that it has been found to retain superconductivity in ultrathin films, it creates an ideal system for studying quasi-two-dimensional superconductivity.

In this work we report the results of first-principles calculations on the electron-phonon coupling in bulk Pb as well as in films of thickness 2–6 ML. Electronic and phonon densities of states (DOSs) are given along with the Eliashberg spectral functions. We find that electron-phonon effects account for the experimental observations, and we propose a simple model which can account for the general trend of the superconducting transition temperature dependence upon film thickness. This study also suggests extensions for future calculations.

Our first-principles calculations are based on pseudopotential density-functional theory within the local-density approximation[14,15] (LDA) for free-standing Pb films. Our calculations utilize a plane-wave basis[16] with a kinetic-energy cutoff of 80 Ry. This basis was employed in conjunction with a norm-conserving scalar-relativistic pseudopotential which included four valence electrons. A grid of $24\times24\times1$ electronic $\mathbf{k}$ vectors was used to describe the ground-state electronic structure. We constructed models of Pb films along the (111) direction to mimic experimental observations. The unit cell was chosen with a simple 1×1 reconstruction in each monolayer. The experimental lattice parameter of bulk fcc Pb is 4.95 Å, while the relaxed LDA lattice constant was found to be 4.87 Å; this slight underestimate is consistent with the expected tendency of LDA to overbind. The fcc in-plane bond length $a/\sqrt{2}$ was imposed by symmetry in the layered system to be 3.44 Å. The layer separation was relaxed, so that each atom was subject to a force of less than 0.01 eV/Å. The calculations have been performed within a supercell arrangement,[17] and the films have been separated by a vacuum layer of 15 Å which is sufficient to eliminate spurious interfilm interactions.

Lattice dynamics were determined using density-functional perturbation theory[18] and the electron-phonon coupling was calculated using a Wannier-Fourier interpolation method.[19–22] A Brillouin-zone mesh of $8\times8\times1$ electronic wave vectors was used to find maximally localized Wannier functions for each thin-film system. Four sp^3-like Wannier functions per Pb atom were used to describe accurately the electronic structure of each layered system. Phonons were calculated on a grid of $4\times4\times1$ wave vectors. The electron-phonon matrix elements $g^{mn}_{\mathbf{kq}\nu}$ were determined at each point on this coarse grid. From the method described in Ref. 21, the electronic eigenvalues, phonon eigenfrequencies, and electron-phonon matrix elements were determined on very fine-sampled Brillouin-zone grids consisting of 250 000 unique electronic wave vectors and 2000 phonon wave vectors.

The superconducting transition temperature (T_c) and the total electron-phonon coupling strength λ were determined through isotropic Migdal-Eliashberg theory.[23]

To begin we calculate the lattice dynamics, electron-phonon coupling strength λ, and Migdal-Eliashberg spectral function α^2F for bulk fcc Pb to verify the method with the calculated pseudopotential as well as to give a basis for comparison of thin-film calculations. The total electron-phonon coupling strength was found to be $\lambda=1.41$, where 10^6 electronic points and 5000 phonon wave vectors were used in the integration of Eq. (4.51) of Ref. 24. This value is consistent

TABLE I. Calculated LDA electronic densities of states at the Fermi level $N(E_F)$ and electron-phonon couplings λ, for layered Pb at different film thicknesses in this work. The Fermi level of the 3 ML film is at a peak in the DOS which tends to destabilize the free-standing film. Beyond this peak, the total DOS at the Fermi level per Pb atom does not vary largely in our calculation. Oscillations in $N(E_F)$ associated with quantum well states have been reported in studies which analyze much thicker films (Refs. 10 and 31). The total electron-phonon coupling of the films approaches the bulk value as the film thickness is increased.

Structure	DOS [states/ (eV spin Pb)]	DOS Fraction of bulk	λ
Bulk	0.482	1.00	1.41
2 ML	0.322	0.67	1.05
3 ML	0.707	1.47	
4 ML	0.467	0.97	
5 ML	0.447	0.93	1.37
6 ML	0.488	1.01	1.38

with many previously published results.[25–28] Using the modified McMillan equation [Eq. (1)], which is appropriate for strong-coupling superconductors,[29] and a Coulomb repulsion parameter of $\mu^*=0.14$, we find agreement between the measured and calculated superconducting transition temperatures at 7.2 K,

$$T_c = \frac{f_1 f_2 \omega_{\log}}{1.2} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right). \quad (1)$$

Table I displays the DOSs at the Fermi level for bulk and 2–6 ML films based on our density-functional theory calculations. We find that the Fermi level for the 3 ML film lies in a peak in the DOS, arising from a quantum well state. This results in an unstable structure under lattice perturbations, yielding many soft phonon modes which drive the free-standing 3 ML slab to a lower-energy state not described by the 1×1 reconstruction. We believe that this may contribute to the experimental difficulty in observing large islands of pristine 3 ML Pb.[6] Similarly, within our calculations, the 4 ML system is unstable to phonon eigenvectors which involve the asymmetric sliding of neighboring atomic sheets. It is worth noting that large pristine areas of 4 ML Pb were not found in the experiments of Ref. 6. Areas of 4 ML were, however, seen in close proximity to 5 ML islands. More recent work indicates that island size effects are of great importance to the superconducting properties of thin Pb films.[9,11,12,30] In the case of our calculations for 4 ML samples, it is possible that either a more complete treatment of bonding to the experimental substrate may stabilize the system or a method to take into account finite-sized films may yield physical results.

The LDA relaxed separation of each monolayer in the assorted films was analyzed. It was found, in agreement with prior studies,[32] that the surface bonds of each system were contracted along the direction normal to the film. Excess surface electrons, from broken bonds arising from the termination of the Pb(111) layers, are concentrated in the interstitial regions of the slab. Increased bonding from these electrons was found to be the cause of the contraction along the out-of-plane direction. This results in an increased spring constant η, which leads to a stiffening of surface phonon modes.

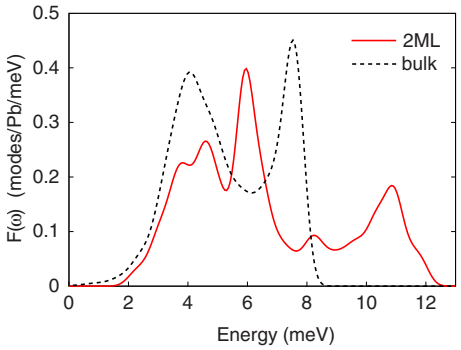

FIG. 1. (Color online) Phonon density of states for bulk Pb fcc (dashed line) and 2 ML Pb film (solid line). The transverse modes of the 2 ML film are split and the out-of-plane TA peak is stiffened by 2 meV. The highest frequency LA peak is stiffened by 3 meV in the 2 ML calculation as compared to the Pb-fcc data. For comparison, the curves are normalized such that $\int F(\omega)d\omega=3$.

The calculated phonon densities of states for bulk and 2 ML Pb are shown in Fig. 1. In the case of the 2 ML film, the degeneracy of the transverse modes has been lifted by the presence of the surface which results in two distinct transverse peaks. Of particular interest is the stiffening of the longitudinal phonon peak by about 40%, or ~3 meV. This stiffening is the result of a stronger Pb-Pb bond arising from the increased electron density in the surface bonds.

We have calculated the Eliashberg spectral function and total electron-phonon coupling for the stable free-standing Pb slabs of thicknesses 2, 5, and 6 ML. The spectral function in the 2 ML system as well as in the bulk is displayed in Fig. 2. The total electron-phonon coupling for each thickness is also given in Table I. By inspecting the spectral function, which gives a total $\lambda=1.05$ in the 2 ML system, we see a reduction in the superconducting transition temperature T_c

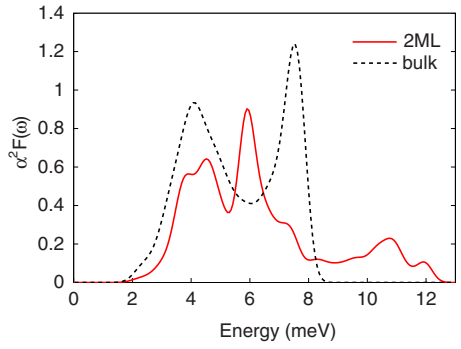

FIG. 2. (Color online) Eliashberg spectral function α^2F for bulk Pb fcc (dashed line) and 2 ML Pb film (solid line). Here, the total electron-phonon coupling $\lambda=2\int\alpha^2F(\omega)\omega^{-1}d\omega$ is decreased from the bulk value of 1.41 to the 2 ML calculated value of 1.05. As can be seen from the above comparison of the spectral functions, the lower coupling in the 2 ML system results from a depression of spectral weight which has also been shifted to higher frequencies.

arising from reduced coupling to the longitudinal frequency phonons. A comparison of the coupling function $\alpha^2(\omega) = \alpha^2 F(\omega)/F(\omega)$ shows a smaller relative coupling to the longitudinal phonons in the thin layered sample. The main conclusion which can be drawn from these data is that the surface phonon modes, which are at an increased frequency, contribute less to the total coupling than the corresponding bulk phonons modes.

We next propose a simple model to account for the observed superconducting transition temperatures over a wide range of Pb film thicknesses. As seen in Ref. 33, T_c is observed to follow a $1/d$ law, where d is the film thickness. In a bulk system, the layer separation is $a/\sqrt{3} \sim 2.86$ Å. If the system is taken to be composed of isolated regions of bulk superconductivity and surface superconductivity, we can assign a specific electron-phonon coupling to each region. As we have calculated a nearly pure surfacelike system with the free-standing 2 ML slab, we take the surface coupling strength $\lambda_{surf}=1.05$. The bulk coupling is then $\lambda_{bulk}=1.41$. In the experimental system, the measured Pb(111) films have been deposited on Si.[34] The effect of the substrate upon the electron-phonon coupling has not been examined in detail in this work; however, we can posit with some justification that the substrate-Pb coupling constant λ_{sub} is fixed for increasingly thick films. The total electron-phonon coupling strength as a function of film width $\lambda(d)$ can be approximated by

$$\lambda(d) = \frac{L}{d}\left[\left(\frac{d}{L} - 2\right)\lambda_{bulk} + \lambda_{surf} + \lambda_{sub}\right]. \quad (2)$$

Here, L is the layer thickness which in the bulk is 2.86 Å along the (111) direction. We fix λ_{sub} so that we obtain the recently measured T_c of the monolayer, 1.83 K,[7] assuming the monolayer electron-phonon coupling is the average of the surface coupling and the substrate coupling. We use Eq. (2) to calculate the electron-phonon coupling and Eq. (1) to estimate the superconducting transition temperature as a function of layer thickness. The resulting trend of T_c with film thickness agrees very well with the experimental data, as shown in Fig. 3. Although this model does not take into account many of the finer details of very thin metallic films, however, it does provide a straightforward interpretation of the gross experimental features.

The above arguments do not account for the details of quantum-size effects which arise from the confined electronic quantum well states. It may be possible, for example, through the stabilization of a film which produces a peak in the electronic DOS to overcome the apparent suppression of T_c by the surface phonons. If, for example, the 3 ML film could be structurally stabilized while retaining its increased electronic DOS, a scaling of $\lambda=1.6$ may be expected. This would lead to a superconducting transition temperature of ~10 K, which is well above the bulk value of 7.2 K. Further studies of the effects of the Pb-Si interface on the electron-phonon interaction is needed.[34] These studies may give us insight about the possible stability of films which exist near quantum well states and on how the complex interplay between surface physics, lattice dynamics, and quantum confinement affects superconductivity in these ultrathin systems.

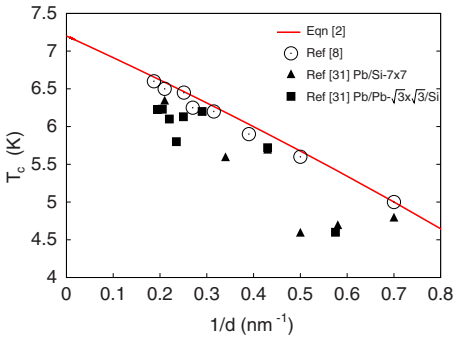

FIG. 3. (Color online) Superconducting transition temperature as a function of layer thickness for the experimental points of Refs. 8 and 33, and the theoretical model [Eq. (2)]. The transition temperature was calculated through the modified McMillan equation [Eq. (34) of Ref. 29]. Frequency moments have been fixed for differing λ's and the Coulomb repulsion parameter is taken to be $\mu^*=0.14$, to obtain the experimental bulk $T_c=7.2$ K.

In conclusion, we find that the observed superconductivity in thin-film samples of Pb is explained through the use of isotropic Migdal-Eliashberg theory. We find, in agreement with experiment, that the total electron-phonon coupling decreases with decreasing film thickness. The variance of the superconducting transition temperature with film thickness can be explained with a simple model relating the surface and bulk electron-phonon coupling. Additional studies which carefully examine the interaction of the metal-substrate interface could yield clues to routes of increased superconducting transition temperature in increasingly thin systems.

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