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Phase transitions in a mercury monolayer

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The physical properties of low-dimensional systems are sometimes vastly different from the properties of their bulk counterparts. Recently, Miedema and Dorleijn made the very interesting prediction, based on semiempirical theory, that there might exist a wide range of substrates on which a monolayer of Hg will be nonmetallic. In a fully *ab initio* study, we have calculated the total energy of free monolayers of Hg as a function of the lattice constant using local-density theory and the full-potential linearized augmented-plane-wave method. There are at least three different phases which are found to play an important role. Near the energy minimum, the variation of the total energy is small over a wide range of values of the lattice parameter, which includes regions of metallic and insulating behavior. Hence our results predict that the interaction with the substrate will determine whether a Hg monolayer is metallic or not.

I. INTRODUCTION

There exist large differences in the physical properties of one-, two-, and three-dimensional systems. A very important consequence of the difference in the dimensionality of condensed-matter systems is a change in the number of atoms which are in close contact with any given atom. Consequently, this change in the coordination number has a profound effect on the nature of the chemical bond between the atoms. For example, diamond with a coordination number of four has a covalent tetrahedral bonding while graphite is a layered π-bonded material. Another example is provided by samarium metal, where the atoms in the bulk are in the trivalent state, but the atoms at the surface are believed to be divalent.[1]

Since the type of chemical bond is related to the coordination number, the largest effects of differences in the dimensionality will be found in systems which have no clear preference for one type of bond or another. The metals in column II of the Periodic Table are in this category, because in the atomic state Be through Ra have completely filled *s* shells and Zn, Cd, and Hg have completely filled *s* and *d* shells. Therefore, there will be a "competition" betweeen a van der Waals modification and a metallic modification.[2] Recently, Miedema and Dorleijn[3] predicted on the basis of Miedema's semiempirical model that a van der Waals—type modification becomes more and more favorable when going to a smaller number of dimensions. The effect is most pronounced in mercury where a free monolayer is said to be predominantly nonmetallic.

Divalent metals are an exceptional case since in the atomic state they only have completely filled electronic levels. Therefore, semimetallic behavior occurs because in the solid the Fermi surface intersects the boundary of the first Brillouin zone. The energy of the *d* band in the group-II*B* transition metals is considerably below the Fermi energy; only in solid Hg is there a slight overlap between the *d* band and the valence band. The special character of the metallic bond in divalent metals has a number of interesting consequences: For example, a metal-nonmetal phase transition has been observed in liquid Hg at elevated temperatures and pressures.[4]

We can also describe the formation of the metallic bond in divalent metals in the following alternative way. Consider a number of divalent atoms which are well separated in space. By reducing the interatomic distance, the atomic levels will broaden into bands. The only way to gain energy is through a lowering of the average energy of the highest occupied band, which must be caused by the interaction of this band with the lowest unoccupied bands. This gives rise to van der Waals—type bonding. If the atoms are close enough, the valence *s* band will start to overlap with the unoccupied *p* band and the system will become a metal, which is the equilibrium (bulk) situation for all elements of columns II*A* and II*B* of the Periodic Table.

There are many physical properties which reflect the weaker nature of the metallic bond in the divalent metals. For example, the heat of vaporization and the dimer dissociation enthalpy of the divalent metals are much smaller than corresponding values for ordinary metals.[3] Miedema and Dorleijn have made an extensive analysis of these data and have made predictions for the cohesive energy of the van der Waals modification of the divalent metals for configurations of different dimensionalities.[3] Comparing these results with the data for the normal metallic configuration shows that the van der Waals modification becomes more and more favorable when the number of dimensions of the system is lowered. For Ca, Sr, and Ba a linear chain of atoms is definitely metallic and a dimer is a borderline case. However, a linear chain of Cd, Zn, or Hg atoms is predicted to be nonmetallic and in the case of Hg even a free monolayer is expected to be in the van der Waals modification.

Nowadays, systems with reduced dimensionality are experimentally accessible. One can prepare small particles by forcing a metal into cavities of a porous material. Also, one can simulate free monolayers by depositing a metal on a substrate of low surface energy. Therefore, Miedema and Dorleijn predict that "it is possible that there is a wide range of low surface energy substrates on which monolayers of Hg will be nonmetallic."[3]

In this paper, we present results of self-consistent *ab initio* all-electron band-structure calculations for free monolayers of mercury and use these results to discuss possible phase transitions in such a system. Section II discusses the theoretical and computational methods which we have employed. Section III contains our results for mercury monolayers in hexagonal- and square-lattice configurations using both the Hedin-Lundqvist and the Wigner approximation for the exchange and correlation potential. Finally, in Sec. IV we present a discussion of our results and draw conclusions regarding possible phase transitions.

II. METHODOLOGY

The calculation of the electronic part of the total energy of a solid requires the solution of a complicated many-body problem. However, using density-functional theory it is possible to prove the important theorem that the total energy is a functional of the one-particle density only.[5] As a consequence, one is able to replace the many-body problem by an equivalent single-particle problem.[6,7]

The resulting single-particle equations enable us to calculate the one-particle density of the interacting electrons. Since the effective potential which appears in these equations depends on the one-particle density we have to solve these equations in a self-consistent way. The total energy derived in this way represents the total energy of the interacting electrons. However, the energy eigenvalues are only zeroth-order approximations to excitation energies: only the Fermi energy has an exact meaning.[7] The error increases with the distance of the eigenvalue to the Fermi energy, the effect being largest in systems where the valence band contains *d* or especially *f* electrons.

Several standard methods to solve the single-particle equations exist. We use the full-potential linearized augmented-plane-wave (FLAPW) method[8,9] in which there are no shape approximations for the potential for the valence band. The core electrons are treated fully relativistically and here we retain only the spherical part of the potential, which is justified because of the small spatial extent of the wave functions. The valence electrons are treated semirelativistically, e.g., we neglect spin-orbit coupling.

We have performed self-consistent all-electron band-structure calculations for a free monolayer of Hg formed as either a hexagonal or a square lattice at several values of the lattice parameter. As approximations to the local exchange and correlation potential we have used both the formula of Hedin and Lundqvist[10] and the Wigner interpolation formula[11] for the correlation energy combined with the Gáspár-Kohn-Sham form for the exchange. The value of the muffin-tin radius ($R_{\mathrm{MT}}=2.5$ a.u.) was kept the same for all geometric configurations. As a result, the ratio of the volume of the interstitial region and the volume inside the muffin-tin spheres depends on the value of the lattice constant and hence we have to adjust the number of APW basis functions in each case in order to guarantee the same absolute accuracy in the convergence of the total energy. For this reason, we have used a large number of APW basis functions for a one atom per unit cell calculation, namely more than 150. The values of the energy parameters were chosen to be -0.8 Ry (near the center of the *d* band) in all cases; because of our large basis size the total energy is almost independent of this choice. For example, if we set the *s* and *p* parameters equal to the Fermi energy (~ -0.3 Ry) the total energy changes by less than 0.1 mRy. The logarithmic radial mesh for the integrations inside the muffin-tin spheres employs 381 points and a step size of 0.03; its use gives an error in the total energy of less than 1 mRy. However, this error is mainly due to the core electrons and will therefore be of a systematic nature, because the core-electron density hardly changes. We have estimated the error due to the changing valence density to be much less than 0.1 mRy. Since we are investigating a metal-nonmetal transition there are drastic changes which occur in the Fermi surface. Therefore, we have used 66 $\bar{k}$ points in the irreducible part of the Brillouin zone together with a triangular integration, resulting in an error in the total energy of less than 0.1 mRy.

III. RESULTS

Many-body quantities which are truly represented in density-functional theory are the single-particle density, the work function, and the total energy. We have calculated the total energy as a function of the atomic volume for two different lattice configurations and for two different local approximations of the exchange and correlation potential. In this case, the atomic volume is an area given by $S=a^2$ for the square lattice and $S=\frac{1}{2}a^2\sqrt{3}$ for the hexagonal lattice, a being the lattice parameter. The results are shown in Fig. 1. The relative error in the total energy is 0.1 mRy, while there is a systematic error of roughly 1 mRy. Of course the error due to the local-density approximation is much larger, e.g., the difference in total energy between the two local approximations which we have employed is 7 Ry. Figure 1 shows that both local approxi-

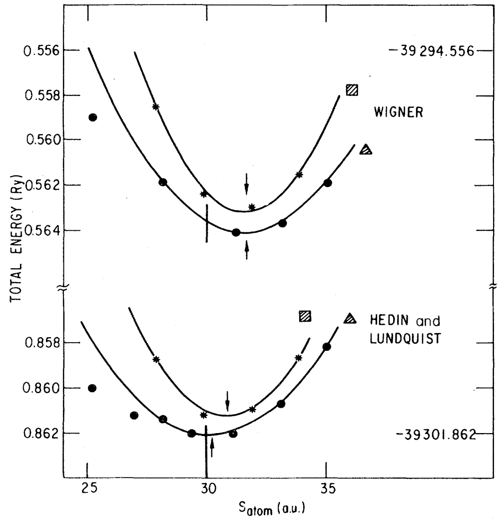

FIG. 1. Total energy of a free monolayer of Hg for a hexagonal (▲) and a square (▨) lattice as a function of the atomic volume. Upper part gives the results using the Wigner formula and lower part gives the Hedin-Lundqvist results. Vertical lines indicate the metal-nonmetal transition for the hexagonal lattice. Drawn lines are a parabolic fit to the points near the minima.

TABLE I. Fitted total energy as a function of the atomic volume: $E=\frac{1}{2}\alpha(S-S_0)^2+E_0$. All quantities are in atomic (rydberg) units.

	E_0	S_0	α
Hexagonal lattice			
Hedin-Lundqvist	$-39\,301.862\,15$	30.206	$0.343\,00\times10^{-3}$
Wigner	$-39\,294.564\,13$	31.584	$0.375\,18\times10^{-3}$
Square lattice			
Hedin-Lundqvist	$-39\,301.861\,34$	30.843	$0.588\,32\times10^{-3}$
Wigner	$-39\,294.563\,19$	31.614	$0.658\,44\times10^{-3}$

mations to the exchange and correlation potential qualitatively give the same results, the hexagonal lattice having the lowest energy and the energy differences being comparable. We have fitted the points near the energy minima to a parabola (see Table I). These fits do confirm the relative accuracy of 0.1 mRy in our calculations.

The charge density does not change very much near the minima in the total energy. There are 1.8 electrons per atom outside the muffin-tin spheres and these electrons are easily accomodated in the interstitial regions. At smaller values of the lattice constant the number of electrons inside the muffin-tin spheres increases and the *d* bands start to overlap. In the hexagonal lattice this is the case for values of the area occupied by one atom less than 27 a.u., where the interstitial charge suddenly starts to decrease. This effect is clearly seen in the total-energy curve. The calculated points are below the parabola because we gain energy due to the combined effect of the direct overlap of the *d* bands and the hybridization with the free-electron-like band.

The single-particle eigenvalues are almost independent of the choice of the approximation to the exchange and correlation potential. The *d* band is located 7—9 eV below the Fermi energy and is (3—2)-eV wide, depending on the value of the lattice constant (See Fig. 2). The bottom of the free-electron-like band is always hybridized with this *d* band, but the interaction becomes smaller with increasing values of the lattice parameter. For large values of the lattice constant the free-electron band is separated into an occupied *s* band and an empty *p*-like band.

The work function changes from 3.9 to 5.0 eV (see Fig. 3) as a function of the atomic volume. There is no difference between the values for the two types of exchange and correlation approximations. We see a clear nonanalytic behavior near the metal-nonmetal transition. At this point the density of states at the Fermi level changes very rapidly from 0—7 states/Ry atom (Fig. 4). In the square lattice the jump is smaller. This is a purely geometrical effect; the boundary of the first Brillouin zone in a hexagonal lattice resembles a sphere more closely than in a square lattice. Therefore, when the system becomes a semimetal the number of electron and hole pockets will be larger in the hexagonal phase, resulting in a larger value of the density of states at the Fermi level.

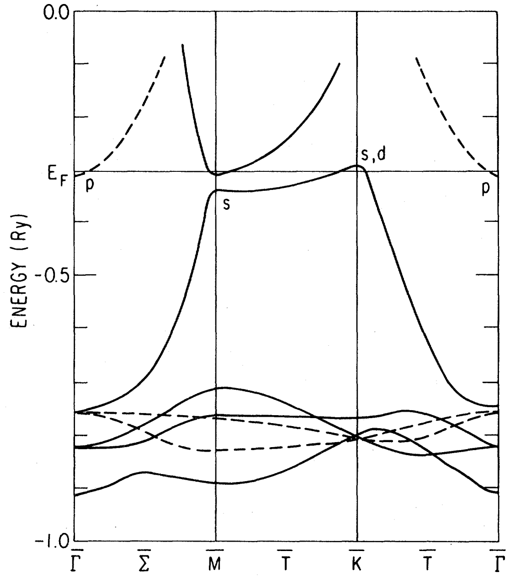

FIG. 2. Typical band structure for a free monolayer of mercury in the hexagonal phase. We have indicated the dominant orbital character of the wave functions near the Fermi level. *d* bands are 7 eV below the Fermi level and they are hybridized with the bottom of the *s* band.

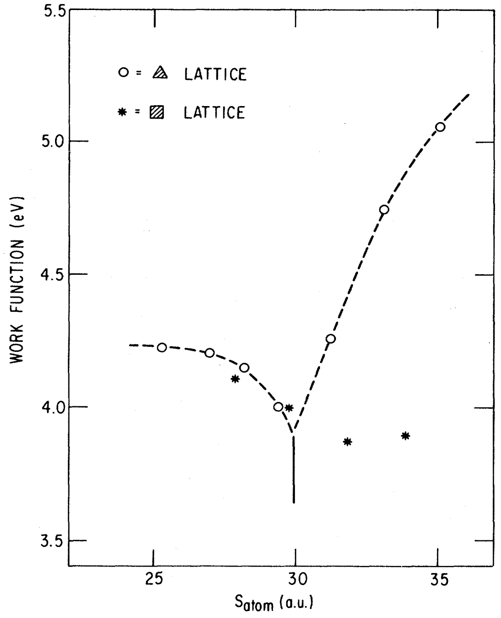

FIG. 3. Work function as a function of the atomic volume. Vertical line indicates the metal-nonmetal transition for the hexagonal lattice. Dashed line is added as a guide for the eye.

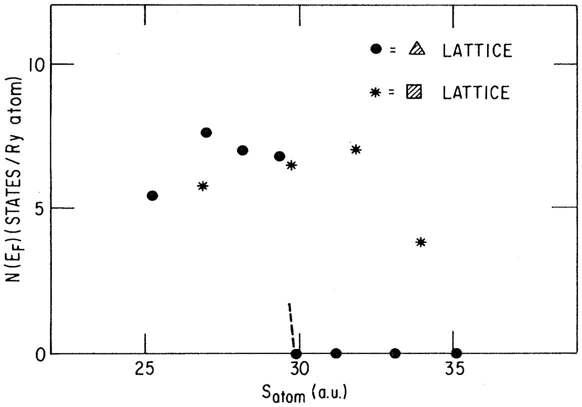

FIG. 4. Density of states as a function of the atomic volume. Position of the metal-nonmetal transition is very accurately estimated from the behavior of the bands near the Fermi level as a function of the lattice parameter.

IV. DISCUSSION

The total-energy curves in Fig. 1 show that the ground state of a free mercury monolayer is a hexagonal nonmetallic structure. However, in an experiment one can only simulate a free monolayer by depositing a monolayer on a substrate of low surface energy. Depending on the nature of the interactions between the substrate and the monolayer we will either find a square-lattice configuration, a metallic hexagonal configuration, or a nonmetallic hexagonal configuration. Since the difference in total energy between the square and the hexagonal lattice is less than 1 mRy (or 158 K) we predict that room-temperature measurements always will give a mixture of all phases. In order to detect the metal-nonmetal phase transition in the hexagonal structure, one either has to use different substrates (at low temperature) which fix the lattice constants at different values or one has to apply pressure.

If we consider the parabolic fits to the total energy as harmonic-oscillator potentials for the atomic nuclei, we can derive an estimate for the energy of the zero-point motion of the atoms. Using the values given in Table I we find this energy to be 0.7 mRy for the hexagonal lattice and 0.9 mRy for the square lattice. This indicates that experiments on quasifree monolayers of mercury might be hard to interpret and that we probably do need the substrate-adsorbate interaction to stabilize a particular phase.

There still remain two approximations which can influence our results. First, we have treated the valence electrons in a semirelativistic way, and second, we use the local-density approximation. The dominant effect of the first approximation is due to the incorrect treatment of the $p_{1/2}$ electrons, which now have zero density at the nucleus. In a bulk material like Pb this introduces errors in the energy levels on the order of 30 mRy.[12] Since in our case the metallic behavior is caused by the interaction between the 6s and the 6p electrons, the semirelativistic approximation will have its largest effects near the Fermi level.

The important p states in our calculations are the states near $\bar{\Gamma}$. When we reduce the value of the atomic area, these states are lowered in energy and they are responsible for the metallic behavior of the film. However, these p states have p_z symmetry, i.e., their charge distribution is perpendicular to the film. As a consequence, 90% of their density is outside of the muffin-tin sphere. Because the effect of the semirelativistic approximation is only important near the origin, this indicates that the error in the Hg monolayer is greatly reduced compared to the error we would have made in a bulk calculation. The important p states will only drop by a few mRy and hence the position of the metal-nonmetal phase transition is shifted to a value of the atomic volume which is increased by less than 1%. Nevertheless, in the Hedin-Lundqvist case this is sufficient to make the ground state metallic. The effect on the total energy is also expected to be small, which can already be deduced from Fig. 1 where the points in the metallic and nonmetallic regions are both on the same parabola and no discontinuity can be seen. On the other hand, the p_z character of these p states makes them very sensitive to the interaction with a substrate and this will be an important factor in determining the conductivity of an adsorbed Hg monolayer.

The second approximation we have used is the local-density approximation. Near a metal-to-nonmetal transition the cooperative behavior of the electrons changes dramatically and it is an open question how well this situation is described in the local-density approximation. The plot of the work function as a function of the atomic volume (Fig. 3) indicates that upon using the local-density approximation we find nonanalytic behavior at the point where the system changes from a semimetal to an insulator. Although the difference between the two local approximations we have used is only qualitative, we do not know how large the changes would be using nonlocal potentials or the exact exchange and correlation potential (which is, of course, only known after solving the complete many-body problem). This is another reason why we are interested in the results of experiments on adsorbed mercury monolayers, because these experiments would supply additional information concerning the quality of the local-density approximation in describing a metal-nonmetal transition.

In this paper we have studied the electronic properties of free monolayers of mercury. We have found that at least three different phases are important and that they are close in energy. Experiments of adsorbed mercury monolayers on suitably chosen substrates should reveal the existence of these phases. From a theoretical point of view the metal-nonmetal transition in the hexagonal phase is of special interest as a test case for local-density theory. Clearly experimental results are needed in order to compare with our theoretical predictions.

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[1] A. Rosengren and B. Johansson, Phys. Rev. B 26, 3068 (1982).

[2] N. F. Mott, Philos. Mag. 6, 287 (1961).

[3] A. R. Miedema and J. W. F. Dorleijn, Philos. Mag. B 43, 251 (1981).

[4] R. W. Schmutzler and F. Hensel, J. Non-Cryst. Solids 8, 718 (1972); V. El-Hanany and W. W. Warren, Phys. Rev. Lett. 34, 1276 (1975); U. Even and J. Jortner, Phys. Rev. Lett. 28, 31 (1972); F. Hensel, Ber. Bunsenges. Phys. Chem. 80, 786 (1976).

[5] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[6] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[7] See W. Kohn and P. Vashista, in Theory of the Inhomogeneous Electron Gas, edited by N. H. March and S. Lundqvist (unpublished).

[8] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B 24, 864 (1981).

[9] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B 26, 4571 (1982).

[10] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[11] See D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963), Eq. 3.58.

[12] A. H. MacDonald, W. E. Pickett, and D. D. Koelling, J. Phys. C 13, 2675 (1980).