PHYSICAL REVIEW B VOLUME 47, NUMBER 20 15 MAY 1993-II

Cu/Pd multilayers: An atomistic structural study

G. W. Fernando
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973
and Department of Physics, University of Connecticut, Storrs, Connecticut 06269

J. Mei*
Department of Physics, State University of New York at Stony Brook, Stony Brook, New York 11794

R. E. Watson, M. Weinert, and J. W. Davenport
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973
(Received 26 August 1992; revised manuscript received 28 January 1993)

The embedded-atom method (EAM) has been used to perform molecular-dynamics (MD) calculations of Cu/Pd multilayer films. In a recent publication, we presented our results on the elastic properties of these multilayers from our EAM-MD technique. In this paper we illustrate the simulation technique in detail. Comparisons are made with first-principles (local-density) calculations with respect to structural aspects of the multilayer. The local-density results follow trends similar to those seen in the EAM-MD approach. Various assumptions used in these calculations are critically examined.

I. INTRODUCTION

It is a well known fact that the recent advances in growth techniques have revolutionized the search for new materials. Although natural multilayers such as $MoSi_2$ do exist, artificially grown metallic and nonmetallic multilayers have begun playing increasingly important roles in condensed-matter and materials physics over the past decade. These can be regarded as a class of materials with properties that are not necessarily representative of the properties of their elemental components or of commonly ordered compounds involving these components. This paper is concerned with such a property, namely the possible anomalies of the elastic properties of metallic multilayer films.

This work was motivated by the controversial nature of the so-called "supermodulus effect," which is identified as anomalous enhancement of the elastic constants of a metal-metal multilayer film. These enhancements have been reported (see the first two references in Ref. 1) in many transition-metal multilayer systems such as Cu/Ni, Cu/Pd, Ag/Pd, and Au/Ni, as small (10–20 Å) repeat lengths (wavelengths) through bulge-test experiments. The orientation of these films seems to affect the enhancements, and with (111) stacking, there are reports of up to 300% increases in the biaxial modulus. Other classes of experiments to be discussed later have not been able to verify these enhancements.

The various theoretical attempts in trying to look for possible mechanisms for anomalous enhancements can be divided into two main categories. One has to do with singularities in the dielectric function, or Fermi surface-Brillouin-zone-type interactions introduced by the multilayering. The other is based on coherency strains. Coherency in the present case is defined as arrangements where atom sites in a given layer match with those of neighboring layers according to fcc (or any other appropriate) stacking. It refers to matchings of intraplanar ordering between neighboring planes, and not to any regular interplanar ordering. It is argued that the layers, in trying to remain coherent, are under some strain, and that these strains could give rise to anomalous behavior in the elastic constants. See the references listed in Ref. 1 for more details.

In the following sections we will describe our attempt to understand possible anomalies by carrying out a realistic molecular-dynamics simulation of a selected multilayer system and some related first-principles results. Dynamical calculations were performed in order to allow for various relaxations that these systems might want to undergo. We do indeed see some such relaxations, although we cannot possibly hope to cover all the various disordered situations (vacancies, dislocations, etc.) that might be relevant.

II. SYSTEM

The systems used in our molecular-dynamics (MD) calculations are Cu/Pd multilayer films with an equal number of layers of Cu and Pd atoms. Initially, each layer consists of 32 atoms which we define as the parallel base of our MD cell. By changing the number of layers, a series of MD runs have been carried out with the total number of atoms in the system ranging from 192 to 1024.

Both Cu and Pd are nonmagnetic metals having the fcc crystal structure under normal conditions. The multilayer system Cu/Pd has been the subject of an early bulge test, as well as more recent experiments. We have performed molecular-dynamics calculations on the superlattice Cu/Pd in an effort to study its elastic properties.[2] For computational simplicity, our simulations have been performed with films stacked in the (001) crystal direction. The structure of the films used in the MD calculations corresponds to n ordered layers of Cu atoms deposited on n ordered layers of Pd atoms, so as to resemble fcc stacking. Periodic boundary conditions are used both in the plane of the films and in the perpendicular direction. The wavelength corresponding to n was varied from about 1.5 to 5.7 nm, which covers the range of experimental measurements. For each value of n, we have calculated the biaxial modulus by applying external biaxial stresses in the plane of the film and monitoring the resulting in-plane strains.

The starting number of atoms in each layer (32 for most of the MD calculations) was the same for all the MD runs. We have also performed similar calculations, starting with 72 atoms per layer for several values of n in order to look for possible size effects. When compared with the case of 32 atoms per layer, we found that the biaxial modulus was insensitive to the size of the parallel base, at least in this test case.

III. INTERATOMIC POTENTIAL

The potentials we have used are derived from the embedded-atom method (EAM).[3] In this method, the total energy is given in terms of a short-ranged pair potential and an embedding function which is density dependent and contains many-body effects. We have used an analytical EAM model which has been successfully applied to calculate thermodynamic properties of Cu.[4] This model is similar to that of Johnson[5] but the interaction range goes beyond nearest neighbors. The experimental data of lattice parameters, elastic constants, cohesive energies, and vacancy-formation energies of the pure metals have been used to determine the model parameters. The shorted-ranged, pairwise interaction between Cu and Pd was constructed by taking an arithmetic average of those for Cu-Cu and Pd-Pd. To check the accuracy of this model, we have calculated the lattice parameter of the alloy Cu_3Pd and found agreement to better than 99% with experiment. Other tests include some comparisons of energetics with more-accurate first-principles heats of formation, showing that the energies obtained here are reasonable.

The short-ranged pairwise interaction in our EAM model has an attractive as well as a repulsive part [see Eq. (16) of Ref. 4]. This term, together with the many-body term, takes into account the effects of charge-density overlap between localized d orbitals. By fitting to the elastic properties and vacancy-formation energy, this pair interaction is expected to give reasonable binding between atoms in the pure metals. Taking an arithmetic average of the pair interactions of the pure metals to construct the pairwise term in the interface potentials is a common approximation. For Cu and Pd, which belong to neighboring columns of the Periodic Table (and hence have similar valence d-electron counts) and which form the same type of crystal structure, we expect the above arithmetic average to give an approximately correct description of the interface pairwise term. The s and the d orbitals of Cu and Pd are primarily responsible for interface bonding and this could mean that a simple arithmetic average is inadequate for the pairwise interaction term at the interface. We intend to examine this approximation in the future, especially since the interface seems to be playing a crucial role in determining the elastic properties of the multilayers.

IV. SIMULATION TECHNIQUE

We have used the variable cell MD scheme proposed by Parrinello and Rahman.[6] In this scheme, the Lagrangian function of a N-body system under an uniform external pressure p can be written as

$$L=\tfrac{1}{2}\sum_{i=1}^{N} m_i \mathbf{v}_i^2 - U(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) + \tfrac{1}{2}W\,\mathrm{Tr}\left[\frac{dh^t}{dt}\frac{dh}{dt}\right] - p\Omega\ , \tag{1}$$

where the first term is the total kinetic energy, U is the potential energy, and $\Omega=\det h$ is the volume of the system. The matrix $h=(\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3)$ defines the MD cell dimensions with $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ being the three cell vectors. The superscript T denotes the transpose of a matrix (or tensor). In this method, h becomes a dynamical variable and the Lagrangian function L has a term $\frac{1}{2}W\,\mathrm{Tr}[(dh^T/dt)(dh/dt)]$ which could be interpreted as the kinetic energy of an external piston. W is an adjustable parameter (piston mass) which has dimensions of mass. Andersen[7] has provided a physically attractive criterion for the choice of the piston mass. In our simulations, the value of W is adjusted to obtain a proper relaxation time of the MD cell and to make the instantaneous internal pressure of the system given by $\frac{1}{3}\mathrm{Tr}(\Pi)$ (the Virial theorem[8]) relax rapidly to the external (piston) pressure. Here Π is the pressure tensor with its elements given by

$$\Pi_{\alpha,\beta}=\frac{1}{\Omega}\left[\sum_{i=1}^{N} m_i v_{i\alpha} v_{i\beta} + \sum_{i<j} f_{ij} r_{ij} \hat{r}_{ij,\alpha} \hat{r}_{ij,\beta}\right]\ , \tag{2}$$

where r_{ij} is the distance between atoms i and j, $\hat{\mathbf{r}}_{ij}=(\hat{r}_{ij,1},\hat{r}_{ij,2},\hat{r}_{ij,3})$ is the unit vector of $(\mathbf{r}_i-\mathbf{r}_j)/r_{ij}$, and $\mathbf{f}_i=\sum_{j(\neq i)} f_{ij}\hat{\mathbf{r}}_{ij}$ is the total internal force acting on the ith atom with the expression of f_{ij} given by Eq. (19) of Ref. 4. With such a choice of W, the piston kinetic energy is found to be negligible compared to the various other terms in energy that appear in the Lagrangian, even for a system with $N=192$.

More generally, when an external stress (specified by a tensor $\mathbf{S}$) is loaded to the system, the Lagrangian function has the form

$$L_s=L-\tfrac{1}{2}\mathrm{Tr}(\Sigma G)\ , \tag{3}$$

where $G=h^T h$ and $\Sigma=h_0^{-1}(\mathbf{S}+p)(h_0^T)^{-1}\Omega_0$. h_0 is the MD cell matrix of a reference system and $\Omega_0=\det h_0$. We have chosen h_0 to be the time average of h at zero external stress in the following simulations.

Our MD time step Δt is 2.0362×10^{-15} sec. The Gear predictor-corrector algorithm[9] has been used for numerical integrations. For each simulation run the system is allowed to evolve for about 5000 time steps and averages are taken during the next 2000 time steps using standard techniques for low-temperature MD under zero stress. This should be viewed as a search for metastable phases. The biaxial modulus Y_B was then calculated by applying a biaxial stress in the plane of the film and evaluating the time average (over 2000 time steps) of the corresponding in-plane strain ϵ_B.

To illustrate a typical simulation, we plot the particle density, MD box dimensions, internal pressure, and internal energy as functions of time for a test run in Fig. 1. As shown in the figure, each simulation run consists of the three stages (indicated by 1, 2, and 3 in Fig. 1). The first stage is the zero-external-stress simulation at room temperature starting from a uniform fcc configuration with a tetragonal MD cell. The system relaxes by itself during this stage searching towards the energetically favorable state, as can be seen by looking at the oscillations of the particle density, three box dimensions (L_x, L_y, and L_z), and internal energy. The equilibration of L_z takes a longer time (compared with that of L_x and L_y) because of a drastic relaxation of the interplanar distances along this direction. After 4000 time steps, this state is cooled down to a low-temperature (30-K) and the corresponding strain is measured. The stress applied is constant and uniform in the plane spanned by x and y directions. The external stress produces an average strain (here a compressed strain) in the plane. The box length in the perpendicular direction L_z increases, indicating a positive Poisson effect. The difference in internal energy between the third and the second stages yields an estimate of the elastic deformation energy. A typical value for the standard deviation of the pressure σ_P is shown in Fig. 1. This value is about 0.006 GPa and should be compared with the magnitude of 100 GPa of the bulk modulus for Cu and Pd.

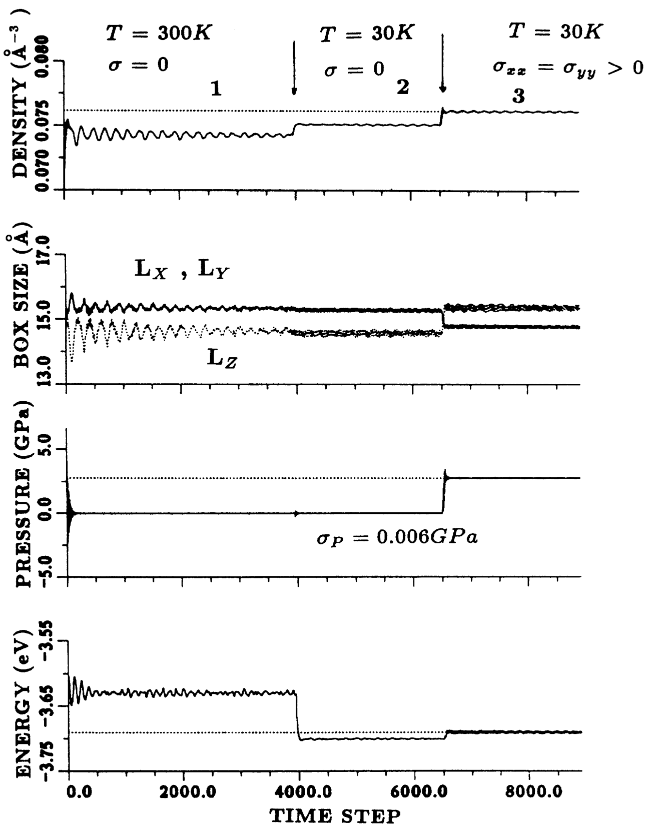

FIG. 1. Simulation results of a test run which shows internal energy, pressure, MD box dimensions, and particle density as functions of time steps for a system with four layers of Cu and four layers of Pd atoms stacked along (001). The simulation has three stages, which are shown by the numbers 1–3 in the figure. The values of temperature T and external stress σ are shown at the top of the figure for each stage. σ_P is a typical value of the standard deviation of the pressure of our simulations, and is very small in comparison with the magnitude of bulk modulus. L_x and L_y measure the MD box dimensions in the plane of (001) (along x and y directions) and L_z measures the dimension along the perpendicular (001) direction.

According to our experience, Y_B has a relatively large (statistical) uncertainty for small ϵ_B (under 1.0%). In order to obtain a reasonably accurate value, a number of different biaxial stresses were loaded and the (extrapolated) limiting value of Y_B as $\epsilon_B \to 0$ was identified as the biaxial modulus of the multilayer film corresponding to the given modulation wavelength. This procedure was repeated for multilayers of different modulation wavelengths. As another check, the biaxial moduli of the pure metals were also calculated with the same procedure and found to be in reasonable accord with experiment.

V. MOLECULAR-DYNAMICS RESULTS

The relaxed interplanar distances in the perpendicular direction of this system under zero stress, particularly for Cu, show large changes compared to bulk. Figure 2 shows these relaxed interplanar distances over a period of about 2000 time steps for a cell that is 28 layers thick (repeat length is about 5 nm). As indicated in the figure, the first 14 layers contain Cu atoms while the rest is Pd. The bulk interplanar distances of both Cu and Pd are shown by dotted lines. The inset in the figure shows the in-plane structure factor (averaged over 2000 time steps). The peak corresponds to a value of about $7.3a_0$ for the in-plane lattice constant (which is wavelength dependent). Both Cu and Pd planes give rise to an identical in-plane structure factor, indicating almost perfect coherency.

The large changes of the interplanar distances are both qualitatively and quantitatively reasonable. Let us define $a_{\parallel}(\Lambda)$ to be half of the in-plane lattice constant in the coherent planes for a given wavelength Λ. For the relaxations shown in Fig. 2, $a_{\parallel}=3.65a_0$ and the average interplanar distances for Cu and Pd are 3.0 and $3.73a_0$, respectively. A simple calculation of an average volume per atom for each species turns out to agree to better than 99.5% with the bulk metallic values, i.e., the equilibrium values are such that the metallic volume per atom is conserved for each species. This is in excellent agreement with the results of our first-principles calculations, in which the volumes are conserved to a similar degree. Note that the equilibrium value of $a_{\parallel}$, as indicated by the structure factor in Fig. 2, is not the average of the bulk Cu and Pd values, but is closer to that of Pd. Again, this result agrees with the first-principles calculations, where the $a_{\parallel}$ that corresponds to the minimum of the energies $E_{\mathrm{Cu}}+E_{\mathrm{Pd}}$ is seen to be off the mean value of the Cu and Pd metallic values by about 2.4%, closer to the Pd value.

Although the films remain coherent, the equilibrium structural parameters for the multilayers show significant changes from their initial values in our MD simulation. We also like to stress that coherency was only an initial condition, and during the simulation there were no explicit constraints forcing the films to be coherent. Even with initial conditions somewhat away from coherency, the films rapidly relax back to being coherent.

The in-plane coherency of the films makes a direct comparison between the first-principles calculations and the MD simulations reasonable. It should be noted again that the first-principles calculation performed here do not have the interface bonding effects, which, we believe, play an important role in the elastic behavior of thin, metallic multilayer films. The important point here is that the atomic volume conservation for the coherent Cu/Pd multilayer films obtained from the fully relaxed MD simulations is consistent with the local-density-approximation (LDA) first-principles total-energy calculations.

Although the interface bonding between Cu and Pd atoms seems to have no effect on the volume-conservation result, it does affect the equilibrium atomic configuration (such as the relative interplanar distances between the Cu and Pd layers and the absolute values of the in-plane lattice constant for a given repeat length) of the system under study and it is necessary for understanding the elastic anomalies that are described here.

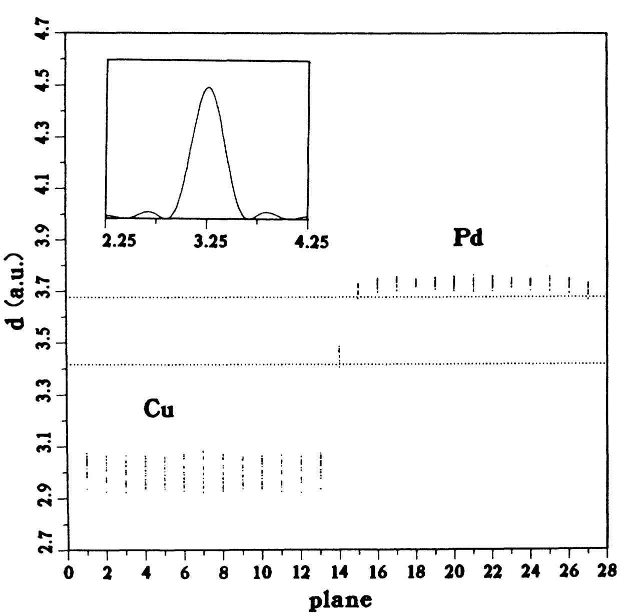

FIG. 2. Interplanar distances over a time period of 2000 time steps after equilibration under zero stress for 14 layers of fcc Cu on 14 layers of fcc Pd, stacked along (001). The horizontal dotted lines show the (observed) bulk interlayer spacings for Cu (at 3.42 a.u.) and Pd (3.68 a.u.), which were used to fit to the embedded-atom method. The modulation wavelength Λ is about 5 nm. The inset of the figure shows the in-plane one-dimensional (1D) structure factor for 14Cu/14Pd. The horizontal scale is in Å^{-1}. The peak corresponds to a value of 3.65 a.u. for $a_{\|}$. Note that $a_{\|}$ depends on Λ. Both Cu and Pd planes give rise to an identical curve after equilibration, indicating almost perfect coherence.

The behavior of the biaxial modulus as a function of modulation wavelength obtained from our MD calculations is shown in Fig. 3. The interesting result we see for coherent Cu/Pd multilayer films with (001) stacking is a decrease of the biaxial modulus by about 50% with increasing modulation length ranging from 1.5 to 4.5 nm. We also know that for large modulation lengths, the biaxial modulus should be around the average value of the ones corresponding to the pure metals, indicated by the arrow in the figure. The recovery back to bulk may be due to mechanisms such as vacancy formations and dislocations, which were not considered in our MD simulations. Our calculations do not show a supermodulus effect. However, the softening of the biaxial modulus reported in Ref. 2 suggests that elastic anomalies could exist for coherent multilayers, and this result has some experimental support in the form of longitudinal sound velocity and other improved measurements.[10] A very important conclusion of our study is that these resulting elastic anomalies cannot be explained by the continuum elastic theory alone because the interface bonding plays an important role. The total-energy change due to layering may be written as[11]

$$\Delta E = \Delta E_{\text{structural}} + \Delta E_{\text{bonding}} \ . \tag{4}$$

Continuum theories, to date, have no input with respect to the bonding energies at the interface. We believe that without addressing this issue, it is not possible to make realistic predictions about the elastic properties of these multilayers. The initial softening followed by an increase

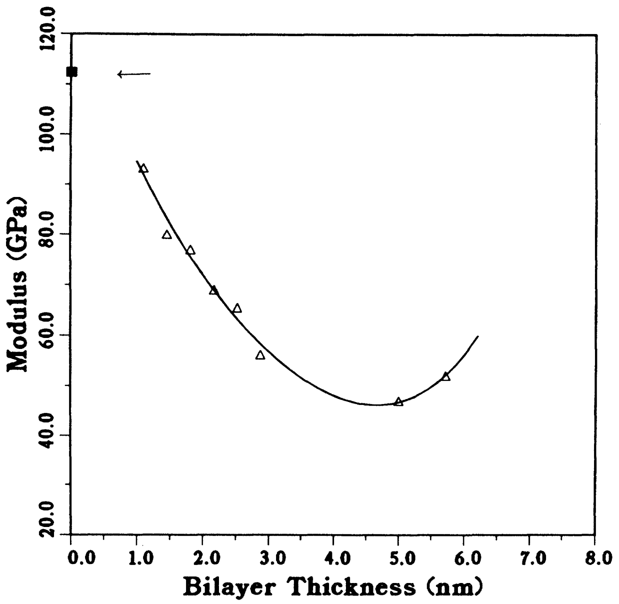

FIG. 3. Biaxial modulus for (fcc) Cu/Pd coherent multilayer stacked along the (001) direction vs the modulation wavelength (bilayer thickness) Λ. The arrow indicates the calculated average value of Cu and Pd biaxial moduli for the same stacking, which is about 113 GPa. The interface effects play a crucial role here.

of the biaxial modulus shown in Fig. 1 of Ref. 2 can be understood by considering the two competing effects in Eq. (4), elastic deformation energy (usually positive) and interface bonding energy (usually negative). These effects are also functions of the repeat length, and the sum of their curvatures will eventually determine the behavior of the biaxial modulus as a function of Λ, the repeat length.

VI. FIRST-PRINCIPLES CALCULATIONS

This section is concerned with providing some first-principles results as well as comparisons with our variable-cell molecular-dynamics simulations of Cu/Pd multilayer systems, described above. The first-principles work has been carried out separately for the elemental metals Cu and Pd allowing for distortions. These distortions are usually referred to as Bain distortions, and are applied in the (001) fcc planes. The perpendicular lattice constant (usually denoted by *c*) is determined through a variational minimization, for a given value of the parallel [to the (001) planes] lattice parameter (which is $2a_{\parallel}$ according to our notation). The interface effects present in a multilayer are not included in the first-principles calculation reported here, since these were done for separate, elemental metals. One purpose for carrying out such calculations is to understand the variations of volume per atom under the Bain distortions as well as the energetics associated with such distortions and their relevance to the multilayer system Cu/Pd. Of course, full multilayer calculations for varying repeat lengths would be able to look for any possible Brillouin-zone-induced singularities in the elastic constants, but these calculations will involve hundreds of atoms, and first-principles, full potential calculations have yet to reach this target for transition-metal systems.

The first-principles calculations were done using the local density approximation for the exchange and correlation effects, which yields an effective single-particle potential. The single-particle wave function is expanded employing a (linear-augmented) Slater-type-orbital (LASTO) basis. Interested readers are referred to Ref. 12 for details of this technique. Full-potential (i.e., potential with no shape approximations) as well as muffin-tin-potential calculations were done. It is important to note that this effective single-particle problem can be solved quite accurately without any other significant approximations using our full-potential LASTO method. This has been documented, for example, in Ref. 13 for the 5*d* transition metals.

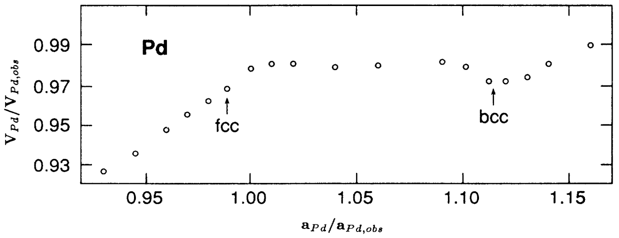

FIG. 4. The ratio of the (full potential) calculated volume to the observed volume of Pd following the Bain distortion. Note that v/v_{obs} varies linearly in the vicinity of the fcc structure but saturates, as it must, with increasing a/a_{obs}. The volumes display a local minimum near the bcc point.

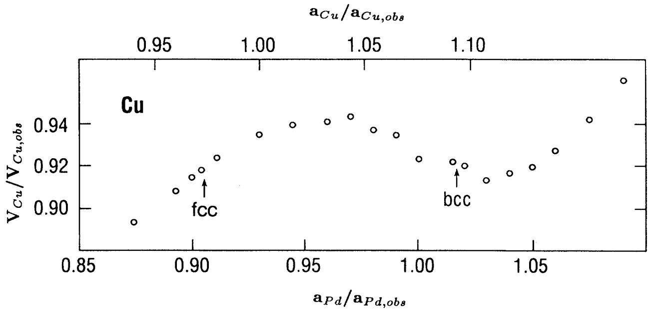

FIG. 5. The same for Cu as in Fig. 4, again showing the linear variation near the fcc point and a minimum near the bcc point.

Figures 4 thru 8 display the essential results from the first-principles calculations. The calculated volumes per atom for Cu and Pd show similar behavior along the Bain distortion. Near the fcc point, the variation in volume is approximately linear, indicating a degree of insensitivity of the perpendicular lattice parameter *c* to the variations of the parallel lattice parameter $a_{\parallel}$. Note that the volume per atom *V* is given by

$$V(a_{\parallel})=c(a_{\parallel})a_{\parallel}^{2} \ . \tag{5}$$

A saturation effect in volume follows the linear regime, as expected. In the vicinity of the bcc point, the changes in volume are more significant (nonlinear), showing clear signs of more sensitivity of *c* with respect to changes in

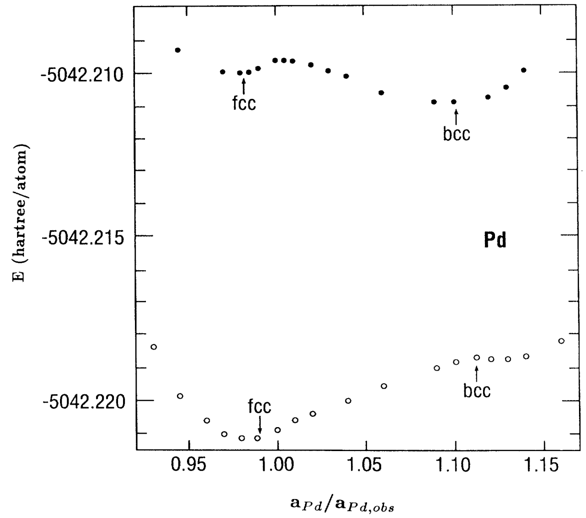

FIG. 6. The total energy per atom in hartree along the Bain distortion for Pd. The open circles denote the full potential results while the closed circles denote the muffin-tin values. There is a clear local minimum around the fcc point, which is below the bcc point by about 2 mH per atom, in the full potential curve.

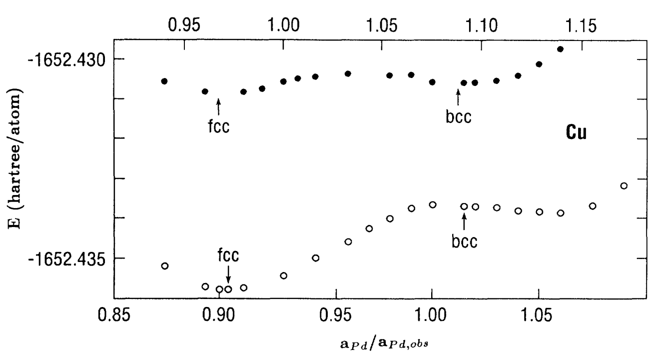

FIG. 7. The same for Cu as in Fig. 5, with qualitatively similar features.

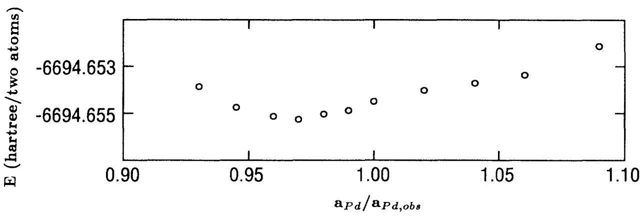

FIG. 8. The sum of the total energies of Cu and Pd as a function of the scaled parallel lattice constant. Note that there is a minimum in this total-energy sum and it occurs at a parallel lattice parameter which is closer to bulk fcc Pd than to bulk fcc Cu. Hence, the distortion energies alone show a preference towards Pd (parallel lattice parameter) in a possible Cu/Pd coherent arrangement.

$a_{\parallel}$. In spite of all the variations present in the volumes per atom, we note that the changes in volume are only of the order of a few percent throughout the Bain distortion region examined here.

The elemental metallic total energies calculated within the LDA for both Cu and Pd show their expected minima near the fcc point, which is reassuring. The differences in energy between the bcc and fcc structures are of the order of a tenth of an eV. The sum of these two total energies points to an important effect. As seen in Fig. 8, this sum shows a minimum in energy for $a_{\parallel}$ closer to bulk Pd than to that of bulk Cu. This result indicates that the distortion energies alone show a preference towards the bulk Pd lattice parameter in a possible coherent arrangement of Cu and Pd layers. This shows that one should be careful in using average values for these lattice parameters when attempting to obtain accurate estimates of elastic anomalies. As previously discussed, our molecular-dynamics simulations with embedded-atom potentials also showed this effect.

VII. DISCUSSION

We have presented details with regard to MD simulations and first-principles calculations on the multilayer system Cu/Pd. These calculations do not show a supermodulus effect, but point to anomalies in the elastic properties which are about an order of magnitude smaller than the changes labeled supermodulus effect, and opposite in sign. The first-principles calculations support the results obtained from MD simulations. We have seen that significant distortions away from the bulk values are possible in the multilayer films and these should be taken into account in any realistic treatment. The interfaces do play an important role in determining physical properties, and as an example, we have seen the parallel lattice parameter of coherent Cu/Pd multilayers deviating from the average value of the Cu and Pd lattice constants.

However, there are several inadequacies in the present set of calculations. The embedded-atom potentials are short-ranged potentials, although they do go beyond nearest neighbors. Any singularities introduced due to Brillouin-zone–Fermi-level interactions arising from multilayering will not be included in the energetics of the MD simulations based on our embedded-atom potentials. As mentioned previously, the arithmetic averaging done when constructing the pairwise term in the interface potentials may be inadequate due to the nature of the bonding orbitals. There is also the possibility of disorder-induced anomalies in these elastic constants. Our simulations, which conserve the particle number, were able to search only for lattice distortions, away from the standard, fcc structures, and obviously there were no vacancies, etc. However, we believe that this present study provides a useful, dynamical, microscopic picture of a possible scenario with regard to transition-metal multilayer systems.

ACKNOWLEDGMENTS

We wish to thank Bernard R. Cooper for helpful discussions. This work carried out at Brookhaven National Laboratory and has been supported by the Division of Materials Sciences, Office of the Basic Energy Sciences of the U.S. Department of Energy, under Contract No. DE-AC02-76CH00016.

---

*Present address: Department of Physics, West Virgina University, Morgantown, WV 26506.

[1] W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977); T. Tsakalakas and J. E. Hilliard, *ibid.* **54**, 734 (1983); see also R. W. Cahn, Nature **324**, 108 (1986); B. W. Dodson, Phys. Rev. B **37**, 727 (1988); M. L. Huberman and M. Grimsditch, Phys. Rev. Lett. **62**, 1403 (1989); A. Banerjea and J. R. Smith, Phys. Rev. B **35**, 5413 (1987); W. E. Pickett, J. Phys. F **12**, 2195 (1982); R. C. Cammarata, Scr. Metall. **20**, 479 (1986); A. F. Jankowski and T. Tsakalakos, J. Phys. F **15**, 1279 (1985); R. C. Cammarata and K. Sieradzki, Phys. Rev. Lett. **62**, 2005 (1989).

[2] J. Mei and G. W. Fernando, Phys. Rev. Lett. **66**, 1882 (1991).

[3] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).

[4] J. Mei, J. W. Davenport, and G. W. Fernando, Phys. Rev. B **43**, 4653 (1991).

[5] R. A. Johnson, Phys. Rev. B **37**, 3924 (1988); **39**, 12 554 (1989).

[6] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980); J. Appl. Phys. **52**, 7182 (1981).

[7] H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).

[8] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980).

[9] C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations* (Prentice-Hall, Englewood Cliffs, NJ, 1971).

[10] B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1988); B. M. Davis, D. N. Seidman, A. Moreau, J. B. Ketterson, J. Mattson, and M. Grimsditch, Phys. Rev. B **43**, 9304 (1991).

[11] M. Weinert, R. E. Watson, J. W. Davenport, and G. W. Fernando, Phys. Rev. B **39**, 12 585 (1989).

[12] G. W. Fernando, J. W. Davenport, R. E. Watson, and M. Weinert, Phys. Rev. B **40**, 2757 (1989); J. W. Davenport, *ibid.* **29**, 2896 (1984).

[13] G. W. Fernando, R. E. Watson, M. Weinert, J. W. Davenport, and J. Wang Phys. Rev. B **41**, 11 813 (1990).