PHYSICAL REVIEW B **68**, 045413 (2003)

Vibrational properties of Cu(100)-$c(2\times2)$-Pd surface and subsurface alloys

I. Yu. Sklyadneva
Institute of Strength Physics and Materials Science, Russian Academy of Sciences, 634021, Tomsk, Russia
and Donostia International Physics Center (DIPC), 20018 Donostia/San Sebastián, Basque Country, Spain

G. G. Rusina
Institute of Strength Physics and Materials Science, Russian Academy of Sciences, 634021, Tomsk, Russia

E. V. Chulkov
Departado de Física de Materiales and Centro Mixto CSIC-UPV/EHU, Facultad de Química, UPV/ EHU, Apardado 1072,
20018 Donostia/San Sebastián, Basque Country, Spain
and Donostia International Physics Center (DIPC), 20018 Donostia/San Sebastián, Basque Country, Spain

(Received 27 January 2003; published 15 July 2003)

Using interaction potentials from the embedded-atom method we investigated the structural and vibrational properties of a Cu(100)-$c(2\times2)$-Pd surface alloy and an underlayer $c(2\times2)$ alloy with a mixed CuPd second layer. The calculated surface phonon frequencies are in agreement with the experimental values obtained by electron energy-loss spectroscopy. From the calculated local phonon densities of states we find that surface effects are most pronounced in the first two layers for both systems studied. The results also indicate a very strong Pd-Cu bonding accompanied by a weaker bonding of the Cu surface atoms to their nearest neighbors. This has considerable influence on the surface phonon frequencies.

DOI: 10.1103/PhysRevB.68.045413 PACS number(s): 68.35.Ja, 68.35.Md, 68.47.De, 81.05.Bx

I. INTRODUCTION

Thin alloy films at surfaces are of great interest from both fundamental and technological points of view due to the effect of alloying on the surface electronic structure, magnetic properties, and catalytic activity which can be quite different from those of the corresponding bulk materials. For Cu(100), a number of metal adsorbates such as Au, Ag, Mg, and Pd at a coverage of $\sim$0.5 ML form surface alloys with a $c(2\times2)$ structure.[1–10] One of the most extensively studied metal-on-metal system is Pd/Cu(100).[1–7,10–14] Earlier low-energy electron diffraction (LEED) measurements[2,4] showed that at room temperature the deposited Pd atoms intermixed with the top substrate layer and at a coverage of $\sim$0.5 ML a Cu(100)-$c(2\times2)$-Pd surface alloy was formed rather than an ordered $c(2\times2)$ overlayer. The structure of the mixed CuPd surface layer was found to be almost planar with Pd atoms slightly rippled outwards.[2] Experimental confirmation of a surface alloy model was also obtained by photoemission experiments,[2] a LEED study,[5] and Rutherford-backscattering spectrometry.[3] The alloying of Pd with the top layer of the Cu(100) substrate was also supported theoretically via first-principles[6] and semiempirical[5,7] calculations. However, medium-energy ion scattering (MEIS) data[5] suggest in qualitative agreement with low-energy ion scattering measurements[12,14] that the surface structure is quite complicated with some fraction of the deposited Pd atoms located at the subsurface. This conclusion is supported by both thermal-desorption experiments[5,11] and scanning tunneling microscopy investigations[13] which indicate that appreciable amounts of pure Cu are present at the surface together with domains of a $c(2\times2)$-CuPd surface alloy. From a thermodynamical point of view a Cu-rich surface would be energetically favorable due to the positive surface energy difference between Pd ($2.05\ \mathrm{J\,m^{-2}}$) and Cu ($1.85\ \mathrm{J\,m^{-2}}$).[15] In addition, the exothermic Pd-Cu interaction suggests that the energy of such a system can also be lowered by increasing the number of Pd-Cu bonds. To investigate the stability of the Cu(100)-$c(2\times2)$-Pd surface Hannon *et al.*[16] measured the dispersion of vibrational modes at the surface along the $\overline{\Gamma X}$ direction using electron energy-loss spectroscopy (EELS). It was found that the room-temperature spectrum exhibited only one surface mode at the $\overline{X}$ point. However, upon annealing of the surface another high-frequency peak appears and then dominates the spectrum. The evolution of the vibrational spectrum upon annealing shows that the changes occur even at very low temperatures that are far below 423 K at which Pd diffuses into the bulk.[4] The measured mode frequencies were compared to the values from slab calculations performed along the $\overline{\Gamma X}$ direction with parameters taken from effective-medium theory (EMT). The evaluations were carried out for a slab of seven layers with the last three layers fixed at the bulk positions. Analysis of the EMT-derived force constants indicated the strong bonding of the Pd atoms to both in-plane and second-layer Cu neighbors which gave rise to nearly degenerate (the energy difference is $\sim$0.83 meV) Pd and Cu vibrations at the $\overline{X}$ point despite the large mass difference. In the experiment these modes were not individually resolved and the measured peak at 11.79 meV was attributed to the superposition of the Cu and Pd modes. To identify the peak at 15.88 meV appearing upon annealing of the surface the authors calculated the vibrational spectrum for Cu overlayer islands on top of the surface alloy. The evaluated energy of Cu vibrations normal to the surface was found to be significantly higher than that of the surface alloy and lower ($\sim$14.06 meV) than that for the underlayer alloy at the $\overline{X}$ point. Using this result the high-frequency peak was attributed to vertical vibrations of Cu in the Cu overlayer islands which are small at room temperature, but increase rapidly in size as the temperature grows. On the other hand, a study of the thermal stability of the Pd/Cu(100) surface[17] indicated the possibility of a temperature-induced transition at 353 K from a Cu(100)-$c(2\times2)$-Pd surface alloy to a $c(2\times2)$ underlayer structure consisting of a CuPd mixed second layer capped by a Cu monolayer. Later the kinetics and mechanism of the transition as well as the structure of the underlayer alloy were examined by LEED.[18]

In this paper we present a full comparative study of the vibrational properties for the Cu(100) surface with one-layer surface and subsurface CuPd alloys along all symmetry lines by using a thick-film model. We first examine the structural characteristics and then extend our study to the vibrations to gain information on metal-metal bonding in the alloy films and to compare the calculated phonon spectra, local densities of states, and force constants of a Cu(100)-Pd surface and underlayer $c(2\times2)$ alloys.

II. CALCULATION METHOD

For calculations of the structural and dynamical properties we use two-dimensional periodic slabs with surfaces perpendicular to the [100] direction. The slab thickness of 30 layers is found to be sufficient to effectively decouple the two opposite slab surfaces. Increasing the number of layers does not change substantially the results of the calculations. We also assume that the top layer of a Cu(100)-$c(2\times2)$-Pd surface alloy and the second layer of an underlayer $c(2\times2)$ alloy have a mixed composition of 50% Cu and 50% Pd. A side view of these two surface structures is shown in Fig. 1.

The calculations are performed using the embedded-atom method (EAM).[19,20] We employ the version of Foiles *et al.*[20] to construct embedding functions and pair interaction potentials for Pd and Cu. The parameters of the model are determined empirically by fitting to the experimental data such as sublimation energy, the equilibrium lattice constant, elastic constants, vacancy-formation energy of the pure metals, and the heat of solution of a Cu-Pd alloy. The electron density is approximated by the superposition of atomic electron densities computed in this work within the local-density approximation.[21,22] This method which provides many-body interaction potentials has been successfully applied to a variety of bulk, surface, and interface problems of pure metals and alloys.[20,23–30]

III. CALCULATION RESULTS AND DISCUSSION

A. Cu(100)-$c(2\times2)$-Pd surface alloy

To obtain the equilibrium structure we relaxed the surface alloy using a molecular-dynamics method. The Cu and Pd atoms were initially arranged above the fourfold sites of the relaxed Cu(100) substrate in a $c(2\times2)$ structure. Then the atoms were allowed to move according to the calculated forces until the equilibrium positions were achieved. Since the pure metals have substantially different lattice constants [$a(\mathrm{Cu})=3.615$ Å and $a(\mathrm{Pd})=3.89$ Å] the system has a rather large lattice mismatch of 7.8%. The results show that the effect of Pd on the outermost interlayer spacings of the Cu(100) substrate is small. The Cu-Cu interlayer distance was found to be close to the bulk one. It is only slightly contracted ($d_{12}=1.1\%$, in percentage of the bulk interlayer spacing) as in the case of the clean Cu(100) surface.[31] While the Cu surface atoms exhibit a small inward relaxation the Pd atoms (filled circles, Fig. 1) relax outward. This leads to a small rippling of 0.025 Å (δ_1) within the outermost mixed CuPd layer. This effect has to be attributed mainly to the size difference between Cu and Pd because the semiempirical method used in this work does not account for changes in the electronic band structure upon Pd alloying. These results are in close agreement with the LEED intensity analysis[2,5] which showed that the structure of the Cu(100)-$c(2\times2)$-Pd surface was almost planar with the Pd atoms relaxed by 0.02–0.03 Å outward from the Cu sublattice. The first Cu-Cu interlayer distance (d_{12}) was found to be nearly the same as

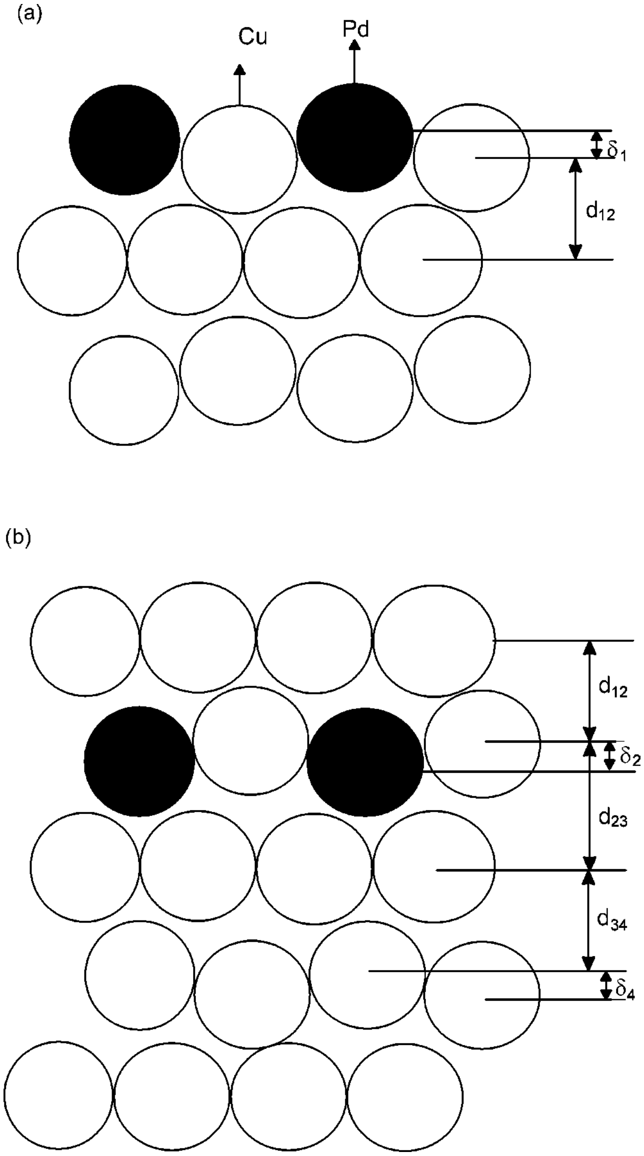

FIG. 1. Side view of the Cu(100)-$c(2\times2)$-Pd (a) surface and (b) underlayer alloys. Also shown are the structural parameters.

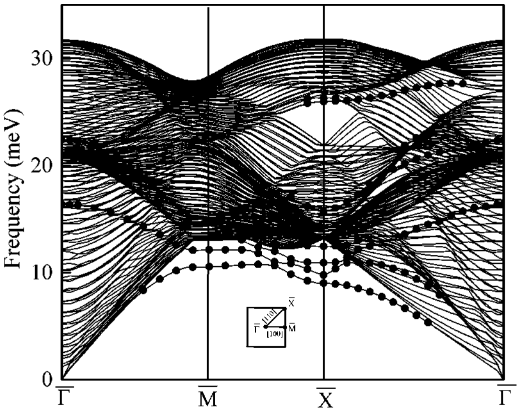

FIG. 2. Calculated phonon dispersion curves for the Cu(100)-$c(2\times 2)$-Pd surface alloy. Surface states are indicated by filled circles.

the bulk value.[2] The MEIS data[5] give slightly larger rippling ($\delta_1 = 0.04$–0.08 Å) than that obtained from LEED measurements assuming that the substrate does not relax. The values of rippling calculated using the EMT (Ref. 16) and EAM simulations[5] are much larger in magnitude (0.11 Å and 0.12 Å). But the calculations were performed for a seven- and nine-layer slabs, respectively.

We have calculated the phonon spectrum along the high-symmetry directions of the $c(2\times 2)$ cell (Fig. 2) for a relaxed 30-layer Cu(100) slab with the mixed top layer of alternately arranged Pd and Cu atoms. Surface states are denoted by filled circles. The calculated surface mode frequencies at the symmetry points are summarized in Table I. We found four surface phonons outside the bulk. The two lowest modes at $\overline{X}$ are characterized by shear horizontal displacements of both Cu and Pd in the top mixed layer. The next two states at $\overline{X}$ (labeled as the Cu and Pd modes in Table I) and both modes below the bulk continuum at $\overline{M}$ correspond to separate motions of the Pd or Cu atoms along the surface normal. Note that these shear vertical surface states are the only modes completely localized on Pd(Cu) atoms in the top layer. The dispersion of these phonons shows substantial flattening near the zone boundary, so one can suggest that surface stress exists within the mixed layer, similar to the case reported for Fe films on the Cu(100) surface.[32] For small wave vectors these Cu modes do not exist while the motion of the Pd atoms couples to the vertical vibrations of the Cu sublattice. Another surface state with in-plane polarization is mainly localized in the second Cu layer and has a frequency of 15.72 meV at $\overline{X}$. Besides these modes there are high-energy gap modes, which are mostly longitudinal and have a substantial weight in the top layer. Our results are comparable to those obtained by EMT calculations for a seven-layer slab[16] which gave 11.87 meV and 12.7 meV for the Pd and Cu modes at $\overline{X}$, respectively. In the EELS experiment,[16] focused on the $\overline{\Gamma X}$ ([110]) direction which is not folded back by the $c(2\times 2)$ cell of the surface alloy, the room-temperature spectrum exhibits only one surface mode at $\overline{X}$ (11.79 meV) which is lower in energy than the experimental Rayleigh mode frequency for a clean Cu(100) surface [13.4 meV (Refs. 33 and 34)] and is slightly higher than the corresponding value for the Pd(100) surface [11.17 meV (Ref. 35)]. In Ref. 16 the measured peak was related to the superposition of the Cu and Pd modes which cannot be resolved experimentally due to the small energy difference between them.

TABLE I. Surface phonon frequencies (meV) at the symmetry points. Atomic displacements are shown in brackets (Z—normal to the surface; XY—within the surface plane). The subscripts (1,2) denote the layer numbers with maximum vibrational amplitude.

	Surface alloy	Underlayer alloy
$\overline{\Gamma}$	$16.38[Z_1]$	$17.58[Z_1]$
	$22.38[Z_2]$	$19.98[Z_2]$
		$22.33[(XY)_1]$
$\overline{M}$	$10.51[\mathrm{Pd},Z_1]$	$11.25[\mathrm{Cu}(Z_1),\mathrm{Pd}(Z_2)]$
	$12.08[\mathrm{Cu},Z_1]$	$12.37[\mathrm{Cu}(Z_1,Z_2)]$
$\overline{X}$	$9.02[(XY)_1]$	$7.78[(XY)_1]$
	$9.76[(XY)_1]$	$11.08[(XY)_1]$
	$11.17[\mathrm{Pd},Z_1]$	$11.62[\mathrm{Pd},(XY)_2]$
	$12.45[\mathrm{Cu},Z_1]$	$12.49[\mathrm{Pd},(XY)_2]$
	$15.72[(XY)_2]$	$15.51[\mathrm{Cu},Z_1]$
		$15.80[\mathrm{Cu},Z_1]$
	$25.97[(XY)_1]$	$23.95[(XY)_1]$
	$26.30[(XY)_1]$	$24.98[(XY)_1]$

Of considerable interest is the degree to which the force constants at the clean Cu(100) surface change upon formation of the alloy. Analysis of the interatomic interactions shows that the force constant between the Cu and Pd atoms in the top layer (the nearest-neighbor surface atoms are Cu and Pd in this case) as well as the force constant for the interaction Pd_1-Cu_2 (the numbers indicate atomic layers) along the surface normal are 60% and 40% larger in magnitude, respectively, than the nearest-neighbor intralayer and interlayer force constants for the clean Cu(100) surface. On the other hand, the force constant representing the interaction Cu_1-Cu_2 is softened by 6% compared to the clean surface value. Thus, we find a very strong Pd-Cu bonding accompanied by weaker bonding of the Cu surface atoms to their nearest neighbors in the layer below. In addition, the interaction between the Pd atoms in the top layer is found to be ~25% smaller than that at the Pd(100) surface. These changes in the force constants upon Pd alloying together with the mass difference between Cu and Pd atoms determine the shifts of surface mode frequencies in the phonon spectrum and the energy separation between the modes. While the larger atomic mass of Pd tends to soften the surface phonons except for the Cu shear vertical mode the bonding at the surface tends to push them to higher energies. For the Cu and Pd modes the energy difference is decreased from 2.48 meV (the effect of the difference in mass) to 1.24 meV. The longitudinal gap modes shifted to higher energies are located at the upper edge of the energy gap and as a

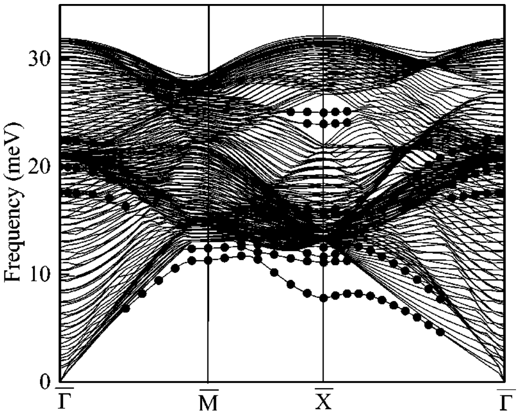

FIG. 3. Calculated phonon-dispersion curves for the Cu(100)-$c(2\times2)$-Pd underlayer alloy. Surface states are shown by filled circles.

result acquire a typical resonant character. This may be the reason why these modes were not measured by EELS.[16] It should be noted that any of the calculated surface modes does not correspond to the measured high-energy peak at 15.88 meV which occurs as the Cu(100)-$c(2\times2)$-Pd surface is annealed.[16]

B. Cu(100)-$c(2\times2)$-Pd underlayer alloy

Before calculating the phonon spectrum the atomic coordinates of the layers were relaxed to the equilibrium positions as in the previous case. The main structural parameters to be determined are the first, second, and third interlayer spacings (d_{12}, d_{23}, and d_{34}, see Fig. 1). While in the previous case the rippling effect is restricted to the surface CuPd layer, in the case of an underlayer alloy it occurs in the second CuPd (δ_2) and fourth (δ_4) layers. The buckling in the Cu top and third layers is ruled out by symmetry constraints. The calculations show an expansion of both the first and the second Cu-Cu interlayer distances relative to the bulk unlike the case of a clean Cu(100) surface where the top interplanar separation is contracted.[27] The changes are $d_{12}=1.4\%$ and $d_{23}=2.8\%$. Our values are smaller than those obtained in Ref. 18 using tensor LEED analysis ($d_{12}=3.3\%$ and $d_{23}=6.6\%$), but the tendency is the same. The change in the second Cu-Cu distance is larger than that in the first one due to the buckling effect. The deeper interlayer spacings are very close to the bulk Cu. The rippling in the mixed CuPd layer where the Pd atoms move inwards from the surface and the rippling in the fourth layer where the Cu atoms located just below the second-layer Pd atoms move upwards (see Fig. 1) are found to be small and do not differ substantially: $\delta_2=0.03$ Å and $\delta_4=0.02$ Å. Our results are in reasonable agreement with the tensor LEED study of Barnes *et al.*,[18] except for the magnitude of the rippling in the fourth layer which is surprisingly large in Ref. 18 ($\delta_4=0.2\pm0.1$ Å).

The calculated values of surface phonon frequencies at the symmetry points are summarized in Table I and the dispersion curves along high-symmetry directions are shown in Fig. 3. As in the previous case a group of modes is found below the bulk bands. However, at $\overline{X}$ all of them are connected with vibrations of atoms within the surface plane in contrast to the clean Cu(100) surface and the Cu(100)-$c(2\times2)$-Pd surface alloy. The lower two states at $\overline{X}$ correspond to motion of the top-layer Cu atoms in the surface plane along the two perpendicular directions. The calculation of force constants indicates that interactions between the nearest-neighbor Cu atoms in the surface layer are ~7.6% weaker than those at the clean Cu(100) surface. Concerning the bonding between Pd and Cu atoms, it is quite similar to the previous case of the top CuPd alloy. The interlayer force constants coupling the Pd atoms to their first- or third-layer Cu nearest neighbors are 30%–50% larger than the bulk ones. The Pd-Cu in-plane bonds are very strong, too. The magnitude of the corresponding force constant is increased by ~60% relative to the bulk value. As in the previous case such an increase comes at the expense of the bonding between Cu atoms in the first three layers which is reduced in magnitude by ~20% compared to the clean Cu(100) surface. The deeper layers behave like those in the bulk. As a consequence the frequency of the lowest surface state at $\overline{X}$ is shifted down. But the other mode connected with displacements of the Cu surface atoms towards their nearest-neighbor Pd atoms in the second layer is shifted up and the energy separation between these two modes becomes rather large (3.31 meV). The next two modes at $\overline{X}$ are characterized by appreciable localization (up to 60%) at the Pd sublattice with shear horizontal atomic vibrations. Despite of the strong Cu-Pd bonding they peel off from the bottom of the bulk bands and lie outside the bulk continuum. The only surface states at $\overline{X}$ connected with motion of atoms along the surface normal are localized in the top Cu layer and lie in the bulk band region at ~15.72 meV. The shift of these modes to higher energies is mainly governed by the Cu-Pd forces which increase substantially.

To illustrate the changes in the phonon spectrum we have calculated the local phonon densities of states (DOS) up to the fourth layer. They are presented in Figs. 4 and 5 together with that for the central layer (dotted line). As one can see the layer DOS start to settle at the third layer where there are only small differences from the bulk DOS. The force constants are found to restore to their bulk values at the third layer too. The largest differences compared to the bulk occur in the mixed CuPd layer in the case of a surface alloy (Fig. 4) and in the two outermost layers for an underlayer alloy (Fig. 5). We have calculated the phonon DOS for Cu and Pd atoms in the mixed layers separately. The vibrational modes related to the displacements of atoms in the mixed CuPd layers are present everywhere from low frequencies to the high-energy gap. In the case of a surface alloy the main feature is the pronounced low-frequency Pd peak below the bulk DOS. It is shifted to lower frequencies compared to the corresponding Cu peak which lies close to the bulk transverse bands. In the upper frequency range, the phonon modes connected with vibrations of Cu mixed layer atoms are mainly situated, except for the surface state, at the energy gap (~26.06 meV). In the case of an underlayer alloy the most pronounced peak is connected with the top-layer Cu

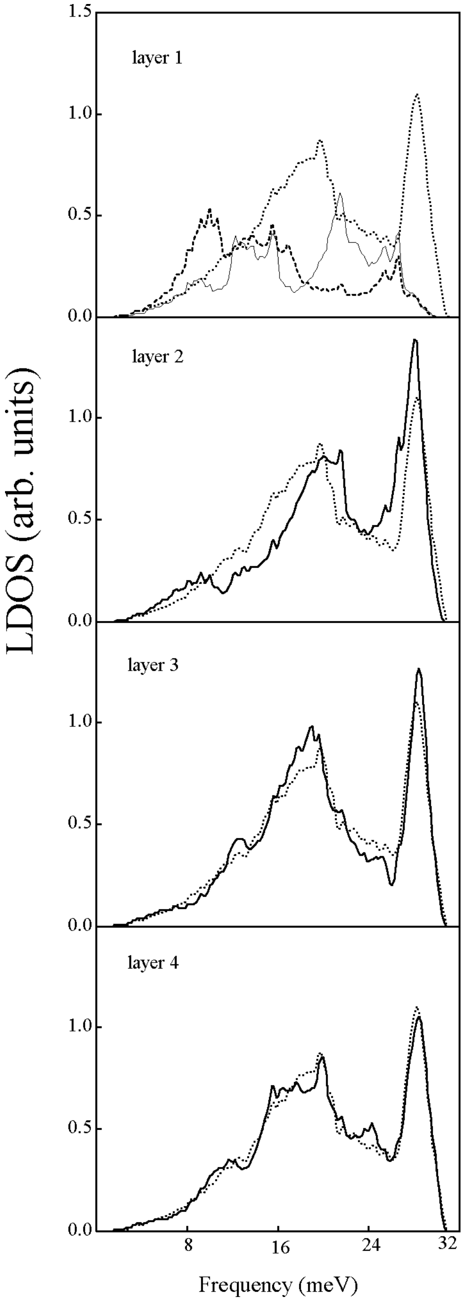

FIG. 4. Local density of states (solid lines) for the Cu(100)-$c(2\times2)$-Pd surface alloy together with the bulk DOS (dotted lines). The solid and dashed lines for layer 1 show the phonon DOS for Cu and Pd atoms, respectively.

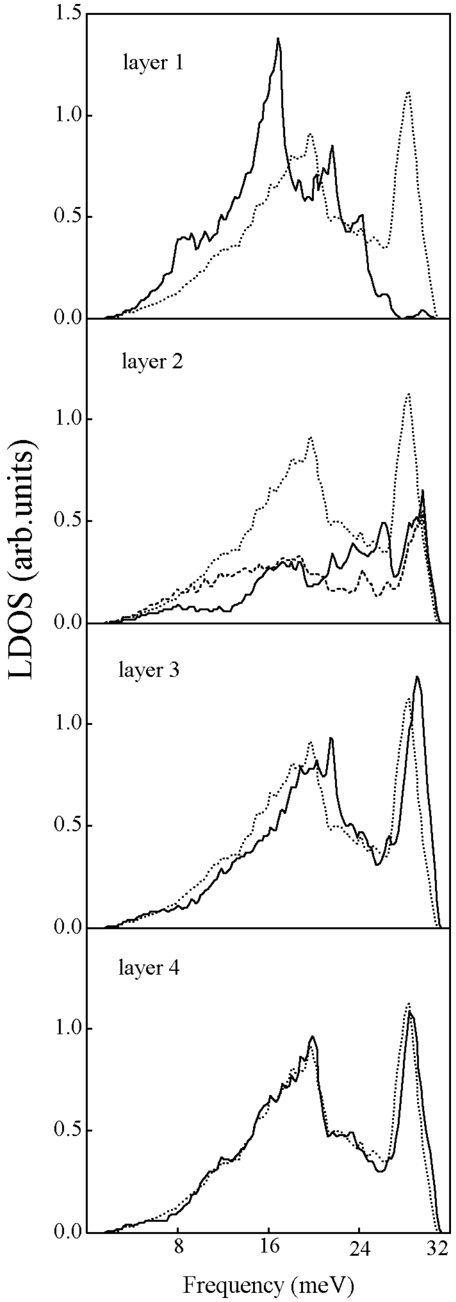

FIG. 5. Local density of states (solid lines) for the Cu(100)-$c(2\times2)$-Pd underlayer alloy together with the bulk DOS (dotted lines). The solid and dashed lines for layer 2 show the phonon DOS for Cu and Pd atoms, respectively.

vibrations in the direction perpendicular to the surface. As for the mixed layer density of states it is more bulklike than that in the previous case. Thus unlike the surface alloy the frequencies of Cu vibrations along the surface normal are shifted to the higher energies in the case of an underlayer alloy. The measured high-frequency shear vertical mode which grows upon annealing of the Cu(100)-$c(2\times2)$-Pd surface appears at 15.88 meV. So this high-frequency peak can be related to the vibrations of pure Cu over the mixed CuPd layer.

IV. CONCLUSION

We present the results of a comparative study of the structural and vibrational properties of a Cu(100)-$c(2\times2)$-Pd surface alloy and an underlayer $c(2\times2)$ alloy with a mixed CuPd second layer. Analysis of the interatomic interactions showed a very strong Cu-Pd bonding compared to the nearest-neighbor Cu-Cu interactions. From the calculated local phonon densities of states we find that the layer DOS start to settle at the third layer where there are only small differences with the bulk DOS, and the force constants almost restore to their bulk values. In the case of a Cu(100)-$c(2\times2)$-Pd surface alloy the largest differences compared to the bulk occur in the mixed CuPd layer and the main feature is the pronounced low-frequency Pd peak below the bulk DOS. In the case of an underlayer $c(2\times2)$-CuPd alloy the most pronounced peak is connected with the top-layer Cu vibrations in the direction perpendicular to the surface. The results also indicate that the energy of Cu top-layer vibrations along the surface normal is higher for an underlayer alloy compared to that for a surface alloy. Thus, the measured high-frequency peak can be related to the vibrations of pure Cu over the mixed CuPd layer. The growth in intensity of this mode upon annealing of the Cu(100)-$c(2\times2)$-Pd surface suggests a temperature-induced transition from a $c(2\times2)$-CuPd surface alloy to an underlayer $c(2\times2)$-CuPd alloy, consisting of a mixed second layer capped by a Cu monolayer.

ACKNOWLEDGMENT

This work was supported by the Ministry of Science of Russia (Grant No. 40.012.1.1.1153) and the University of Basque Country.

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[1] G.W. Graham, Surf. Sci. **171**, L432 (1986).

[2] S.C. Wu, S.H. Lu, Z.Q. Wang, C.K.C. Lok, J. Quinn, Y.S. Li, D. Tian, F. Jona, and P.M. Marcus, Phys. Rev. B **38**, 5363 (1988).

[3] T.D. Pope, G.W. Anderson, K. Griffiths, P.R. Norton, and G.W. Graham, Phys. Rev. B **44**, 11 518 (1991).

[4] A.R. Koymen, K.H. Lee, G. Yang, K.O. Jensen, and A.H. Weiss, Phys. Rev. B **48**, 2020 (1993).

[5] T.D. Pope, M. Vos, H.T. Tang, K. Griffiths, I.V. Mitchell, P.R. Norton, W. Liu, Y.S. Li, K.A.R. Mitchell, Z.-J. Tian, and J.E. Black, Surf. Sci. **337**, 79 (1995).

[6] J. Kudrnovsky, S.K. Bose, and V. Drchal, Phys. Rev. Lett. **69**, 308 (1992).

[7] J.E. Black, Phys. Rev. B **46**, 4292 (1992).

[8] A. Christensen, A.V. Ruban, P. Stoltze, K.W. Jacobsen, H.L. Skriver, J.K. Nørskov, and F. Besenbacher, Phys. Rev. B **56**, 5822 (1997).

[9] M.-S. Chen, D. Terasaki, S. Mizuno, H. Tochihara, I. Ohsaki, and T. Oguchi, Surf. Sci. **470**, 53 (2000).

[10] J.E. Garcés, H.O. Mosca, and G.H. Bozzolo, Surf. Sci. **459**, 365 (2000).

[11] M. Valden, J. Aaltonen, M. Pesa, M. Gleeson, and C.J. Barnes, Chem. Phys. Lett. **228**, 519 (1994).

[12] G.W. Graham, P.J. Schmitz, and P.A. Thill, Phys. Rev. B **41**, 3353 (1990).

[13] P.W. Murray, I. Stensgaard, E. Lægsgaard, and F. Besenbacher, Phys. Rev. B **52**, R14 404 (1995).

[14] Y. Yao, Y.G. Shen, D.J. O'Connor, and B.V. King, Surf. Sci. **359**, 65 (1996).

[15] J. A. Alonso and N. H. March, *Electrons in Metals and Alloys* (Academic, London, 1989).

[16] J.B. Hannon, H. Ibach, and P. Stoltze, Surf. Sci. **355**, 63 (1996).

[17] G.W. Anderson, T.D. Pope, K.O. Jensen, K. Griffiths, P.R. Norton, and P.J. Schultz, Phys. Rev. B **48**, 15 283 (1993).

[18] C.J. Barnes, E. Alshamaileh, T. Pitkänen, P. Kaukasoina, and M. Lindroos, Surf. Sci. **492**, 55 (2001).

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

[20] S.M. Foiles, M.I. Baskes, and M.S. Daw, Phys. Rev. B **33**, 7983 (1986).

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

[22] L. Hedin and B.I. Lundqvist, J. Phys. C **4**, 2062 (1971).

[23] C.M. Gilmore and V. Provenzano, Phys. Rev. B **42**, 6899 (1990).

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

[25] J.E. Black, Z.-J. Tian, and T.S. Rahman, Surf. Sci. **291**, 215 (1993).

[26] I.Yu. Sklyadneva, G.G. Rusina, and E.V. Chulkov, Surf. Sci. **377–379**, 313 (1997).

[27] J.S. Nelson, E.C. Sowa, and M.S. Daw, Phys. Rev. Lett. **61**, 1977 (1988).

[28] U. Kürpick, A. Kara, and T.S. Rahman, Phys. Rev. Lett. **78**, 1086 (1997).

[29] I.Yu. Sklyadneva, G.G. Rusina, and E.V. Chulkov, Surf. Sci. **433–435**, 517 (1999).

[30] Ch. Ghosh, A. Kara, and T.S. Rahman, Surf. Sci. **502–503**, 519 (2002).

[31] H.L. Davis and J.R. Noonan, Surf. Sci. **126**, 245 (1983).

[32] W. Daum, C. Stuhlmann, and H. Ibach, Phys. Rev. Lett. **60**, 2741 (1988).

[33] M. Wuttig, R. Franchy, and H. Ibach, Z. Phys. B: Condens. Matter **65**, 71 (1986).

[34] G. Benedek, J. Ellis, N.S. Luo, A. Reichmuth, P. Ruggerone, and J.P. Toennies, Phys. Rev. B **48**, 4917 (1993).

[35] L. Chen and L.L. Kesmodel, Surf. Sci. **320**, 105 (1994).