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Structural and Vibrational Properties of Cu(111)-Pt Surface Alloy

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Abstract_Investigations of surface alloys are important in various applications because the electronic structure and geometric arrangement of the surface atoms strongly influence the reactions taking place on the surface. Therefore, a deeper understanding of the physical and chemical phenomena associated with the creation of surface alloys appears to be essential in order to further progress in catalysis. In the present paper, we present the calculation of vibrational properties of the Cu(111)-Pt surface alloy formed by depositing Cu atoms onto the Pt(111) surface substrate. The surface phonon frequencies and local vibration density of state (LDOS) are calculated with the use of the matching theory. New surface modes have been found on the Cu(111)-Pt surface alloy along the high-symmetry directions, in comparisonwith the clean surface Pt(111). From the calculated LDOS, wehave found that the LDOS spectra starts to settle at the fourth layer, where there are only small differences with the perfect bulk spectrum.

***Keywords*— Surface alloys, Vibration properties, Matching theory, High-symmetry directions**

I. INTRODUCTION

The study of surfaces is an interesting topical theme in the field of surface and interface physics. It makes it possible to explain important phenomena such as adsorption, diffusion as well as crystal growth. The surface is the place of interactions between the material and its environment. Therefore, surfaces play an essential role in a large number of nanotechnology applications. They are often used as supports for nano-objects and intervene directly in the properties of the material that we wish to create. At the atomic scale, a surface represents a very asymmetric environment where the atoms have a modified coordination and electronic structure compared to the atoms of the volume. As a result, the surface structure can be radically different from a simple crystal termination [1].

The first work on the physics of surface vibrations was carried out by Lord Rayleigh, in 1882, who studied the propagation of waves on the continuous media surface [2]. Subsequently, in 1911, Love addressed another type of surface wave that can exist when a layer of one isotropic material is supported by a substrate of another isotropic material type [3].

In addition, the surface of a solid lowers the frequencies of volume vibrations, causing the appearance of localized vibration waves and variations in the phonon density of states. Consequently, it must contribute, in a specific way, to the solid vibrational properties [4].

The formation of alloys is a complicated subject in materials science.The alloy concernedin the present research work is Cu–Pt. These are very interesting alloys from the point of view of their catalytic and magnetic properties. For this reason, these surface alloys have been widely studied by several authors [5]-[10], for their technological and scientific interest, in adsorption, reactivity, catalysis, etc.

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II. VIBRATIONAL DYNAMICS OF A PERFECT WAVEGUIDE

The atoms in a face-centered cubic crystal structure in the [111] direction are arranged in the following way: an ordered stack of planes (ABC ABC, ...) which is a hexagonal structure as shown in figure1.

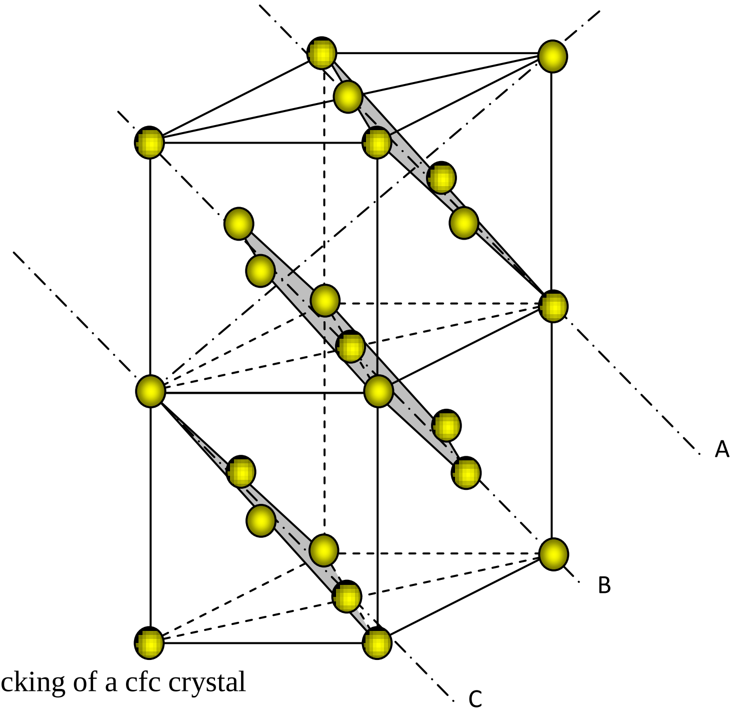

Fig. 1 ABC atomic stacking of a cfc crystal

The study of the volume region following direction [111] is shown in figure 2. A copper atom in volume is surrounded by 12 first neighbors located at a distance of $a\sqrt{2}$, and 6 second neighbors at a distance a.

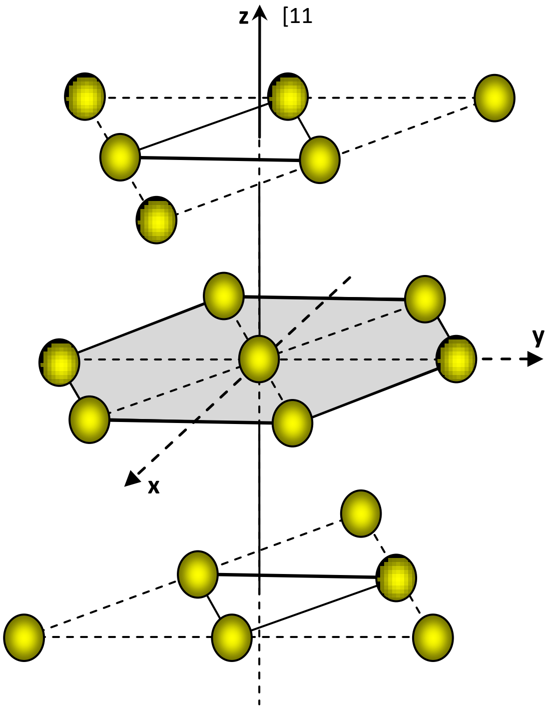

Fig. 2First and second neighbors of an atom structure following the [111] direction in a volume following the direction [111].

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Writing the equations of motion for an atom in the volume region makes it possible to determine the volume vibrational dynamics of the platinum substrate far from the surface region. To study the motion of these atoms, we apply Newton's second law:

$$m(l)\,\frac{d^2\vec{r}i}{dt^2} = \sum \vec{F} \qquad (1)$$

Taking into account the harmonic approximation, which is a simple description of the total interaction potential made possible by the very small atomic displacements in the vicinity of equilibrium, associated with the central forces model, the equation of motion of an atom occupying the site *l* is written in the form:

$$\omega^2 m(l) u_\alpha(l,\omega) = \sum_{l'\neq l}\sum_{\beta}\left(\frac{r_\alpha r_\beta}{r^2}\right) k(l,l')\left[u_\beta(l',\omega) - u_\beta(l,\omega)\right] (2)$$

The equations of motion can be put in matrix form:

$$[\Omega^2 I - D(e^{i\varphi_x}, e^{i\varphi_y}, Z, r)]|u\rangle = 0 \qquad (3)$$

Where *D* represents the dynamic matrix in volume, it is (3×3) of size, and *I* is an identity matrix of the same size as that of matrix *D*.

The mathematical condition for the matrix system (3)to obtain non-trivial solutions is that the determinant is zero, that is to say:

$$det[\Omega^2 I - D(e^{\varphi_x}, e^{\varphi_y}, Z, r)] = 0 (4)$$

The equations system resolution, given by relation (4), gives access to the dispersion curves that have been calculated in the reciprocal lattice of the hexagonal lattice following the directions of high symmetries of the first Brillouin zone *ΓM*, *ΓK* and *KM*, with:

$$\Gamma = (0,0,0),\ \mathrm{K} = \left(0, \frac{2\pi}{\sqrt{3a}}, 0\right)\ \text{et}\ \ \mathrm{M} = \left(\frac{2\pi}{3\mathrm{a}}, \frac{2\pi}{\sqrt{3a}}, 0\right)$$

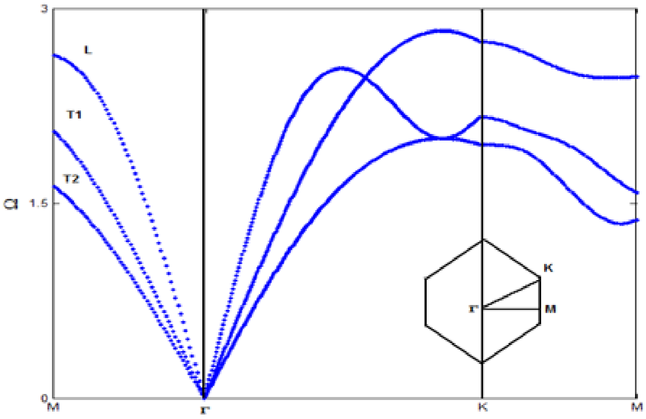

Fig. 3Dispersion curves of a perfect cfc [111] structure in high symmetry directions.

The dispersion curve is shown in figure 3. The latter represents the phonon modes of the face-centered cubic structure along the [111] direction, as a function of the wave vectors taken along the high symmetry directions in the first Brillouin zone. In the first direction Γ-M, we notice that the dispersion curve contains three types of branches: two transverse branches (noted T_1 and T_2), for which the vibrations propagate perpendicularly to the atoms motion, and a longitudinal branch (noted L) for which the direction of propagation of the vibration and the atoms motion are collinear. The same behavior is well observed in the Γ-

K direction. While along the K-M direction, we notice the existence of three transverse and longitudinal modes. Thevibrations set is described for the first Brillouin zone wave vectors.Consequently, we obtain two eigenmodes per branch.

III. DESCRIPTION OF THE ORDERED SURFACE ALLOY CU-PT (111)

The model system that we have chosen is indicated in figure 4. It is obtained by deposition of Cu between two Pt layers, and in the middle, Pt atom has been placed in the centre of six adjacent Cu atoms. The two metals, copper and platinum, crystallize in a face-centred cubic structure with lattice parameters of 3.615 Å and 3.77 Å respectively.

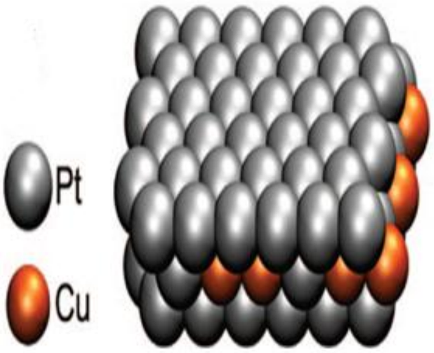

Fig. 4A schematic representation of the Cu- Pt(111) ordered surface alloy.

IV. DYNAMIC MATRIX OF THE CU-PT ALLOY SURFACE SYSTEM[111]

The motion equations governing the vibrational displacements of different atom sites of the system, in the presence of the surface, are obtained from equation (2).

The system dynamic matrix *D* considered, with a Cu-Pt(111) alloy surface, finds its origin by writing the vibrational motion equations of the atoms (A), (B), (C), (D), and (E) , shown in figure 5.

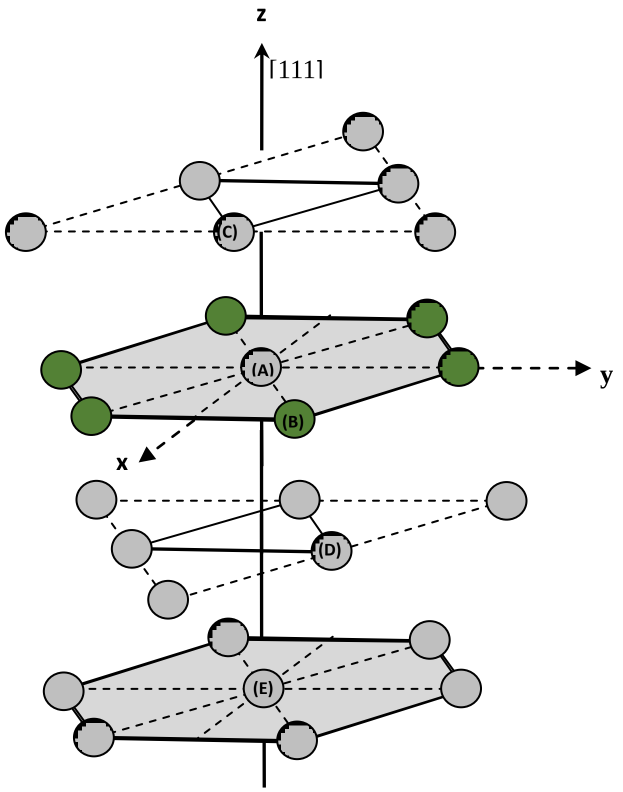

Fig. 5Schematic representationof the Cu-Pt (111) alloy surface.

The set of equations for the atoms vibrational motion defined previously constitutes a homogeneous linear system. This can be put in the form of a rectangular matrix *D*, containing more unknowns (18) than equations (15), such as:

$$[D]|U\rangle = |0\rangle \qquad (5)$$

and :

$$\dim\ [D] = 12 \text{ x } 18$$

$$\dim\ |u\rangle \ = 18 \text{ x } 1$$

$$\dim\ |0\rangle \ = 12\text{x } 1$$

where $|u\rangle$is a column vector describing the vibrational displacements of all elementary cell atoms of the considered zone.

V. MATCHING MATRIX

Our objective in this study is to establish the matching relationships between atoms vibrational displacements belonging to the alloy surface and the vibrational fields of the evanescent modes in volume. For this, we will represent the sites atomic displacements belonging to the matching region by a linear combination of vector {R} defining a finite space. Knowledge of the phase factors [Z, 1/Z], characterizing the evanescent modes due to the presence of the surface and determined from the previous study in volume, makes it possible to make this matching state.

For an atom belonging to the matching region of our alloy surface system, we can describe its vibrational displacements by means of the following relation:

$$u_\alpha\left(n_x, n_y, n_z\right) = \sum_i^{i=3} \mathrm{Z}_i^{n_z} P(\alpha, i) R \qquad (6)$$

Here α represents one of the three Cartesian directions, and P(α,i) are the weighted weights associated with the different evanescent modes. They are determined using the cofactors of the dynamic volume matrix *D* defined previously.

The vector |u⟩ describing all the vibrational displacements of all elementary cell atoms of the considered zone can be broken down into two parts: the first is denoted by |irr⟩; it is constituted by the atomic displacements of fiveirreducible sites elements forming the surface region, that is to say, the atoms (A), (B), (C) and (D). As for the second noted by |rac⟩, it is formed by the displacements associated with the matching sites (E), this for the base |R⟩. So, we write:

$$|u\rangle = \begin{pmatrix} |irr\rangle \\ |rac\rangle \end{pmatrix} (7)$$

and

$$dim|irr\rangle = (12 \text{ x } 1)$$

$$dim|rac\rangle = (6 \text{ x } 1)$$

From there, the matching of the atoms can be described using the following expressions:

$$|u\rangle = \begin{pmatrix} |irr\rangle \\ |rac\rangle \end{pmatrix} = \begin{bmatrix} I_d & 0 \\ 0 & R_1 \\ 0 & R_2 \end{bmatrix} \begin{pmatrix} |irr\rangle \\ |R\rangle \end{pmatrix} (8)$$

where I_d is an identity matrix of dimension (12×12); and R_1, and R_2 are square matrices of dimension (3 × 3).

By putting$D_r = \begin{bmatrix} I_d & 0 \\ 0 & R_1 \\ 0 & R_2 \end{bmatrix}$, the equations system (8) can be expressed using this matrix as follows:

$$|u\rangle = \begin{pmatrix} |irr\rangle \\ |rac\rangle \end{pmatrix} = \begin{bmatrix} I_d & 0 \\ 0 & R_1 \\ 0 & R_2 \end{bmatrix} \begin{pmatrix} |irr\rangle \\ |R\rangle \end{pmatrix} = D_r \begin{pmatrix} |irr\rangle \\ |R\rangle \end{pmatrix} (9)$$

The matrix $D_r$of dimension (18×12) is called matching matrix.

Using this relationship, we can rewrite the equations system (9) as follows:

$$[D(12\text{x}18)]\,.\,[D_r(18\text{x}12)] \begin{pmatrix} |irr\rangle \\ |R\rangle \end{pmatrix} = |0\rangle \qquad (10)$$

Or

$$[D_s(12\text{x}12)] \begin{pmatrix} |irr\rangle \\ |R\rangle \end{pmatrix} = |0\rangle (11)$$

with D_s defined as being the matrix product of the two matrices D and D_r.

This, for values of the ratios of the force constants, the eigenmodes of surface phonons located in the vicinity of the ordered metal alloy surface Cu-Pt(111), are determined using the following compatibility relation

$$det[D_s(12\text{x}12)] = 0 (12)$$

VI. THE STATES LOCATED AT THE LEVEL OF A CLEAN PT(111) PLATINUM INTERFACE AND AT THE LEVEL OF A CU-PT(111) ALLOY INTERFACE

The vibrational properties of our Cu-Pt(111) metal alloy surface system are presented in this part.We have calculated the localized phonons of the clean surface Pt(111), whichwill be used as a reference system in order to know the copper atoms influence on this surface.

The calculated surface phonons are indicated by black lines for the Pt(111) clean surface and the alloy surface. Those lines are, in general, along the high symmetry directions (ΓM), (MK), and (KΓ) as shown in figures6 and 7.

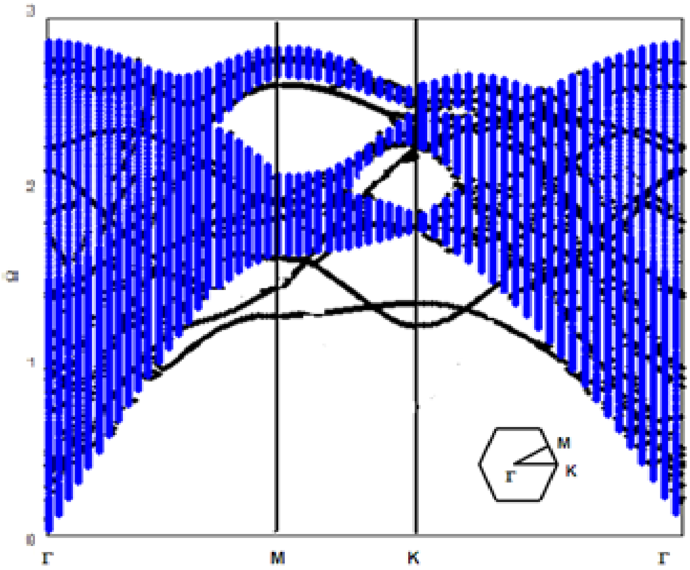

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Fig. 6The surface phonon dispersion curves calculated for the clean surface Pt(111) with the bulk phonon band. Surface conditions are indicated by solid lines.

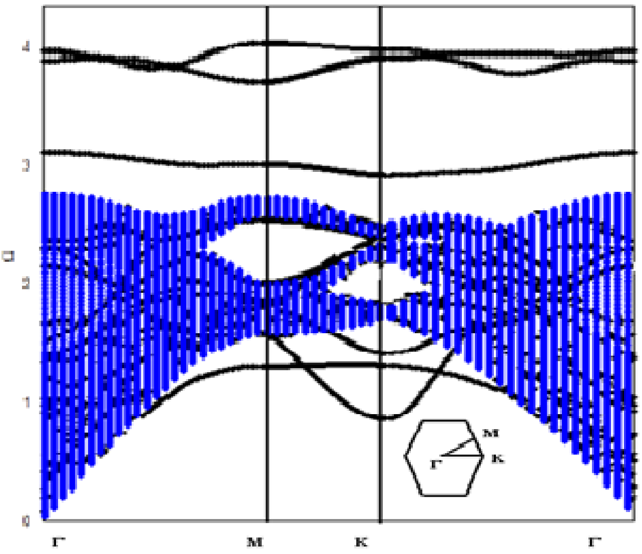

Fig.**7**The surface phonon dispersion curves calculated for the Cu-Pt(111) alloy surface with the bulk phonon band. Surface conditions are indicated by solid lines.

Ourfindings for the Pt(111) clean surface are shown in figure 6. Our calculations detail the presence of three localized phonon branches located under the volume phonon band.

The lowest of these is called the Rayleigh branch. At the longest wavelengths (i.e. near the point Γ), this mode essentially corresponds to the vertical vibrational deformations of the surface

Our results show a resonance branch in the interval (MK), near the lower limit of the volume band, which subsequently becomes a surface phonon branch in the last interval. Our numerical results show a resonance in the interval (KΓ). They also show the existence of two phonon branches at higher energies.

In figure 7, the results correspond to the surface phonons of the ordered Cu-Pt(111) alloy surface. The Rayleigh branch for the Pt(111) surface is maintained and modified only very slightly for the alloy surface.

However, three new branches appear below the volume band along the high symmetry directions (ΓM), (MK) and (KΓ). The phonon branches in the two energy gaps are strongly modified by the presence of copper atoms in the interior layer of the alloy surface.

Given that the effective atomic mass decreases and elastic constants increase in a mean-field representation for the outer layer, it is likely that the phonon branches of the Pt(111) surface be pushed toward high energiesin the ordered alloy surface, to be replaced by resonances in higher energy gaps.

Furthermore, in the surface phonon branches of the alloy surface in comparison to those of the clean Pt(111) surface, new optical phonon branches appear.

One of them appears just at the upper limit of the volume phonon band while the other two are located higher above this band. It is clear that these new branches of surface phonons are induced by the presence of copper atoms surrounded by six closest neighbors of copper atoms in the interior atomic layer.

VII. THE LOCAL VIBRATIONAL DENSITIES OF STATES

The local vibrational densities of states of our system are calculated numerically per atomic site in the inner surface layer. These densities of states are given in arbitrary units, as a function of the normalized frequency Ω in the first Brillouin zone. Furthermore,thelocalvibrationdensitiesofstates(LDOS)intheorderedsurfacealloy can be calculated by using the Green'sfunction formalism. TheGreen'sfunctionsarecalculated in a direct manner from thesquare matrix established by the matching formalism. The final expression of this LDOS is given by the following equation [11, 12]

$$N(\Omega) = \sum_{\varphi_x,\varphi_y}\sum_{p\alpha}\rho_{(\alpha,\beta)}^{(p,p')}(\Omega,\varphi_x,\varphi_y) \quad = -\frac{2\Omega}{\pi}\sum_{\varphi_x,\varphi_y}\sum_{p\alpha}\lim_{\varepsilon\to 0^+}\left[ImG_{\alpha\beta}^{pp}(\varphi_x,\varphi_y,\Omega^2+i\varepsilon)\right] \quad (13)$$

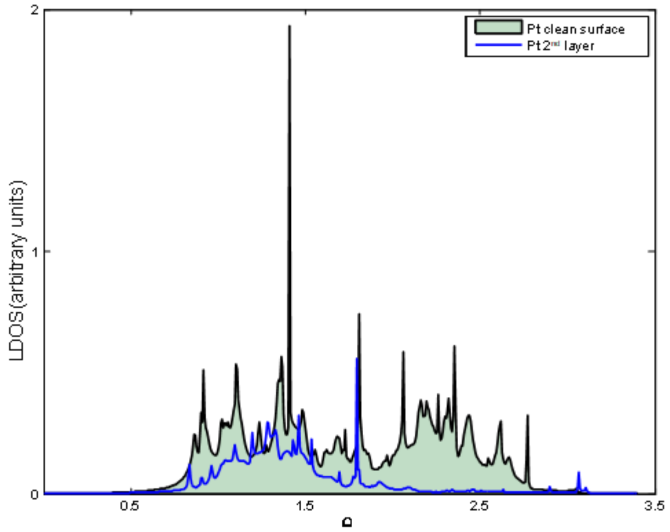

Fig. 8Local vibrational densities of states of the Pt atomic sites in the second atomic layer of the alloy surface with that of the vibrational density of states of the clean Pt(111) surface.

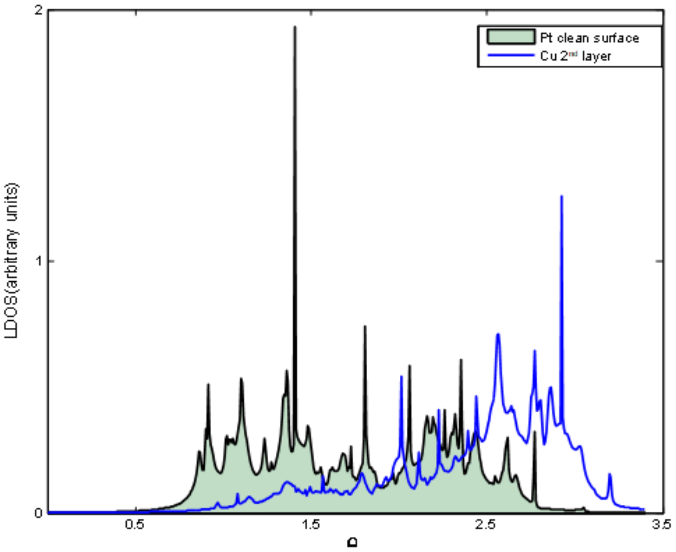

Fig. 9Local vibrational densities of states of the Cu atomic sites in the second atomic layer of the alloy surface with that of the vibrational density of states of the clean Pt(111) surface.

The first observation is that the surface alloy LDOS extends to higher energies. The second observation which we can note is the remarkable diminution of the LDOS for the layer 2 (Pt) site spectrum on the surface alloy, in comparison with that for the layer 2 (Pt) site in the clean Pt(111) surface.Furthermore,the LDOSforthe layer2(Cu)site inthe surface alloy presents aremarkably strong and widespread spectrum in comparison with that for the layer 2 (Pt) site. Note in particular the increased DOS towards the higher energy limit for the layer 2 (Cu) site. These differences are certainlydue to the presence of Cu atoms in the surface alloy, corresponding to a net transfer of vibrational activity from the Pt sites to the Cu sites, reminiscent of the charge transfer from the Pt to the Cu sites.

VIII. CONCLUSION

The present research work bears on an investigation of the vibrational properties of the ordered Cu-Pt(111) alloy surface obtained by the deposit of Cu atoms on the surface of a platinum(111) substrate. The matching method used here for the analytical and numerical calculations of these surface vibrational properties turns out to be a basic and effective theoretical tool.

Overall, the most remarkable result in our calculations is the appearance of new phonon branches for the Cu-Pt(111) surface in comparison with the clean Pt(111) surface. Indeed, the ordered alloy surface system exhibits three such branches of surface phonons.

As for the results of the states densities, they show a remarkable decrease in the spectrum of the vibrational states densities of the platinum atomic sites in the alloy surface, in comparison to that of the platinum atomic site in the second layer in the clean Pt surface(111).

These differences are essentially due to the presence of copper atoms in the alloy surface, which corresponds to a net transfer of vibrational activity from the platinum atomic sites to those of copper.

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