# Calculation of Vibrational Spectra for Surface Atoms: FCC Transition Metals

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A (self-consistent) tight-binding type electronic theory is used to calculate the atomic relaxation and force constants between atoms near the (001) surface of fcc transition metals (Ni, Pd and Pt). Assuming the Born-Mayer potential for the short-range core repulsion energies, we have derived simple analytic expressions for the force constants near the surface. We then calculate the local vibrational spectra and Debye parameters for the surface atoms, employing the recursion method originally introduced by Haydock et al. for the electronic structure calculation of solids. It is shown that the inclusion of electronic effects (electronic rearrangement and surface relaxation) is important for the vibration of surface atoms.

## 1. Introduction

Recently, there has been a considerable interest in the study of atomic vibration at transition metal surfaces [1—3]. Vibrational information on the clean surface as well as on chemisorbed layers has been obtained using low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HRELS) and other methods [2]. Stimulated by these experimental observations, a number of theoretical studies of the problem have been carried out [4—13]. Except in a few cases [9—12], however, the previous theoretical work has been performed assuming the surface force constants unchanged relative to the bulk values.

It is the purpose of the present paper to investigate the atomic vibrations near the (001) surface of fcc transition metals (Ni, Pd and Pt), taking into account the surface relaxation and changes in the force constants between atoms near the surface. Most of the previous experimental work has been concerned with the atomic vibration in the low index surface planes of fcc transition metals [6, 13 to 16]. To calculate the surface relaxation and changes in the force constants, we use a tight-binding type electronic theory coupled to the moments approach [17].

We employ the recursion method (continued fraction technique) [18] to obtain the local vibrational spectra for atoms near the surface of fcc transition metals (Ni, Pd and Pt). The recursion method has a number of advantages compared, for instance, to the so called slab method [1], which has been frequently used in the studies of lattice dynamics of solid surfaces. Since the recursion (continued fraction) method is a "real space" method, it allows to study solid surfaces with localized perturbations, such as an isolated adsorbate atom. Phonon densities are determined by allowing the atoms of interest to interact with successive neighbouring shells.

We then calculate the Debye parameter for surface atoms and compare the results with those for bulk atoms as well as those obtained by LEED experiments [6, 14—16]. In particular, we shall show that the inclusion of electronic effects (electronic rearrangement and surface relaxation) is important: The vibration spectra of surface atoms are considerably changed when the electronic rearrangement and surface relaxation are taken into account. Furthermore, in certain circumstances (i.e., for particular fcc transition metals) the atomic vibration parallel to the surface plane can be influenced (softened) significantly, and the effective Debye parameters for vibrations parallel and normal to the surface, $\theta_{\parallel}$ and $\theta_{\perp}$, become nearly equal. We will also give some experimental evidences for this behavior.

The format of this paper is as follows. In Sect. 2, we present the method of calculation for the surface force constants, local vibrational spectra and

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Debye parameters. The analytical expressions for the surface force constants are also given in this section. The numerical results and related discussions for the surface atomic vibrations of fcc transition metals (Ni, Pd and Pt) are presented in Sec. 3. The final section 4 is devoted to conclusions.

## 2. Method of Calculation

We use a tight-binding approximation coupled to the moments method [17] to describe the transition metal d-band, and estimate the change in the d-band energy due to the introduction of lattice defects (surface and static atomic displacements). The local density of states $\varrho_i(E)$ of the d-electrons on atom $i$ is approximated by a Gaussian fitted to the first and second moments, $\mu_{1i}$ and $\mu_{2i}$. The influence of s-electrons and s-d mixing is neglected [19, 20]:

$$\varrho_i(E) = (10/\sqrt{2\pi\mu_{2i}'}) \cdot \exp\{-(E-\mu_{1i})^2/2\mu_{2i}'\}, \tag{1}$$

where the factor 10 is due to the degeneracy of the d-band and

$$\mu_{2i}' = \mu_{2i} - \mu_{1i}^2. \tag{2}$$

Taking the free atom level as the origin of the energies, one obtains

$$\mu_{1i} = V_i, \quad \mu_{2i}' = \sum_j \beta_{ij}\beta_{ji}, \tag{3}$$

where $V_i$ is the diagonal matrix element of the self-consistent potential resulting from charge oscillations near the lattice defect (surface plane), and $\beta_{ij}$ an effective resonance integral between atomic sites $i$ and $j$. We assume that the resonance integral $\beta_{ij}$ varies with the interatomic distance $R_{ij}$ as [21, 22]

$$\beta_{ij} = \beta_0 \exp(-qR_{ij}), \tag{4}$$

where the parameter $q$ can be chosen so as to fit the elastic constants or phonon dispersion curve of the given transition metal [11, 12]. It has been shown that, if $R_0$ is the equilibrium interatomic distance, a reasonable value of $q$ can be given for fcc transition metals as $qR_0 = 2 \sim 3$ [11, 21, 22].

One can now calculate the band structure energy as a function of atomic displacements from the expression [19, 20]

$$\delta E_e = \sum_i \left[ \int_{-\infty}^{E_f} E\{\varrho_i(E) - \varrho_0(E)\}\,dE - V_i \int_{-\infty}^{E_f} \varrho_0(E)\,dE - (V_i/2) \int_{-\infty}^{E_f} \{\varrho_i(E) - \varrho_0(E)\}\,dE \right], \tag{5}$$

where $E_f$ and $\varrho_0(E)$ represent the Fermi energy and d-electron density of states for the unperturbed transition metal, respectively. In the following, we assume that the self-consistent potential $V_i$ completely screens the defect (perturbation) and each atom is neutral [19, 20]. In this case $V_i$ can be given by

$$V_i = E_f(1 - \sqrt{\mu_{2i}'/\mu_2}), \tag{6}$$

where $\mu_2$ denotes the second moment for the perfect lattice.

To account for the repulsive core-core interaction energies at small distances, arising from the interatomic d-d repulsion and the increase in sp kinetic energy upon compression, we take a Born-Mayer potential [21, 23]:

$$E_r(R_{ij}) = C_0 \exp(-pR_{ij}). \tag{7}$$

This type of repulsive potential can stabilize the crystal at short distances. The parameter $p$ can be fitted to the phonon dispersion curve (with $q$), while $C_0$ is determined from the bulk equilibrium condition [21—23]. From (5) and (7), one can calculate the change in the total (electronic and repulsive) energies due to the introduction of lattice defects. It is known that this kind of treatment gives a good description of the bulk transition metal elastic constants [21] and the phonon spectrum [11, 12]. Furthermore, it has proved useful in a number of alloy [24], surface [9, 11, 12] and defect [25] problems.

It is now possible to obtain the analytic expressions for the elastic constants between atoms near the surface of transition metals. For the perfect fcc lattice, the force constant $\lambda_0$ between nearest neighbour atoms can be written, in terms of the cohesive energy per atom $E_c$, as [11, 12]

$$\lambda_0 = \frac{|E_c|\,pq(1 - 2q/p)}{(1 - q/p)Z}, \tag{8}$$

where $Z$ is the number of nearest-neighbours (12 for fcc lattice) and

$$E_c = -10\sqrt{\mu_2/2\pi}\exp(-E_f^2/2\mu_2) + \tfrac{1}{2} Z C_0 \exp(-pR_0). \tag{9}$$

Taking into account the broken bonds at the (001) surface, we have derived the following expressions for the force constants $\lambda_{\alpha\beta}(mn)$ between nearest-neighbour atoms in the $m$-th and $n$-th atomic layers ($\alpha(\beta)$ denotes the $\alpha(\beta)$-component of atomic displacements): For example, for atoms in the first ($m, n = 1$) and second ($m, n = 2$) layers,

$$\lambda_{xx}(1,1) = |E_c|/(1 - q/p) Z R_0^2 \{(\sqrt{Z/8} - 1) q R_0 + p q R_0^2 [1 - (2\sqrt{Z/8}) q/p]\}, \tag{10}$$

$$\lambda_{xx}(1,2) = |E_c|/(1 - q/p) Z R_0^2 \{\tfrac{1}{2}(\sqrt{Z/8} - 1) q R_0 + p q R_0^2 [1 - (1 + \sqrt{Z/8}) q/p]\}, \tag{11}$$

$$\lambda_{xz}(1,2) = |E_c|/(1 - q/p) Z R_0^2 \{\tfrac{1}{2}(1 - \sqrt{Z/8}) q R_0 + p q R_0^2 [1 - (1 + \tfrac{3}{4}\sqrt{Z/8}) q/p]\}, \tag{12}$$

$$\lambda_{zz}(1,2) = |E_c|/(1 - q/p) Z R_0^2 \{\tfrac{1}{2}(\sqrt{Z/8} - 1) q R_0 + p q R_0^2 [1 - (1 + \tfrac{3}{4}\sqrt{Z/8}) q/p]\}. \tag{13}$$

Considering the appropriate parameter values, $qR_0 = 2.2 \sim 3.0$ and $pR_0 = 9.0 \sim 13.0$, for fcc transition metals [11, 12, 21], one notices that the force constants near the surface are substantially changed (up to $\sim 30\%$) from the corresponding bulk value $\lambda_0$. These values are further modified when the atomic relaxation near the surface is taken into account. For instance, $\lambda_{xx}(1,1)$ is modified as

$$\begin{aligned}\lambda_{xx}(1,1) = |E_c|/(1 - q/p) Z R_0^2 \{&(\sqrt{Z/8} - 1) q R_0 + p q R_0^2 (1 - (2\sqrt{Z/8}) q/p) \\ &- [q^2 R_0^2 / 4(1 - 2 q R_0)] \Delta_z/d_0\},\end{aligned} \tag{14}$$

where $\Delta_z$ denotes the change in interlayer spacing ($d_0$) between the first and second layers. For a small atomic displacement (relaxation) at the surface, $\Delta_z$ may be written as

$$\begin{aligned}\Delta_z/d_0 = 6(3 - \sqrt{6})/\{&(27 + 10\sqrt{6}) q R_0 \\ &- (12\sqrt{6}) p R_0\}.\end{aligned} \tag{15}$$

To calculate the local vibrational spectra for atoms close to the surface, we use the recursion method (continued fraction technique) originally introduced by Haydock et al. [18] for electronic structure calculations of solids. Within the framework of the harmonic approximation, the local vibrational spectra $g_{i\gamma}(\omega)$ can be expressed as

$$g_{i\gamma}(\omega) = -\frac{\operatorname{Im}}{\pi} 2\omega G_{ii}^{\gamma\gamma}(\omega^2 + i0), \tag{16}$$

with

$$G_{ii}(\omega^2) = \cfrac{1}{\omega^2 - a_1{}^i - \cfrac{b_1{}^i}{\omega^2 - a_2{}^i - \cfrac{b_2{}^i}{\omega^2 - \dots}}}, \tag{17}$$

where $\gamma$ denotes the $\gamma(= x, y$ and $z)$ component of the vibrational state of atom $i$. The coefficients $a_n^i$ and $b_n^i$ can be calculated using the recursion method [26–28]:

$$a_n^i = \frac{\{n|\tilde{D}|n\}}{\{n|n\}}, \quad b_n^i = \frac{\{n|n\}}{\{n-1|n-1\}}, \tag{18}$$

where $\tilde{D} = \tilde{M}^{-1/2} \tilde{\Phi} \tilde{M}^{-1/2}$. $\tilde{M}$ and $\tilde{\Phi}$ are the mass tensor and force constant matrix, respectively.

We also calculate the Debye parameters from the formula [29]

$$\Theta(n) = \frac{\hbar}{k_B} \left( \frac{n+3}{n} \langle \omega^n \rangle \right)^{1/n}, \quad n = -2, -1, 1 \text{ and } 2, \tag{19}$$

where

$$\langle \omega^n \rangle = \int_0^{\omega_{\max}} \omega^n g_i(\omega) \, d\omega. \tag{20}$$

In (20), $\omega_{\max}$ represents the bulk maximum frequency ($m\omega_{\max}^2 = 16\lambda_0$; $m$ is the atomic mass). From the surface Debye parameters (for the vibrations normal and parallel to the surface), it may be possible to discuss the softening of atomic vibrations at the surface.

## 3. Numerical Results and Discussions

The present numerical calculations have been performed for the (001) surfaces of Ni, Pd and Pt using the parameter values listed in Table 1. In Table 1 we also give the bulk modulus B and the maximum frequency $\omega_{\max}$ for the perfect lattice calculated

Table 1. Parameter values $qR_0$ and $pR_0$, and calculated bulk moduli $B$ and maximum bulk frequencies $\omega_{\max}$.

| | Ni | Pd | Pt |
|---|---|---|---|
| $qR_0$ | 2.2 | 2.6 | 2.6 |
| $pR_0$ | 11.0 | 13.0 | 13.0 |
| $E_c$ (eV/atom) | 4.3 | 4.0 | 6.0 |
| $B$ (eV/atom) | 11.6<br>(12.3) | 15.0<br>(17.6) | 22.5<br>(26.5) |
| $\omega_{\max}$ ($10^{12}$ Hz) | 8.36 | 6.42 | 5.75 |

$B$ given in the parentheses are experimental values.

from the parameter ($pR_0$ and $qR_0$) values. The bulk modulus $B$ is calculated using the formula derived by Ducastelle [21] and given in units of eV/atom. Both $B$ and $\omega_{\max}$ are in good agreement with the corresponding experimental values [7, 21].

We investigate the local vibrational spectra for atoms close to the surface using two different calculational methods. Firstly, we calculate the vibrational spectra for the unrelaxed surface configuration assuming the same force constants as in the bulk crystal. This kind of approximation has been widely used in the literature [13]. Secondly, we calculate the vibrational spectra taking into account the effects of atomic relaxation and electronic rearrangement (d-band deformation). For both calculations, the continued fraction is terminated to reproduce the first 32 moments using the usual square root function [18].

In Fig. 1, we present the local vibrational spectra $g_{iz}(\omega)$ for atoms in the first (a), second (b) and third (c) layers of Ni(001), together with the spectrum (d) for the bulk atom. The corresponding results for $g_{ix}(\omega)$ are shown in Figure 2. Here, $z(x)$ denotes the atomic vibration normal (parallel) to the surface and $i$ represents the atom in the $i$-th layer. The dashed and solid curves represent the vibrational spectra obtained for the unrelaxed (force constants unchanged) and relaxed (electronic effects included) surfaces, respectively. One notices in Figs. 1 and 2 that the surface effects (bond breaking at the surface) are large for the two calculations: Even for the atoms in the third layer, the vibrational spectrum is considerably different from that for the bulk atom.

First, we discuss the vibrational spectra for the unrelaxed surface (dashed curves). As shown in Fig. 1, the surface spectral density $g_{1z}(\omega)$ is dominated by a single, prominent peak which lies below the lower peak in the bulk phonon spectrum. This peak (near $\sim 0.4\,\omega_{\max}$) has its origin in a Rayleigh surface wave as discussed by Black et al. [30]. The peak position is in good agreement with

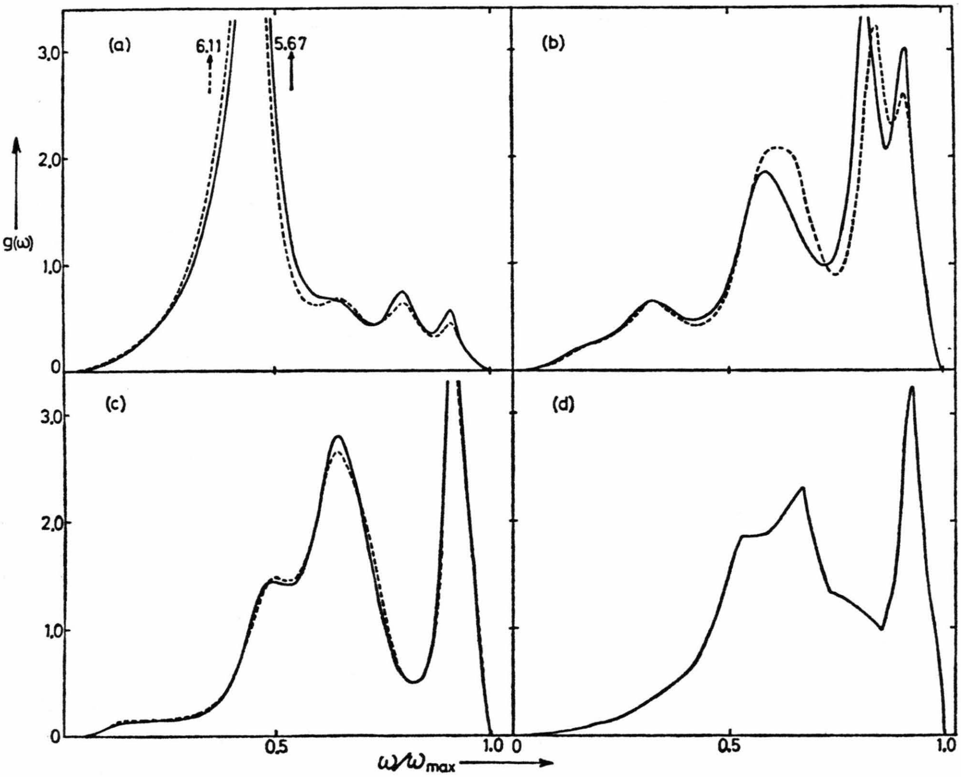

Fig. 1. Vibrational spectra $g_{iz}(\omega)$ (normal to the surface) for atoms close to the (001) surface of Ni; first (a), second (b) and third (c) layers. Bulk phonon density of states is shown in figure (d).

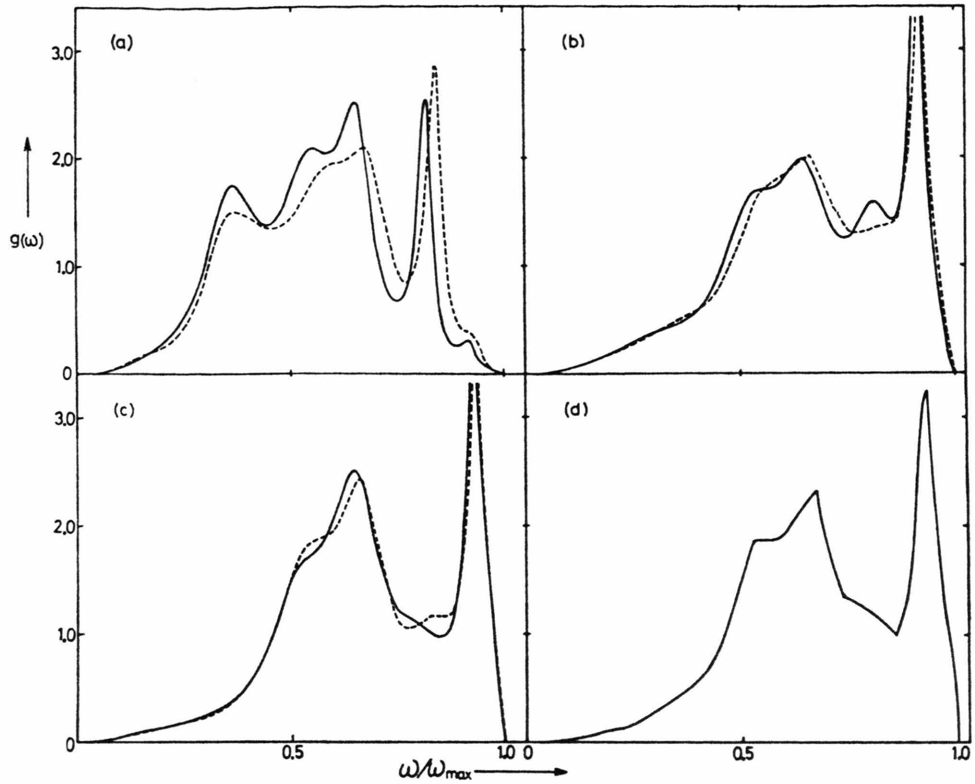

Fig. 2. Vibrational spectra $g_{ix}(\omega)$ (parallel to the surface) for atoms close to the (001) surface of Ni; first (a), second (b) and third (c) layers.

that determined by Castiel et al. [7] using the slab method. They obtained, using a 21 layer slab, the surface states near the frequency of $\sim 0.4\ \omega_{\max}$ for the fcc transition metals: The positions of surface states have been found to be almost independent of the material.

In contrast to the case of the atomic vibration normal to the surface, the phonon densities $g_{ix}(\omega)$ in Fig. 2 (parallel to the surface) have a rich and complex structure. Here, it is important to note that the phonon spectra $g_{ix}(\omega)$ in Fig. 2 differ substantially from that for the bulk atom, and a considerable softening can be seen in the $g_{1x}(\omega)$ curve, in disagreement with an intuitive expectation: It has been believed that the atomic motion parallel to the surface is quite similar to that for the bulk atom [13]. Accordingly, in the present calculation the effective Debye parameters $\theta_{\parallel}(n)$ for the atomic vibration parallel to the surface becomes considerably smaller than that for the bulk atom, as will be shown later.

Next, we discuss the electronic effects on the surface atomic vibration. As shown in Figs. 1 and 2 (solid curves), the electronic effects are important both for the atomic vibrations parallel and normal to the surface. It can be noticed from Fig. 1 that the peak position of the vibrational spectrum $g_{1z}(\omega)$ is slightly shifted upwards (towards higher frequency) when the electronic effects are taken into account. Furthermore, $g_{2z}(\omega)$ for the atom in the second layer is strongly influenced compared to the corresponding dashed (force constants unchanged) curve. This is related to the fact that the interlayer spacing between the first and second atomic layers is smaller (contraction) than that for the bulk crystal. From (14) one obtains a contraction of the surface interlayer spacing of the order of $\sim 4\%$.

Furthermore, it can be noticed from Figs. 1 and 2 that the electronic effects are larger for the vibration parallel to the surface than for the normal vibration. This results from the fact that the force constants like $\lambda_{xx}(1, 1)$ are considerably reduced compared to $\lambda_0$. Thus we come to the conclusion that the electronic effects (d-band deformation and surface relaxation) must be included in the studies of atomic vibration at transition metal surface. We have also calculated the phonon spectra for atoms close to the Pd(001) and Pt(001) surfaces and found that the qualitative features are the same as for Ni(001).

We turn now to a discussion of the surface Debye parameters. Using (8), we have calculated the Debye parameters of atoms near the (001) surface of fcc transition metals (Ni, Pd and Pt), both for the atomic vibrations normal and parallel to the surface, and presented the results in Table 2. The calculation of the Debye parameters $\theta(n)$ is of significance since they can, in principle, be measured using Mössbauer spectroscopy. One notices in Table 2 that the Debye parameters, $\theta_\perp(n)$, for atomic vibrations normal to the surface are much smaller than those for the bulk atom $\theta_{\text{bulk}}$ and considerably smaller than those for the parallel vibration $\theta_\parallel(n)$. This is in qualitative agreement with the results of LEED experiments [4–6]. However, the calculated values of $\theta_\perp(n)$ are roughly equal to $\sim 70\%$ of those for the bulk atom and are considerably larger than those ($\sim 50\%$ of $\theta_{\text{bulk}}$) obtained by LEED experiments. We think further softening of the atomic vibration can be expected from the spill out of sp electrons at the surface [9]. We are currently investigating the surface atomic vibration taking into account the effects of the spill out of sp electrons [31].

Table 2. Calculated Debye parameters for surface atoms (in K).

| | n | $\theta_{\text{bulk}}$ | $\theta_\perp$ | $\theta_\parallel$ |
|---|---|---|---|---|
| Ni(001) | 2 | 366.2 | 264.6 | 301.4 |
| | 1 | 364.2 | 259.4 | 296.3 |
| | −1 | 368.2 | 258.2 | 288.6 |
| | −2 | 381.5 | 266.5 | 291.5 |
| Pd(001) | 2 | 281.7 | 203.3 | 231.3 |
| | 1 | 280.1 | 199.3 | 227.4 |
| | −1 | 283.2 | 198.3 | 221.5 |
| | −2 | 293.4 | 204.7 | 223.6 |
| Pt(001) | 2 | 251.8 | 181.7 | 206.8 |
| | 1 | 250.4 | 178.2 | 203.3 |
| | −1 | 253.2 | 177.3 | 198.0 |
| | −2 | 262.3 | 182.9 | 199.9 |

$\theta_\perp$ ($\theta_\parallel$) denotes the Debye parameter for atomic vibration normal (parallel) to the surface.

Finally, we point out that $\theta_\parallel(n)$ can become as large as $\theta_\perp(n)$ when the electronic effects (d-band narrowing and surface relaxation) are taken into account and particular sets of parameters $qR_0$ and $pR_0$ are used. If we use $qR_0$ and $pR_0$ with $q/p \approx 1/3$*, (for instance $qR_0 = 3$ and $pR_0 = 9$), we find that $\theta_\parallel(n)$ is nearly equal to $\theta_\perp(n)$. This indicates that force constants like $\lambda_{xx}(1,1)$ can be reduced substancially due to the d-band deformation (narrowing) at the surface, and the reduction of force constants leads to a drastic softening of the atomic vibration parallel to the surface. In this respect, we refer to the experimental work by Morabito et al. [6], where the parallel and perpendicular components of the root mean square displacements were found to be equal for the Ag(100) and Ag(111) orientations.

## 4. Conclusions

We have investigated the atomic vibration at the (001) surface of the fcc transition metals Ni, Pd and Pt using a tight-binding type electronic theory coupled to the moments method. The short range repulsive energies, arising from the interatomic d-d repulsion and the increase in sp kinetic energy upon compression, are taken into account and simulated by a Born-Mayer potential. We have found that the inclusion of electronic effects (narrowing of the d-band and surface relaxation) is important for the vibrational property of surface atoms. Furthermore, it has been found that for particular transition metals the Debye parameter $\theta_\parallel(n)$ (parallel to the surface) can become as large as $\theta_\perp(n)$ (normal to the surface), in agreement with experiments.

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* The ratio $q/p$ must be less than 1/2 for giving positive $\lambda_0$ (see (8)).

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