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A.Šurda

THE FREQUENCY
DISTRIBUTION FUNCTION
OF A DISORDERED SURFACE

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DISTRIBUTION FUNCTION
OF A DISORDERED SURFACE

Локальная функция распределений собственных частот
поверхностных слоев полубесконечного кубического кристалла
со случайно адсорбированными атомами вычислена для поверх-
ности /001/. Использован метод, основанный на приближении
когерентного потенциала. Показаны результаты для различных
концентраций и масс адсорбированных атомов.

The local frequency distribution functions of the
surface layers of a semi-infinite simple cubic crystal
with randomly adsorbed impurities have been calculated
for the (001) surface. A method based on the coherent
potential approximation was used. The results are displayed
for various concentrations and masses of adsorbed impuri-
ties.

1. INTRODUCTION

A knowledge of the surface dynamics of crystals with ad-
sorbed impurities is essential for understanding the proces-
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It can hardly be assumed that the atoms on the surface are
ordered during the process of adsorption, as has been sup-
posed, nearly without exception till now, in studying the
surface effects.

The properties of a monoatomic impurity layer[3] and ad-
sorbed isolated atoms[4,5] on the (001) surface of a simple
cubic lattice were discussed previously. We have investi-
gated the properties, mainly the local density of states,
of a simple cubic crystal with the surface in which there
are isotopic impurities with an arbitrary concentration.
Then, both the former models can be considered to be, in
some aspects, only the limiting cases of our model. The
calculations are based on the CPA method which was found
convenient for our purpose, because it takes into account
the influence of the bulk correctly.

A similar problem for electrons but with inpurities che-
misorbed on the crystal curface was the subject of the
work[6].

2. FORMULATION

In this paper we shall treat a semi-infinite crystal with
a perfect ideal lattice without relaxation or reconstruction
of surface layers. All planes parallel to the surface have
the same symmetry, but the sites in the surface plane are
randomly occupied by particles with different masses. We
shall describe this crystal by the equations of motion in the
harmonic approximation

$$\sum_{\alpha'\ell'} [M_\ell \omega^2 \delta_{\alpha\alpha'} \cdot \delta_{\ell\ell'} - F_{\ell\ell'}^{\alpha\alpha'}] w_{\ell'}^\omega = 0, \tag{1}$$

Шурда А.

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$$\sum_{a'\ell'} [M_\ell \omega^2 \delta_{aa'} \cdot \delta_{\ell\ell'} - F_{\ell\ell'}^{aa'}] w_{\ell'}^\omega = 0, \tag{1}$$

or, in the matrix formulation:

$$(M\omega^2 - F)\vec{u} = 0. \tag{2}$$

In Eq. (1) lower indices specify a particular particle of the crystalline lattice, a, a' label directions of an orthogonal coordinate system. The vector u_ℓ is the displacement of an atom with the mass M_ℓ and F is the force constant matrix. It is supposed that the only nonzero elements are those which correspond to the nearest neighbour interaction.

Our case of an ideal semi-infinite crystal with the mass-disordered surface can be characterized by a force constant matrix of an ideal unperturbed infinite lattice with the exception of the surface area, where the masses of atoms can randomly acquire two values and the elements of the force constant matrix are changed due to the lower symmetry of the bounded crystal.

If we choose the z direction perpendicular to the crystal surface, the force constants depend only on the differences of lattice point coordinates in the directions parallel to the surface, $\ell_1 - \ell_1'$, $\ell_2 - \ell_2'$ and do not depend on the kind of atoms occupying particular lattice sites.

Denoting the mass of particles inside the crystal and of a part of surface particles by M_0 and of the adsorbed ones by M', their difference can be characterized by the quantity $\lambda = (M_0 - M')/M_0$. Then the mass matrix can be expressed like the difference of two matrices

$$M = M_0 - \Delta M,$$

where M_0 is the product of the unit matrix $M_0 = M_0 I$ and ΔM is a random diagonal matrix with the nonzero elements $M_0 - M'$ which correspond to the lattice points occupied by impurity atoms.

After dividing Eq. (1) by M_0 we obtain

$$[(I - \Delta)\omega^2 - \Phi]\vec{u} = 0, \tag{3}$$

where $\Delta = M_0^{-1}\Delta M$, $\Phi = M_0^{-1}F$.

We introduce the Green function defined by equation (3)

$$[(I - \Delta)\omega^2 - \Phi]G = I$$

or, equivalently, $G = [(I - \Delta)\omega^2 - \Phi]^{-1}$ and we use it to evaluate the frequancy distribution function of the lattice vibrations

$$\rho(\omega^2) = -\frac{1}{\pi}\lim_{\epsilon \to 0_+} \text{Im} \, \text{Tr}[(I - \Delta)G(\omega^2 + i\epsilon)]. \tag{4}$$

For the crystal with an infinitely large disordered surface, the distribution function (4) is equal to a configurationally averaged frequency distribution function

$$\rho(\omega^2) = -\frac{1}{\pi}\lim_{\epsilon \to 0_+} \text{Im} \, \text{Tr} <(I - \Delta)G(\tilde{\omega} + i\epsilon)>. \tag{5}$$

The matrix Δ is a random quantity and besides its explicit appearance in Eq. (5), it is contained there also implicity in the Green function.

If we consider the term $\omega^2 \Delta$ as a perturbation, we can write the Dyson equation

$$G = P + \omega^2 P \Delta G \qquad P = (I\omega^2 - \Phi)^{-1} \tag{6}$$

after averaging

$$<G> = P + \omega^2 P <\Delta G>. \tag{7}$$

Instead of an averaged Green function, it is convenient to find the self-energy Σ defined by the relation

$$<G> = P + P\Sigma <G>. \tag{8}$$

Calculating $<\Delta G>$ with the aid of Eqs. (7), (8) and inserting it into (5), one gets an expression for the frequency distribution function, where the random matrix Δ does not appear explicitly

$$\rho(\omega^2) = -\frac{1}{\pi}\lim_{\epsilon \to 0_+} \text{Im} \, \text{Tr}[(1 - \frac{\Sigma}{\omega^2}) <G(\omega^2 + i\epsilon)>]. \tag{9}$$

In the layers parallel to the surface the macroscopic disordered crystal is translationally invariant. Then, the configurationally averaged Green function $<G>$ and therefore, also the self-energy Σ depend only on the difference of x and y components of atomic coordinates. So, in these planes it is advantageous to work in the k-representation and to retain the coordinate representation only in the z-direction.

The coherent potential approximation[7] is a single-site approximation and the self-energy is supposed to be a diagonal matrix in the lower indices denoting the coordinates of a lattice site. If we denote this diagonal self-energy as $\tilde{\Sigma}$ we can define an effective Green function by

$$\tilde{G} = [I\omega^2 - \Phi - \tilde{\Sigma}]^{-1}. \tag{10}$$

In a single-site approximation the correlation among atoms is not considered and, carrying out the conditional averaging, we can suppose that the chosen point is surrounded by an effective medium characterized by the self-energy $\tilde{\Sigma}$.

Then, for the local frequency distribution function it must hold

$$c\rho_\ell^{M' \in n}(\omega^2) + (1-c)\rho_\ell^{M \in n}(\omega^2) = \rho_\ell(\omega^2). \tag{11}$$

When the atom at the point n has the mass M then $\rho_\ell^{M \in n}$ is the local frequency distribution function of the effective crystal at the point ℓ, and c is the probability that the impurity is at the point n.

Combining (6) and (9), Eq. (11) can be rewritten

$$c \, \mathrm{Tr} \, \{(I-D^{M' \in n}) \tilde{G}^{M' \in n}(\omega^2+i\epsilon)\}_{\ell\ell} \, +$$

$$+ (1-c)\mathrm{Tr}\{(I-D^{M \in n})\tilde{G}^{M \in n}(\omega^2+i\epsilon)\}_{\ell\ell} = \mathrm{Tr}\{(I - \frac{\tilde{\Sigma}}{\omega^2})\tilde{G}(\omega^2+i\epsilon)\}_{\ell\ell} \tag{12}$$

$$D_{ij}^{M \in n} = \frac{\tilde{\Sigma}_{ii}}{\omega^2} \, \delta_{ij} - (\frac{\tilde{\Sigma}_{nn}}{\omega^2} - \lambda)\delta_{ni}\,\delta_{nj} \, .$$

When the lattice points ℓ and n are the bulk ones, the equality $\tilde{\Sigma}_{\ell\ell} = 0$ follows from Eq. (12), since then $c=0$. When the point n is at the surface of the crystal for any ℓ we get the Sove-Taylor equation [8]

$$\tilde{\Sigma}(1-(\lambda\omega^2 - \tilde{\Sigma})G_{nn}) = c\lambda\omega^2. \tag{13}$$

The same condition also follows from the requirement that the averaged scattering matrix for a surface atom in the single site approximation is equal to zero.

Solving Eqs. (10) and (13), we get the unknown matrices $\tilde{G}$ and $\tilde{\Sigma}$. The frequency distribution function is given by the right-hand side of Eq. (12).

We have solved the above-mentioned problem for a simple cubic lattice with the lattice constant a and the (001) surface. (The origin of the coordinate system is in the surgace plane, and z-components of the crystal atoms are positive numbers). If we consider only nearest neighbour interactions, the submatrices $F_{\ell\ell'}$ of the force constant matrix,

F are diagonal for the cubic lattice and they are characterized by two independent quantities - a central force constant α and a non-central one, denoted by β [9]. At the surface due to the lower lattice symmetry, they have the following form [10].

$$F_{\pm i,0} = -\begin{pmatrix} \alpha & 0 & \pm\delta \\ 0 & \beta & 0 \\ \mp\delta & 0 & \beta \end{pmatrix} \quad F_{\pm j,0} = -\begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & \pm\delta \\ 0 & \mp\delta & \beta \end{pmatrix}$$

$$F_{k,0} = -\begin{pmatrix} \beta & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix} \quad F_{0,0} = \begin{pmatrix} 2\alpha+3\beta & 0 & 0 \\ 0 & 2\alpha+3\beta & 0 \\ 0 & 0 & \alpha+4\beta \end{pmatrix}$$

$$i \equiv (1,0,0) \quad j \equiv (0,1,0) \quad k \equiv (0,0,1) \quad 2\delta = -\beta$$

The surface symmetry of an averaged crystal is the same as the symmetry of a pure surface, and consequently, the effective Green functions have the same form as the force constant matrix. In this case the Green function $\tilde{G}_{00}$ and the self energy $\tilde{\Sigma}$ are diagonal matrices 3x3, and only two non-zero elements are different

$$\tilde{G}_{00} \equiv \begin{pmatrix} \tilde{G}_{00}^{11} & 0 & 0 \\ 0 & \tilde{G}_{00}^{11} & 0 \\ 0 & 0 & \tilde{G}_{00}^{33} \end{pmatrix} \quad \tilde{\Sigma} \equiv \begin{pmatrix} \tilde{\Sigma}_1 & 0 & 0 \\ 0 & \tilde{\Sigma}_1 & 0 \\ 0 & 0 & \tilde{\Sigma}_3 \end{pmatrix}$$

Then, the matrix equation (13) can be decomposed into two algebraic equations for particular directions, where every element of the matrix $\tilde{G}_{00}$ contains both elements of the self-energy matrix $\tilde{\Sigma}_1$, $\tilde{\Sigma}_3$ is a complicated manner.

Evaluating the Green function $\tilde{G}_{00}$, it is useful to take the advantage of the translational symmetry in the planes perpendicular to the axis z. After performing a two-dimensional Fourier transformation in directions parallel to the surface, the whole problem becomes one-dimensional. The

Green function is parametrically dependent on the vector of 2-dimensional Brillouin zone and the z-component of space coordinates. If the Green function of an ideal crystal with surface is known, we can treat the self-energy $\tilde{\Sigma}$ and the element of rotationally invariant force constant matrix δ as diagonal and nondiagonal perturbations, respectively. Then, the Dyson equation leads to the following terms [11]:

$$\tilde{G}_{00}^{11} = \tilde{G}_{00}^{22} = \frac{1}{4\pi^2} \int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi} [\, P_{00}^{11}(\phi_1,\phi_2) + 4\frac{\delta^2}{M_0^2}\sin^2\phi_1 \, P_{00}^{11^2}(\phi_1,\phi_2)\times$$

$$\times \frac{P_{00}^{33}(\phi_1,\phi_2)}{1 - P_{00}^{33}(\phi_1,\phi_2)Q_{00}(\phi_1,\phi_2)}\, d\phi_1 d\phi_2 \qquad (14)$$

$$\tilde{G}_{00}^{33} = \frac{1}{4\pi^2}\int\limits_{-\pi}^{\pi}\int\limits_{-\pi}^{\pi} \frac{P_{00}^{33}(\phi_1,\phi_2)}{1 - P_{00}(\phi_1,\phi_2)Q_{00}(\phi_1,\phi_2)}\, d\phi_1 d\phi_2$$

$$Q_{00}(\phi_1,\phi_2) = 4\frac{\delta^2}{M_0^2}[\,\sin^2\phi_1 P_{00}^{11}(\phi_1,\phi_2) + \sin^2\phi_2 P_{00}^{22}(\phi_1,\phi_2),$$

$P(\phi_1,\phi_2)$ is the two-dimensional Fourier transform of the semi-infinite crystal Green function with diagonal force constant matrix $(\delta=0)$

$$P_{00}^{11}(\phi_1,\phi_2) = \frac{1}{1 - \tilde{\Sigma}_1 - t}$$

$$t = \begin{cases} \overline{\xi + \sqrt{(\xi^2 - 1)}} & \xi > 1 \\ \xi - i\sqrt{1-\xi^2} & |\xi| < 1 \\ \overline{\xi - \sqrt{(\xi^2 - 1)}} & \xi < -1 \end{cases} \qquad (15)$$

$$\xi = \gamma + 2 - \gamma\cos\phi_1 - \cos\phi_2 - \frac{\tilde{\omega}}{2},$$

where $\gamma = a/\beta$ and we have put $M/\beta = 1$;

$$P_{00}^{33}(\phi_1,\phi_2) = \frac{1}{\gamma - \tilde{\Sigma}_3 - \gamma t} \qquad (16)$$

But in this case $\xi = \frac{1}{\gamma}(\gamma + 2 - \cos\phi_1 - \cos\phi_2 - \frac{\omega^2}{2})$.

If the Green function $\tilde{G}$ is given by (14), (15), (16), the equation (13) for the self-energy is an integral equation, and it is necessary to solve it by successive iterations, in general. But this method does not converge in many frequency regions, and for every region it is necessary to choose different forms of equation (13) as a basis for the iteration process.

The best and always converging iterative procedure appears to be that of Chen [12], where Eq. (13) is cast into the form

$$\tilde{\Sigma}^{(n+1)} = \tilde{\Sigma}^{(n)} + <T_{00}^{(n)}>(I + \tilde{G}^{(n)}<T_{00}^{(n)}>)^{-1} \qquad (17)$$

where we attached the superscript $(n+1)$ to the left-hand side of Eq. (17) and the superscript (n) to the right-hand side in order to outline the iteration scheme of our calculation

$$\tilde{G}^{(n)} = [\,\omega^2 I - \Phi - \tilde{\Sigma}^{(n)}\,]^{-1}$$

$<T_{00}^{(n)}>$ is the averaged T-matrix on a surface site embedded in an effective medium, Green function of which has the self-energy $\tilde{\Sigma}^{(n)}$.

It can be easily seen that if $\tilde{\Sigma}^{(n)} = <\Delta>\omega^2$, $\tilde{\Sigma}^{(n+1)}$ is the self-energy in the average T-matrix approximation. If $\tilde{\Sigma}^{(n+1)} = \tilde{\Sigma}^{(n)}$, the iterative procedure is finished and $<T_{00}> = 0$, i.e., $\tilde{\Sigma}^{(n)}$ is the CPA self-energy.

3. RESULTS

In our calculation we put the ratio γ of central and noncentral elements of the force constant matrix equal to 3 and considered the masses of impurity atoms twice heavier or twice lighter than the mass of a bulk atom. The concentration of impurities was chosen to be $c = 0, 0.2, 0.5, 0.8$ 1. We put δ equal to zero and therefore we neglected the influence of Rayleigh's surface waves on the frequency distribution function (FDF). It can be shown [13] that this approximation has only a small effect on the shape of FDF, and the number and positions of singularities and peaks remain untouched. For our model the local FDF (LFDF) of every surface layer depends on the polarization of vibrations.

At first let us notice the results of calculations for the polarization parallel to the surface. LFDF for various
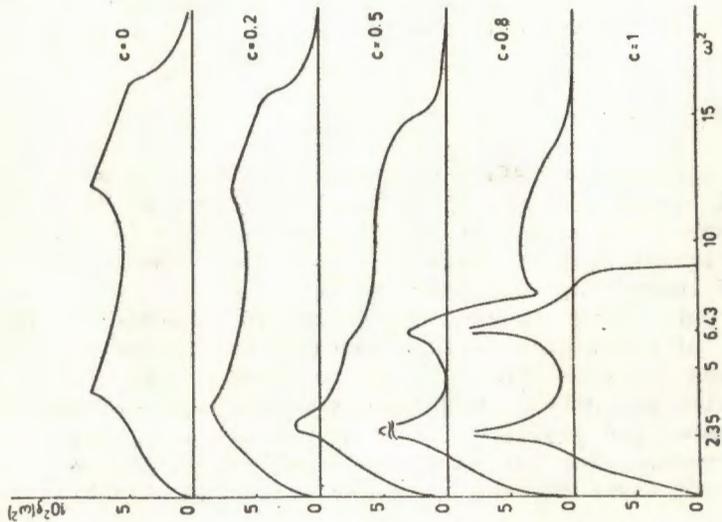
Fig. 2. LFDF of the surface layer for various concentrations of impurities with masses $M' = M_0/2$. The polarization of atomic displacements is parallel to the surface.

Fig. 1. LFDF of the surface layer for various concentrations of impurities with masses $M' = 2M_0$. The polarization of atomic displacements is parallel to the surface.
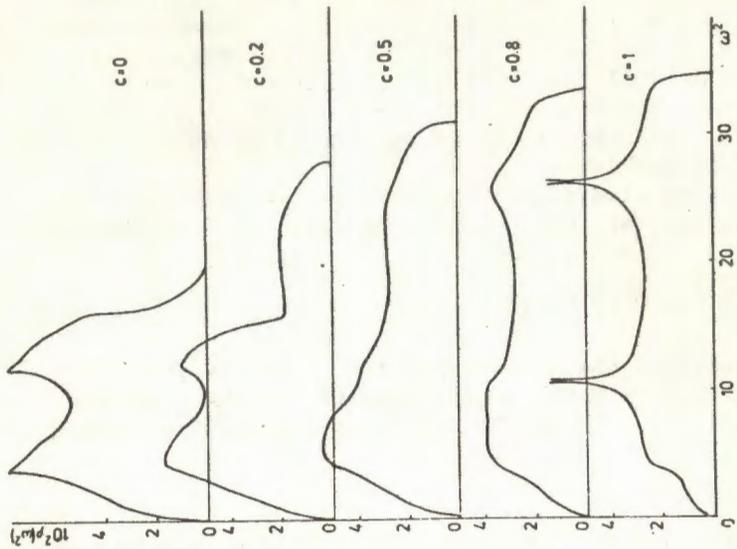
Fig. 3. LFDF's of four layers in the surface area of a pure semi-infinite crystal. (The solid line is the surface layer, two dots and the dashed line on the first layer, dot and dash line an second layer, the dashed line is the third layer under the surface). The polarization of atomic displacements is parallel to the surface.

Fig. 4. LFDF's of four layer in the surface area of a semi-infinite crystal with an adsorbed monolayer. (The full line is surface layer, two dots and dash line are the first layer, the dashed is the second layer, the dot and the dash line are the third layer under the surface). The polarization of atomic displacements is perpendicular to the surface.
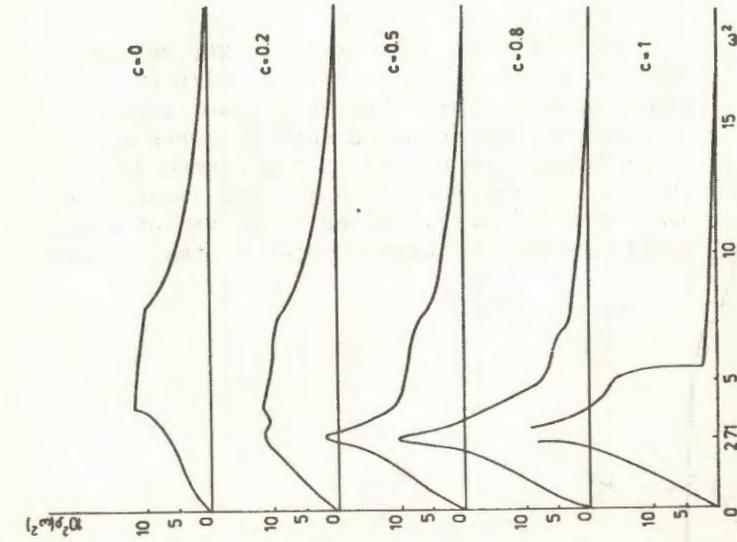
Fig. 5. LFDF of the surface layer for various concentrations of impurities with masses $M' = 2M_0$. The polarizations of atomic displacements is perpendicular to the surface.

Fig. 6. LFDF of the surface layer for various concentrations of impurities with masses $M' = M_0/2$. The polarizations of atomic displacements is perpendicular to the surface.

concentrations of impurities with the twice as heavy masses (half as heavy masses) as the masses of the bulk crystal atoms are in Fig. 1 (Fig. 2). When the surface of the crystal is covered with a monoatomic layer of adsorbed atoms, the surface LFDF has main features of a two-dimensional FDF with two logarithmic singularities and a small contribution from the bulk at the beginning and at the end of the spectrum. Increasing the concentration of the bulk atoms in the surface layer, we can see a successive transition to the spectrum of a semi-infinite crystal with the clean surface displaying two singularities in the slope. The heavier atoms decrease and the lighter ones increase the maximum frequency of surface vibrations. The presence of the surface has an appreciable influence only on the dynamics of surface atoms. LFDF of the planes near the surface differs only slightly from the distribution function of an unbounded crystal. It can be seen from Fig. 3, where LFDF of the surface layer and of the first, second and third layers under the surface

Fig. 7. LFDF of the first layer under the surface for various concentrations of impurities with masses $M' = M_0/2$. The polarizations of atomic displacements is perpendicular to the surface.
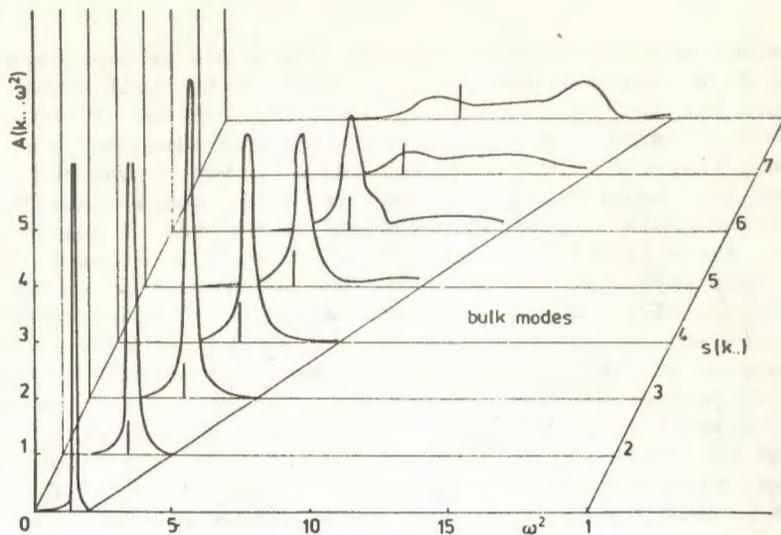
Fig. 8. Spectral density of the surface layer for various vectors $k_{\parallel}$, parallel to the surface. The polarization of atomic dusplacements is parallel to the surface. The impurity concentrations $c=0.8$, $M'=2M_0$, $\rho(k_{\parallel})=4-(3\cos\phi_x+\cos\phi_y)$, $k=(\phi_x,\phi_y)/a$. The short bars denote δ-functions of the spectral density of the semi-infinite crystal with a monoatomic surface layer.

is shown. Similar fast convergence to FDF of an infinite crystal is also observable for the layers under the disordered surface.

Another situation is for the vibration polarized in the perpendicular direction to the surface. There, due to the stronger central component of interatomic forces, the influence of the surface is more distinct also in the deeper layers. As is shown in Fig. 4, for $M'=2M_0$ LFDF only in the 3rd layer has the shape resembling FDF of an ideal crystal. Logarithmic singularity at $\omega^2=2.71$ which has the origin in the existence of localized surface vibrations remains for every layer, though its weight is decreased with the depth. LFDF of the first layer reaches the maximum in the area, where the values of the surface LFDF are small.

When the polarizations of vibrations are perpendicular to the surface, we can also observe a stronger influence of bulk atoms on the dynamics of surface atoms. That is displayed by distinct tails at the end of the spectrum, as

is shown in Fig. 5, and at the beginning of the spectrum, as in Fig. 6. LFDF of layers in the neighbourhood of the surface are also dependent on the concentration of adsorbed atoms. Their influence on LFDF of the 1st layer for various concentrations of impurities is shown in Fig. 7.

The localized surface states appear above or below the band of bulk energies of a semi-infinite crystal with a surface monolayer, and hence, their spectral density at given vector k of the surface Brillouin zome is a δ-function.

The case, when the surface layer contains 80% of adsorbed heavier atoms, is shown in Fig. 8. Now, the localized states can occur below the energy band too, but the original sharp lines are broadened mainly for the higher frequencies. The dispersion relation of these modes are changed slightly, too. The δ-functions for the monoatomic surface layer (denoted by short bars) are shifted against the maxima of the plotted spectral densities.

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