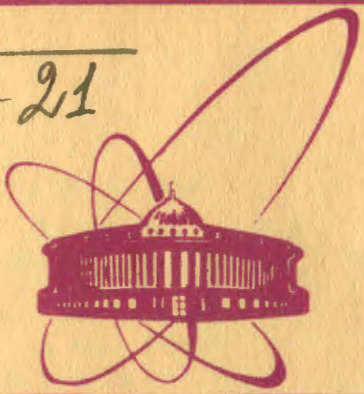

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E17-81-635

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LOCAL FREQUENCY DISTRIBUTION FUNCTION OF A CRYSTAL WITH ADSORBED ATOMS.

Part II

Submitted to "Czechoslovak Journal of Physics B"

1981

1. INTRODUCTION

In the previous paper[1], the formulae for local frequency distribution functions (LFDF) of the atoms in a semi-infinite simple cubic lattice with randomly adsorbed atoms were derived. The procedure was based on the CPA method. The adsorbed atoms were distributed on the (001) surface so that each adatom was bounded only to the one surface atom. The interaction between the adatoms was neglected. In order to investigate the influence of this interaction on LFDF's the Green function of an infinite crystal with a planar defect was derived, too. A limiting case of that model is just a semi-infinite crystal covered by an adsorbed monolayer, i.e., in terms of CPA, a crystal surface with the concentration of the adatoms equal to one ($c = 1$).

For the model discussed in ref.[1], we first present in this paper a detailed analysis of the behaviour of LFDF's of the atoms for the concentration of adatoms equal to one. Using the formulae of paper[1], we give in the second part of this paper, results of numerically calculated LFDF's of the adsorbed atoms as well as of the surface atoms for different concentrations, including the case $c = 1$, and for different kinds of adsorbed atoms. The frequencies of the modes localized at the surface are also calculated.

2. THE GREEN FUNCTION OF A SEMI-INFINITE CRYSTAL WITH AN ADSORBED MONOLAYER

LFDF's of the atoms are given by the imaginary part of the diagonal elements of the Green function matrix $\hat{G}$. Its elements may be obtained by inversion of a certain matrix $\hat{D}$, i.e., $\hat{G} = \hat{D}^{-1}$ the elements of which are matrices presenting the structure of the atomic layers and the interaction between layers in ref.[1] (compare with the equation (9)).

The model used in the previous and also in the present work is a harmonic simple cubic lattice with the (001) surface and with interactions (by means of central α and non-central β force constants between the nearest neighbours only. Further, it is assumed that each of the surface atoms bounds one adsorbed atom by central α' and non-central β' force constants

(the adatoms form a layer). The interaction between the adatoms is not taken into account. The mass of the bulk and the surface atoms is M_0 the mass of the adatoms is M'. Let the origin of the coordinate system be in the surface plane so that the z-components of the coordinates of the surface atoms are equal to 0 and those of the adsorbed atoms are equal to 1. Because we have studied the surface with an adsorbed layer, we use a method for the determination of $\hat{G}=\hat{D}^{-1}$ more simple than that given in ref.[1].

The translational periodicity parallel to the surface in all of the layers leads to the following relation:

$$\hat{D} \Rightarrow \hat{D}(\phi_1 \phi_2) = \begin{bmatrix} \hat{D}^{11}(\phi_1 \phi_2) & 0 & 0 \\ 0 & \hat{D}^{11}(\phi_1 \phi_2) & 0 \\ 0 & 0 & \hat{D}^{33}(\phi_1 \phi_2) \end{bmatrix}$$

where the matrices $\hat{D}^{\kappa\kappa}(\phi_1 \phi_2)$ are analogous to the matrix describing vibrations of a linear chain with a defect at its end. They are independent of each other and have the following form

$$\hat{D}^{\kappa\kappa}(\phi_1 \phi_2) = \begin{array}{c|cccc|c} & \vdots & & \vdots & & \vdots \\ \cdots & M_0\omega^2 - F^{\kappa\kappa}_{-2-2} & \gamma^{\kappa} & 0 & 0 & -2 \\ & \gamma^{\kappa} & M_0\omega^2 - F^{\kappa\kappa}_{-1-1} & \gamma^{\kappa} & 0 & -1 \\ & 0 & \gamma^{\kappa} & M_0\omega^2 - F^{\kappa\kappa}_{00} & \gamma'^{\kappa} & 0 \\ \hline & 0 & 0 & \gamma'^{\kappa} & M'\omega^2 - \gamma'^{\kappa} & 1 \\ \cdots & -2 & -1 & 0 & 1 & \end{array} \qquad (1)$$

where

$$F_{ii}^{\kappa\kappa} = F_{ii}^{\kappa\kappa}(\phi_1\phi_2) = 2\beta OM^{\kappa} + 2\gamma^{\kappa}, \qquad \text{for } i = -1, -2, -3, \ldots$$

$$F_{00}^{\kappa\kappa} = F_{00}^{\kappa\kappa}(\phi_1\phi_2) = 2\beta OM^{\kappa} + \gamma^{\kappa} + \gamma^{\kappa} = F_{-1-1} + \gamma'^{\kappa} - \gamma^{\kappa}$$

with $\gamma^1 = \gamma^2 = \beta$, $\gamma'^1 = \gamma'^2 = \beta'$, $\gamma^3 = \alpha$, $\gamma'^3 = \alpha'$. The quantities OM^{κ} satisfy the relations

$$\begin{aligned} OM^1 &= OM^2 = \alpha/\beta\,(1 - \cos\phi_1) + (1 - \cos\phi_2), \\ OM^3 &= 2 - \cos\phi_1 - \cos\phi_2, \\ \phi_1 &= k_1 a, \quad \phi_2 = k_2 a, \end{aligned} \tag{2}$$

where the vector components k_1, k_2 are associated with the two-dimensional Brillouin zone and a is the lattice parameter.

In order to write the elements $G_{\ell\ell}^{\kappa\kappa} = \{(D^{\kappa\kappa})_{\ell\ell}^{-1}\}$, it is convenient first to separate the displacement of the adatoms and the displacements of the substrate atoms. This procedure reduces (1) to a quasidiagonal blok matrix. The inversion of this block matrix leads to

$$G_{11}^{\kappa\kappa}(\phi_1\phi_2, \omega^2) = \frac{1}{M'} \; \frac{1 - \gamma'^{\kappa} P_{00}^{\kappa\kappa}}{(\omega^2 - \gamma'^{\kappa}/M')(1 - V_{00}^{\kappa\kappa} P_{00}^{\kappa\kappa})} \tag{3}$$

for the adsorbed atoms and to

$$G_{ii}^{\kappa\kappa}(\phi_1\phi_2, \omega^2) = \{[M_0\omega^2 - 2\beta OM^{\kappa})\hat{1} - \hat{A}^{\kappa\kappa} - \hat{V}^{\kappa\kappa}]^{-1}\}_{ii} \tag{4}$$

for the surface and bulk atoms ($i = 0, -1, -2, -3, \ldots$). The matrix $\hat{A}^{\kappa\kappa}$ is the force constant matrix of an ideal semi-infinite linear chain with the free end (in (1) we set $M_0 = M' = OM' = \gamma'^{\kappa} = 0$). Its Green function is defined as

$$\hat{P}^{\kappa\kappa} = \hat{P}^{\kappa\kappa}(\phi_1\phi_2, \omega^2) = [(M_0\omega^2 - 2\beta OM^{\kappa})\hat{1} - \hat{A}^{\kappa\kappa}]^{-1} \tag{5}$$

and its (00) element, which appears in (3), can be calculated. One gets

$$\lim_{\epsilon\to 0^+} P_{00}^{\kappa\kappa} = \lim_{\epsilon\to 0^+} P_{00}^{\kappa\kappa}(\phi_1\phi_2, \omega^2 + i\epsilon) = \frac{1}{\gamma^{\kappa}} \; \frac{1}{1 - t_{\kappa}} \tag{6}$$

with

$$t_{\kappa} = \begin{cases} \xi_{\kappa} + \sqrt{\xi_{\kappa}^2 - 1} & \text{for } \xi_{\kappa} > 1 \\ \xi_{\kappa} - i\sqrt{1 - \xi_{\kappa}^2} & \text{for } |\xi_{\kappa}| < 1 \\ \xi_{\kappa} - \sqrt{\xi_{\kappa}^2 - 1} & \text{for } \xi_{\kappa} < -1 \end{cases}$$

where

$$\xi_1 = \xi_2 = OM^1 + 1 - M_0\omega^2/2\beta,$$

$$\xi_3 = \beta/\alpha(OM^3 - M_0\omega^2/2\beta) + 1$$

and where OM^κ is given by (2). And finally, the matrix $\hat{V}^{\kappa\kappa}$ is the perturbation produced by the adsorbed layer. It has only one nonzero element

$$V_{00}^{\kappa\kappa} = \gamma'^{\kappa} \frac{\omega^2}{\omega^2 - \delta_\kappa} \tag{7}$$

with $\delta_\kappa = \gamma'^{\kappa}/M^\kappa$. Therefore, using (5), the Green function (4) can be also rewritten in the explicit form as follows:

$$G_{ii}^{\kappa\kappa}(\phi_1\phi_2, \omega^2) = P_{ii}^{\kappa\kappa} + \frac{(P_{i0}^{\kappa\kappa})^2 V_{00}^{\kappa\kappa}}{1 - V_{00}^{\kappa\kappa} P_{00}^{\kappa\kappa}} \tag{8}$$

with $V_{00}^{\kappa\kappa}$ defined by (7).

Now, in view of (3) and (8) the local frequency distribution function of the surface atoms and of the atoms of other bulk layers can be expressed as

$$g_i(\omega^2) = -\frac{M}{\pi} \sum_{\substack{\phi_1\phi_2 \\ \kappa}} \lim_{\epsilon\to 0^+} \mathrm{Im}\left[P_{ii}^{\kappa\kappa} + \frac{(P_{0i}^{\kappa\kappa})^2 V_{00}^{\kappa\kappa}}{1 - V_{00}^{\kappa\kappa} P_{00}^{\kappa\kappa}}\right] =$$

$$= \sum_\kappa g_{i,\,\mathrm{clean}}^{\kappa}(\omega^2) + \sum_\kappa \Delta g_i^\kappa(\omega^2), i = 0, -1, -2, -3, \ldots \tag{9}$$

and that of the adsorbed atoms as

$$g_1(\omega^2) = -\frac{1}{\pi} \sum_{\substack{\phi_1\phi_2 \\ \kappa}} \lim_{\epsilon\to 0^+} \mathrm{Im} \frac{1 - \gamma'^{\kappa} P^{\kappa\kappa}}{(\omega^2 - \delta_\kappa)(1 - V_{00}^{\kappa\kappa} P_{00}^{\kappa\kappa})} \tag{10}$$

or, after some simple algebra, in the equivalent form

$$g_1(\omega^2) = \sum_\kappa \left(\frac{\delta_\kappa}{\omega^2 - \delta_\kappa}\right)^2 g_0^\kappa(\omega^2), \tag{11}$$

where in accordance with (9) $g_0^\kappa = g_{0,\,\mathrm{clean}}^{\kappa} + \Delta g_0^\kappa$. The relation (11) is valid for all $\omega^2 \neq \delta_\kappa$. From (11) one sees that LFDF's of the adsorbed atoms have the profile of the surface LFDF's given by (9), modified by $[\delta_\kappa/(\omega^2 - \delta_\kappa)]^2$. The first term on the right-hand side of (9) describes LFDF's of the crystal atoms with a clean surface (the free surface). The second term represents the contribution from the defect $\hat{V}^{\kappa\kappa}$. From (9) and (11) it is seen that singularities and peaks in LFDF's of the

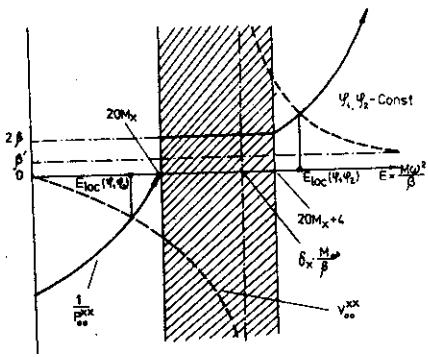


Fig. 1. The graphical solution of (12) for $\kappa=1\equiv x$ and for the dimensionalless frequency $E=M_0\omega^2/\beta$. The solid line corresponds to $[\lim_{\epsilon\to 0^+} \mathrm{Re} P^{xx}_{00}]^{-1}$, the dashed line corresponds to $\lim_{\epsilon\to 0^+} \mathrm{Re}\, V^{xx}_{00}$.

atoms produced by an adsorbed layer may occur only at frequencies $\omega^2=\omega^2_{loc}(\phi_1\phi_2)$ for which

$$\lim_{\epsilon\to 0+} \mathrm{Re}(1 - V^{\kappa\kappa}_{00} P^{\kappa\kappa}_{00}) = 0, \qquad \phi_1\ \phi_2 = \text{const.} \tag{12}$$

The graphical solution of this equation is presented in Fig. 1. The frequency $\omega^2=\delta_\kappa$ is the vibration frequency of the isolated atom bounded to the non-move substrate. For this frequency $g^\kappa_0(\delta_\kappa)=0$ and $g^\kappa_1(\delta_\kappa)\neq 0, \neq\infty$.

(i) Localized surface states

For ω^2 satisfying

$$2OM^\kappa + 4\gamma^* < M_0\omega^2/\beta < 2OM^\kappa$$

$$\gamma^* = 1 \quad \text{for} \quad \kappa = 1,2$$

$$\gamma^* = \alpha/\beta \quad \text{for} \quad \kappa = 3,$$

for a given value of ϕ_1 and ϕ_2, the Green function $P^{\kappa\kappa}_{00}$ is real in the limit $\epsilon\to 0^+$ (see (6)). Therefore the first term of (9) vanishes. The second term is zero except at the frequencies $\omega^2=\omega^2_{loc}(\phi_1\phi_2)$ (the condition (12)). These frequencies contribute by a delta function to $\Delta g^\kappa_1(\omega^2,\phi_1\phi_2)$. Replacing in (9) and (10) the summation over ϕ_1,ϕ_2 by integration we receive

$$\Delta g^\kappa_1(\omega^2) \sim \int_0^{OM^\kappa_{max}} \delta[\omega^2 - \omega^2_{loc}(\phi_1\ \phi_2)]\, z(OM^\kappa)\, d\,OM^\kappa. \tag{13}$$

The functions $z(OM^\kappa)$ are the frequency distribution functions of the square lattice with the dispersion laws (2) and those are known[2]. From (13) it is seen that in $g^\kappa_1(\omega^2)$ the contribution typical for the two-dimensional square lattice density must appear (the logarithmic singularities, the discontinuities in $dz(\omega^2)/d\omega^2$). Owing to the delta function the profile of $z(\omega^2)$ will be modulated.

(ii) Resonance states

For given values of ϕ_1 and ϕ_2, the Green function $P^{\kappa\kappa}_{00}$ is complex in the limit $\epsilon\to 0^+$, for ω^2 from the interval $M_0\omega^2/\beta\in(2OM^\kappa, 2OM^\kappa+4\gamma^*)$.

Therefore both the terms of (9) are nonzero. In addition, if condition (12) is valid, the denominator in (9) shows a resonance behaviour and resonance levels may occur. For frequencies near the resonance frequency ω_R^2, Δg_i^κ may be approximated by

$$\Delta g_i^\kappa(\omega^2) \sim \int_0^{OM^\kappa_{max}} s_i^\kappa(\omega^2) \frac{\Gamma}{(\omega^2-\omega_R^2)^2+\Gamma^2} z(OM^\kappa)\, dOM^\kappa,$$

where $s_i^\kappa(\omega^2) = V_{00}^{\kappa\kappa}\, \mathrm{Re}(P_{i0}^{\kappa\kappa})^2/(\partial\, \mathrm{Re}D/\partial\omega^2)$ and $D = 1 - V_{00}^{\kappa\kappa} P_{00}^{\kappa\kappa}$. The width of the resonance $\Gamma = \mathrm{Im}D/(\partial\, \mathrm{Re}D/\partial\omega^2)\big|_{\omega^2=\omega_R^2}$ is given by

$$\Gamma = \frac{(\omega_R^2)^2 \gamma'^\kappa}{2\delta_\kappa \gamma^\kappa} \sqrt{\frac{2OM^\kappa + 4\gamma^* - M_0 \omega_R^2/\beta}{-2OM^\kappa + M_0 \omega_R^2/\beta}}$$

whereas the condition (12) yields $\omega_R^2 > \delta_\kappa$ and

$$\omega_R^2 = 2\frac{\delta_\kappa}{2 - M'\delta_\kappa/\gamma^\kappa}, \qquad (14)$$

i.e., ω_R^2 in this case is not dependent on ϕ_1 and ϕ_2. One sees that the resonance is well-defined if $M_0\omega_R^2/\beta = 2OM^\kappa + 4\gamma^*$. Further one sees that the known Lorentzian-type of the resonance is "smeared cut" by the factor $s_i^\kappa(\omega_R^2)$. For the surface atoms it is equal to

$$s_0^\kappa(\omega_R^2) = \frac{\gamma'^\kappa \omega_R^4}{(2\gamma^\kappa)^2 \delta_\kappa}\left[\frac{2OM^\kappa + 2\gamma^* - M_0\omega_R^2/\beta}{2OM^\kappa - M_0\omega_R^2/\beta}\right].$$

3. RESULTS AND DISCUSSION

In this section we have shown the numerically computed frequency of the localized modes (12) and the local frequency distribution function (LFDF) of the surface ($g_0 \equiv g_{sur}$) and of the adsorbed atoms ($g_1 \equiv g_{ad}$) for a fixed value of M'/M_0 and variable δ_κ. In our calculation we have put $\alpha/\beta = 3$ and $M_0/\beta = 1$. Therefore the frequencies of the lattice with the clean surface ($\gamma'^\kappa = M' = 0$) lie in the interval $\langle 0,20\rangle$, i.e., in the region $\omega^2 > 20$ only the localized states contribute to the spectrum. The main interest is focused on the case corresponding to the hydrogen on a crystal surface for which the neutron scattering experiments are known. In all numerically computed LFDF's the lines correspond to the concentration of adsorbed atoms $c = 1$ (see (9-11)), the dashed lines correspond to $= 0.25$ (in/1/ see (7-8)).

Table

The localized mode frequencies (12) and resonance frequency (14) for various and the mass ratios: (a) $M'/M_0=0.017$, (b) $M'/M_0=0.5$. $OM^x=2$ and $OM^x=6$ correspond to the logarithmic singularities of the function $z(\omega^2)$, $OM^x=0$ and $OM^x=8$ corresponds to the discontinuities of the derivation of the function $z(\omega^2)$.

a)

β'/β	δ_x	$\omega^2_{loc}(\phi_1,\phi_2)$							ω_R^2
		$OM^x=2$	$OM^x=6$	$OM^x=8$	$OM^x=0$	$OM^x=2$	$OM^x=6$	$OM^x=8$	
0.51	30.75	3.99	11.92	15.81	31.28	31.37	31.63	31.9	-
0.34	20.75	3.99	11.85	15.49	21.12	21.21	21.63	22.27	-
0.30	18.10	3.99	11.79	15.09	18.42	18.52	19.08	10.33	-
0.23	14.00	3.99	11.46	13.20	14.25	14.37	-	-	15.85
0.17	10.00	3.99	9.52	9.8	10.2	10.34	-	-	10.91
0.02	1.1	1.1	1.1	1.1	-	-	-	-	1.11

b)

β'/β	δ_x	$\omega^2_{loc}(\phi_1,\phi_2)$							ω_R^2
		$OM^x=2$	$OM^x=6$	$OM^x=8$	$OM^x=0$	$OM^x=2$	$OM^x=6$	$OM^x=8$	
10.1	20.2	2.92	7.23	8.91	30.65	32.2	36.08	38.38	-
0.55	1.1	0.96	1.06	1.07	-	-	-	-	1.52

(i) Modes polarized parallel to the surface ($\kappa = 1 \equiv x$)

The solution of (12) forms the band with respect to ϕ_1 and ϕ_2. Results for a few value of OM^x (see the relations (2)) are presented in Tables a, b. It is obvious (see Fig.1) that the resonance state may rise, for a given value of ϕ_1 and ϕ_2, only if the localized mode does not exist in the high frequency region. From (12) the dependence of δ_x versus $\omega^2_{loc}(\phi_1\phi_2)$ can be also determined for fixed values of M'/M_0 and OM^x. The results are shown in Fig.2 (compare with Tables).

When $\delta_x > 20$ and $M'/M_0 = 0.017$, then in the frequency interval $\langle 0,20\rangle$ the presence of the adatoms evokes only sharp singularities at the points $\omega^2 = 4$ and $\omega^2 = 12$ (compare with Table a

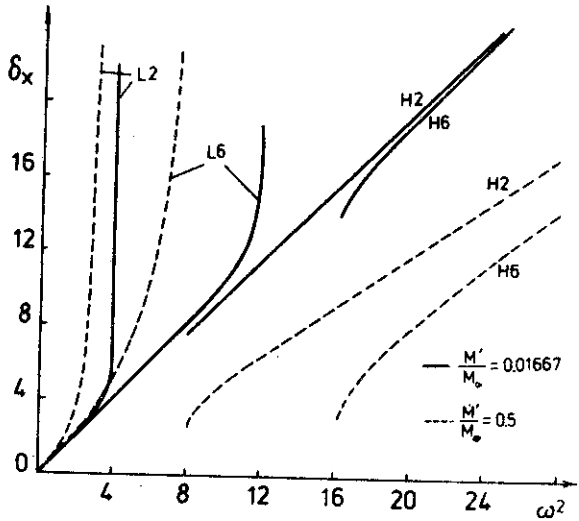


Fig.2. The relation between the parameter δ_x and the localized mode frequencies $\omega^2 = \omega^2_{loc}(\phi_1\ \phi_2)$ for the cases $OM^x=2$ and $OM^x=6$. By the letters L and H we indicate the low frequency and the high frequency localized mode, respectively.

case is not shown. The contribution in the region $\omega^2>20$ has the shape of the modified two-dimensional frequency distribution function.

Figure 3 shows the typical behaviour of g^x_{sur} for δ_x from the region $<0,20>$. In this case, for $c=1$, g^x_{sur} has only three

and with Fig. 2), otherwise the surface LFDF is roughly similar to LFDF of the clean surface (see below, Fig.7) and therefore this

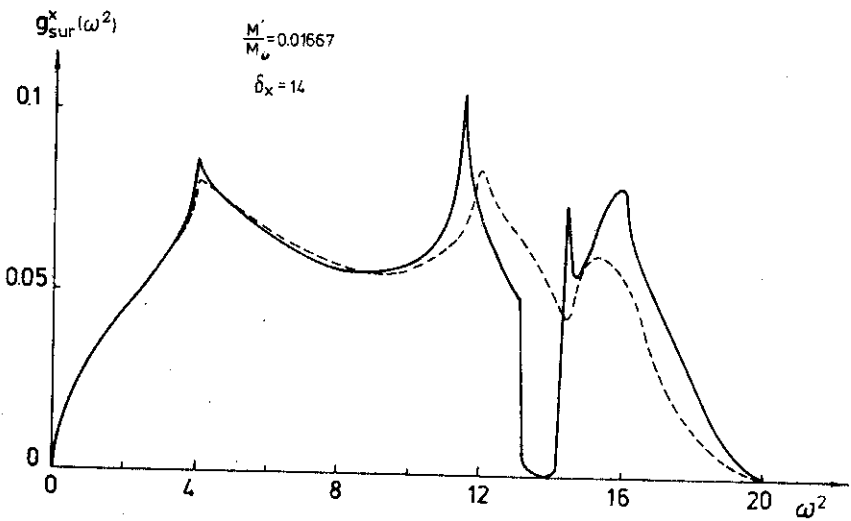
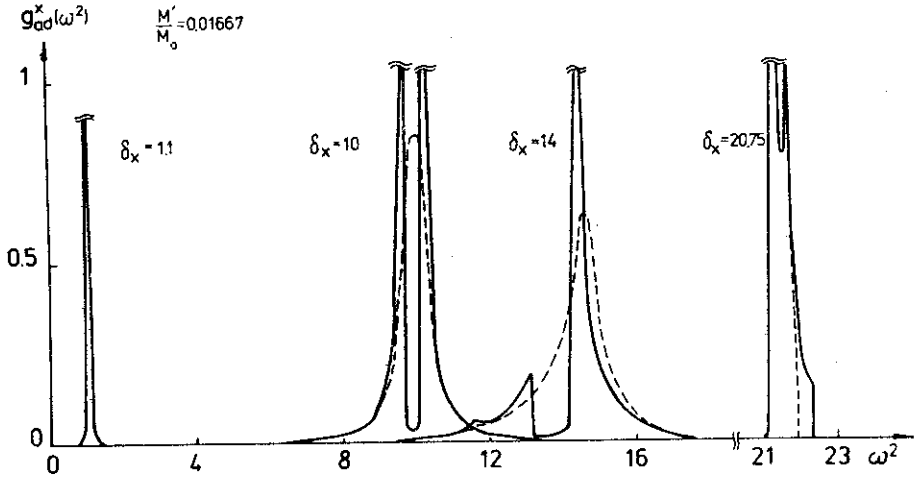
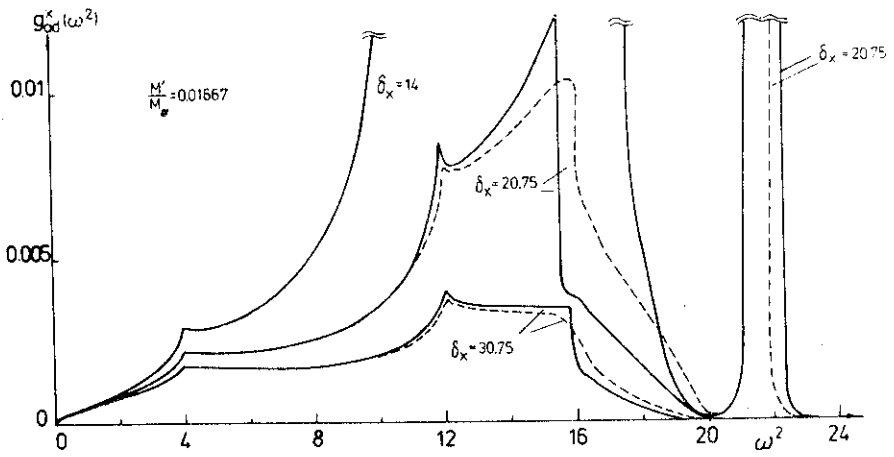


Fig.3. LFDF's of the surface atoms for $\omega^2 \in <0,20>$.



a)



b)

Fig.4. a) LFDF's of the adsorbed atoms for several values of the parameter δ_x (1.1, 10.0, 14.0, 20.75). b) The detail of the low frequency part of the adatom LFDF for δ_x=14 and 20.75. For illustration the case with δ_x =30.75 is also shown.

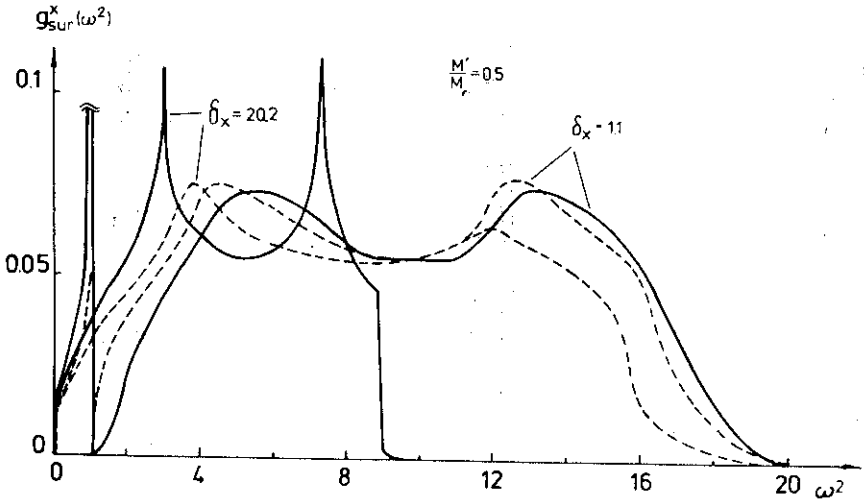


Fig.5. The low frequency part of the surface LFDF for fixed M'/M_0 =0.5 and variable δ_x.

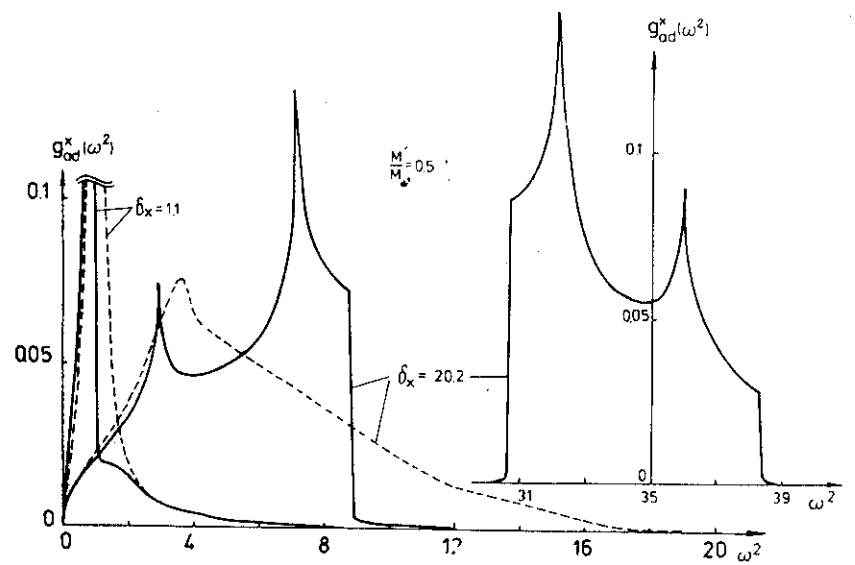


Fig.6. LFDF of the adsorbed atoms for fixed M'/M_0 =0.5 and variable δ_x.

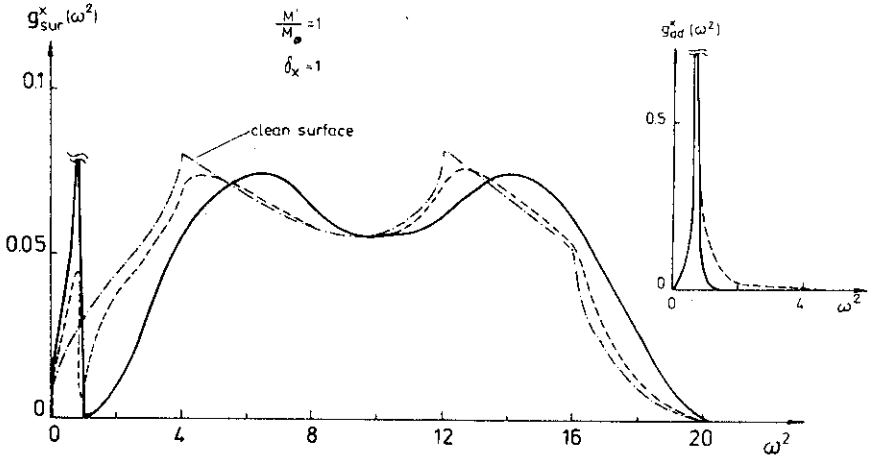


Fig.7. LFDF's of the surface and of the adsorbed atoms for $M'/M_0 = 1$ and $\delta_x = 1$, illustrating the effect of the interaction between atoms in the surface layer. LFDF of the surface atoms of the crystal with a nonadsorbing surface is shown by the dot-and-dashed line (the clean surface).

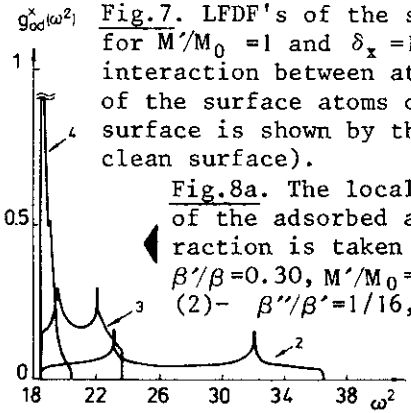
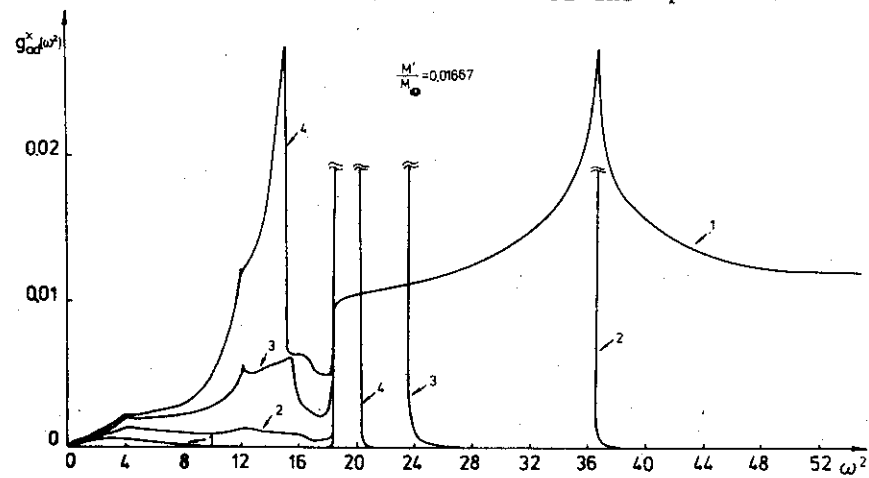


Fig.8a. The local frequency distribution function of the adsorbed atoms if the adatom-adatom interaction is taken into account. For all curves is $\beta'/\beta = 0.30$, $M'/M_0 = 0.017$ and $c = 1$ (/1/- $\beta''/\beta' = 1/4$, (2)- $\beta''/\beta' = 1/16$, (3)- $\beta''/\beta' = 1/64$, (4)- $\beta''/\beta' \approx 0$).

Fig.8b. The detail of the low frequency part of the spectrum.



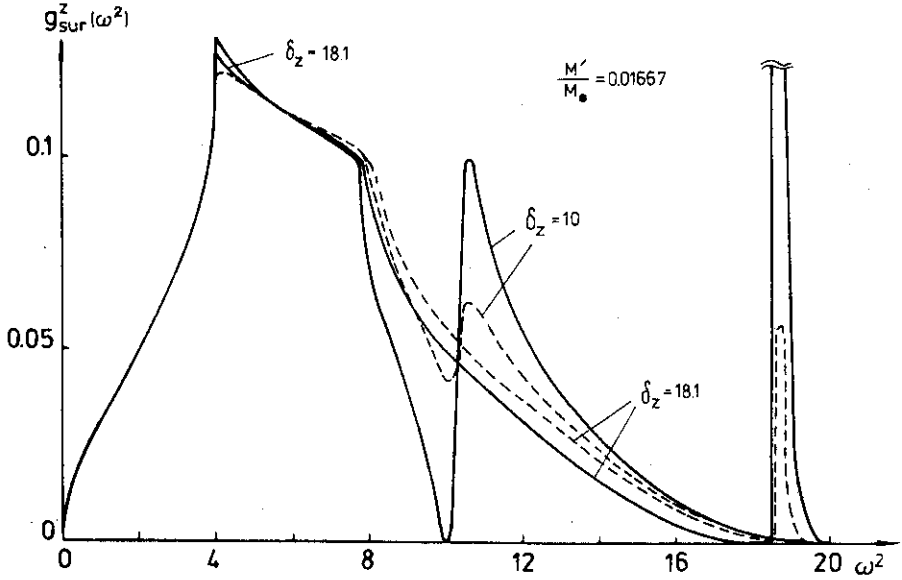


Fig.9. LFDF of the surface atom for fixed M'/M_0=0.017 and variable δ_z.

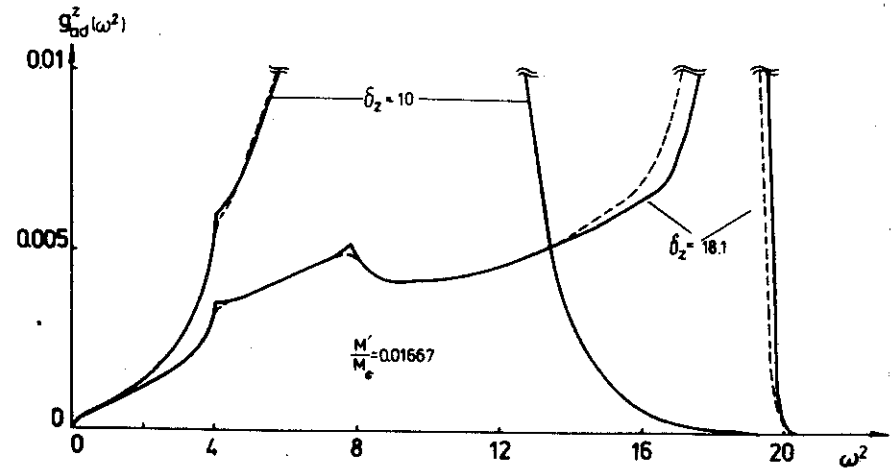


Fig.10. LFDF of the adsorbed atoms for fixed M'/M_0 =0.017 and variable δ_z.

singularities and the resonance state at (ω^2 =15.8. Only for this case the resonance is well-defined. LFDF's of the adsorbed atoms for the parameters δ_x are shown in Fig. 4a. Fig. 4b shows the details of these distribution functions. The effect of the factor $[\delta_x/(\omega^2-\delta_x)]^2$ is clearly seen. For example, for δ_x =14 the peak at the point ω^2=13.2 must be associated with the end of the low frequency band of localized mode frequencies (see Tables).

The influence of the increasing mass of the adatoms on LFDF is illustrated in Figs.5 and 6. The effect of the interaction between atoms of the surface layer is illustrated in Fig.7. For comparison LFDF of the clean surface atoms is shown, too. It is also interesting to study the effect of the adatom-adatom interaction on LFDF of the adsorbed atoms. This interaction is taken into consideration if in (1) the matrix element $D_{11}^{\kappa\kappa}(\phi_1\phi_2)$ is written as

$$D_{11}^{\kappa\kappa}(\phi_1\phi_2) = M'\omega^2 - 2\beta'' OM''^{\kappa}(\phi_1\phi_2) - \gamma'^{\kappa},$$

where α'',β'' are the corresponding force constants between the atoms in the adsorbed layer. $OM''^{\kappa}(\phi_1\phi_2)$ are defined by (2) replacing α,β by α'',β'', respectively. LFDF of the adsorbed atoms is obtained by the same procedure as was used for the noninteracting adatoms. Results are shown in Fig. 8a, 8b.

(ii) Modes polarized normal to the surface ($\kappa = 3 \equiv z$).

Similarly as the x-polarization the vibration in the direction normal to the surface (the z-polarization) can be analysed. In this case the function $z(OM^z)$ has only one singularity. The computed LFDF's of the surface and the adsorbed atoms are shown in Figs.9 and 10.

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Received by Publishing Department
on October 10 1981.