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Dynamics of thin epitaxial layers on (001) surfaces of bcc metals: A Green-function approach

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A general expression has been found for the dynamical Green functions in crystals described by force-constant models with any finite range of the harmonic interactions. The surface and interface response theory has then been applied to obtain the Green functions for this kind of crystals with planar surfaces and/or interfaces. A relatively simple method has been developed with the use of the latter Green functions to evaluate the frequencies and polarization vectors of the localized phonon modes in such systems. The frequencies and the polarization vectors have been obtained for thin epitaxial W layers of different thickness adsorbed on the Fe(001) surface. The validity of the method has been discussed in comparison with slab calculations.

I. INTRODUCTION

The static and dynamical properties of crystal surfaces and interfaces have their origin in a complex interplay of various degrees of freedom which are needed to define the state of the material. In particular, the structure and the dynamics of metallic surfaces are mostly dominated by the behavior of electrons and by their influence on the lattice of cations. The advances in studies of the dynamics of metallic surfaces with the use of electronic degrees of freedom has been recently reviewed by Eguiluz.¹

For some purposes, however, it is often useful and convenient to construct simplified models, in which the complex microscopic interactions are represented by a number of phenomenological parameters capable of describing the degrees of freedom appropriate to the given kind of experiment. The harmonic Born-von Kármán dynamical theory, which falls into this category of models, has been successfully used as a basis for the study of metallic surfaces (see, for example, Refs. 2–5). In this type of theory all the interactions are reduced to effective force constants describing the increase in the potential energy of the crystal when the atoms are displaced from their equilibrium positions. The introduction of a phenomenological temperature dependence into the surface force constants has allowed the modeling of the surface instabilities also known as surface-reconstruction phase transitions.⁶ In turn, the inclusion of anharmonic terms in the force-constant model has made it possible to describe the structure and the dynamics of surfaces which come into existence as a result of the surface-reconstruction phase transitions.^{7–10}

A particularity of the lattice-dynamical models applied to crystalline surfaces, especially those undergoing reconstruction phase transitions, is that in order to model at the same time the bulk and the surface properties the surface force constants have to be made different from the bulk force constants.¹¹ Modifications of force constants in

some regions of the material are quite natural when one considers the dynamics of systems composed of different crystals bridged by coherent interfaces. The experimental works with this kind of materials are now more and more precise as a result of the development of the appropriate scattering techniques. Recently, the dynamics of thin epitaxial Pb films on the Cu(111) surface has been studied by means of helium-atom scattering.¹² The interpretation of such and similar experiments, which are expected to appear in an increasing number in the near future, requires a model capable of reproducing the frequencies and the polarization vectors of the surface and interface phonon modes.

The majority of the cited lattice-dynamical calculations^{5,7,10} aimed at modeling the dynamics of the clean surfaces have been done with the use of the slab method in which a limited number of atomic planes serves as a model of the system with surfaces. In the present work we put forward an alternative Green-function approach based on the surface and interface response theory.¹³ This theory takes advantage of the fact that the materials with surfaces and/or interfaces show well-defined bulk properties in the majority of their volumes, whereas some perturbations occur in a relatively narrow surface or interface region. This observation allows one to obtain a fairly simple expression for the Green function of the system with surfaces and interfaces whenever the bulk Green functions are known for the constituent bulk subsystems. Such an approach is, therefore, well adapted to the study of epitaxial films, superlattices, and other composite materials.

As an example of a system with surfaces and interfaces we have chosen thin epitaxial films of tungsten adsorbed on the (001) surface of iron crystal in its bcc phase. Although no measurements of the surface dynamics have been done until now in these systems, we have selected them for the present calculations because the force-constant models of Fe and W surfaces are well known

and elaborated in the existing literature.^{6,7,10} This allows us to compare our results with those already obtained by other techniques.

In Sec. II we give some useful details of the force-constant model for Fe and W. The formula for the bulk Green function in systems with harmonic interactions extended to finite but otherwise unlimited number of neighbor atoms is derived in Sec. III. The corresponding Green function for the system with clean surface and for the thin epitaxial films is given in Sec. IV. Section V presents the method for evaluation of the surface and interface phonon frequencies and their polarization vectors. The numerical results of the present method applied to the epitaxial W films of different thickness adsorbed on the Fe(001) surface are summarized in Sec. VI.

II. FORCE-CONSTANT MODEL FOR BCC METALS

The total potential energy V of a crystal which is assumed to be composed of atoms interacting by central pairwise forces is given in the harmonic approximation by the following expression:⁶

$$V = V_0 + \sum_{j \neq i} \alpha_{ij} (dR_{ij}) + \frac{1}{2} \beta_{ij} (dR_{ij})^2, \quad (1)$$

where V_0 is a constant independent of the interatomic distances and dR_{ij} is the variation of the distance between the atoms i and j . Following Castial *et al.*⁶ and Fasolino and Tosatti¹⁰ we shall retain here the harmonic interactions among first- and second-nearest neighbors only. Consequently, out of the second-order force con-

TABLE I. Values of the force constants of Fe and W as fitted by Castial *et al.* (Ref. 6) in units of $(10^{12} \text{ Hz}) \times m$.

Element	λ	β_1	β_2
Fe	-0.45	12.73	5.14
W	-0.04	6.11	4.37

stants β_{ij} only β_1 and β_2 (for the first- and the second-nearest neighbor, respectively) will differ from zero. The corresponding first-order force constants α_1 and α_2 fulfill the following condition of the minimum of the energy with respect to the lattice parameter a :

$$-\alpha_1 \sqrt{2/3} + \alpha_2 = \lambda a \quad (2)$$

where a is the lattice parameter, i.e., the equilibrium distance between the second-neighbor atoms in the bcc structure. Table I gives the values of the force constants β_1 , β_2 , and λ for Fe and W fitted by Castial *et al.*⁶ to the experimental bulk dispersion curves.

Choosing a Cartesian coordinate system with its axes parallel to the elementary cubic cell of the bcc crystal and performing the following Fourier transform:

$$u_i(\mathbf{r}) = u_i(\mathbf{k}, \omega) \exp(-i\omega t) \exp(i\mathbf{k} \cdot \mathbf{r}), \quad i = 1, 2$$

$$u_3(\mathbf{r}) = -iu_3(\mathbf{k}, \omega) \exp(-i\omega t) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3)$$

of the displacements $u_i(\mathbf{r})$, $i = 1, 2, 3$ of the atoms placed in equilibrium at the points \mathbf{r} , one obtains the Hermitian dynamical matrix

$$D(\mathbf{k}, \omega) = \bar{D}(\mathbf{k}) - I\omega^2$$

$$= \begin{pmatrix} \Lambda_1(1 - C_1 C_2 C_3) + \Lambda_2(1 - C'_1) + \Lambda_3(2 - C'_2 - C'_3) - \omega^2 & (\Lambda_1 + 4\Lambda_3)S_1 S_2 C_3 & i(\Lambda_1 + 4\Lambda_3)S_1 C_2 S_3 \\ (\Lambda_1 + 4\Lambda_3)S_1 S_2 C_3 & \Lambda_1(1 - C_1 C_2 C_3) + \Lambda_2(1 - C'_2) + \Lambda_3(2 - C'_1 - C'_3) - \omega^2 & i(\Lambda_1 + 4\Lambda_3)C_1 S_2 S_3 \\ -i(\Lambda_1 + 4\Lambda_3)S_1 C_2 S_3 & -i(\Lambda_1 + 4\Lambda_3)C_1 S_2 S_3 & \Lambda_1(1 - C_1 C_2 C_3) + \Lambda_2(1 - C'_3) + \Lambda_3(2 - C'_1 - C'_2) - \omega^2 \end{pmatrix} \quad (4)$$

where

$$C_i = \cos(k_i a / 2), \quad S_i = \sin(k_i a / 2), \quad C'_i = \cos(k_i / a),$$

$$\Lambda_1 = (8\beta_1 - 16\lambda) / 3m, \quad \Lambda_2 = 2\beta_2 / m, \quad \Lambda_3 = 2\lambda / m, \quad (5)$$

$i = 1, 2, 3$; m is the atomic mass.

For our purpose of studying planar surfaces and interfaces perpendicular to the crystallographic direction [001] we still need a matrix $H_0(k_1, k_2, l_3, l'_3; \omega)$ which is the harmonic energy matrix Fourier transformed with respect to k_1 and k_2 , i.e., the wave-vector components parallel to the surface. Here l_3 and l'_3 label the atomic planes [001] in such a way that the first-neighboring planes have their l_3 indices different by 1. The explicit form of the energy matrix,

$$H_0(k_1, k_2, l_3, l'_3, \omega) = H_0(k_{\parallel}, \Delta l_3; \omega), \quad \Delta l_3 = l'_3 - l_3$$

is easily deduced from the matrix $D(\mathbf{k}, \omega)$:

$$D_{ij}(\mathbf{k}; \omega) = D_{ij}(k_{\parallel}, k_3, \omega) = \sum_{\Delta l = -2}^2 H_{0,ij}(k_{\parallel}, \Delta l_3; \omega) \exp(ik_3 \Delta l_3 a / 2), \quad (6)$$

$$\begin{aligned}
H_{0,11}(k_{\parallel}, 0; \omega) &= \Lambda_1 + \Lambda_2(1 - C'_1) + \Lambda_3(2 - C'_2) - \omega^2, \\
H_{0,22}(k_{\parallel}, 0; \omega) &= \Lambda_1 + \Lambda_2(1 - C'_2) + \Lambda_3(2 - C'_1) - \omega^2, \\
H_{0,33}(k_{\parallel}, 0; \omega) &= \Lambda_1 + \Lambda_2 + \Lambda_3(2 - C'_1 - C'_2) - \omega^2, \\
H_{0,11}(k_{\parallel}, 1; \omega) &= H_{0,22}(k_{\parallel}, 1; \omega) = H_{0,33}(k_{\parallel}, 1; \omega) \\
&= H_{0,11}(k_{\parallel}, -1; \omega) = H_{0,22}(k_{\parallel}, -1; \omega) = H_{0,33}(k_{\parallel}, -1; \omega) = C_1 C_2 \Lambda_1 / 2, \\
H_{0,12}(k_{\parallel}, 1; \omega) &= H_{0,21}(k_{\parallel}, 1; \omega) \\
&= H_{0,12}(k_{\parallel}, -1; \omega) = H_{0,21}(k_{\parallel}, -1; \omega) = -(\Lambda_1 + 4\Lambda_3) S_1 S_2 / 2, \\
H_{0,13}(k_{\parallel}, 1; \omega) &= -H_{0,31}(k_{\parallel}, 1; \omega) = -H_{0,13}(k_{\parallel}, -1; \omega) \\
&= H_{0,31}(k_{\parallel}, -1; \omega) = (\Lambda_1 + 4\Lambda_3) S_1 C_2 / 2, \\
H_{0,23}(k_{\parallel}, 1; \omega) &= -H_{0,32}(k_{\parallel}, 1; \omega) = -H_{0,23}(k_{\parallel}, -1; \omega) \\
&= H_{0,32}(k_{\parallel}, -1; \omega) = (\Lambda_1 + 4\Lambda_3) C_1 S_2 / 2, \\
H_{0,11}(k_{\parallel}, 2; \omega) &= H_{0,22}(k_{\parallel}, 2; \omega) = H_{0,11}(k_{\parallel}, -2; \omega) = H_{0,22}(k_{\parallel}, -2; \omega) = -\Lambda_3 / 2, \\
H_{0,33}(k_{\parallel}, 2; \omega) &= H_{0,33}(k_{\parallel}, -2; \omega) = -\Lambda_2 / 2.
\end{aligned} \tag{7}$$

III. BULK GREEN FUNCTION

By definition, the bulk Green function $G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega)$ fulfills the following condition:

$$\sum_{l''_3 = -\infty}^{\infty} \sum_{l'''_3 = 1}^3 G_{0,ii''}(k_{\parallel}, l_3, l''_3; \omega) H_{0,i''i'}(k_{\parallel}, l'_3, l'''_3; \omega) = \delta_{ii'} \delta_{l_3 l'_3}. \tag{8}$$

The explicit expression for the elements $G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega)$ can be obtained by performing the inverse Fourier transform with respect to k_3 of the matrix $D^{-1}(\mathbf{k}, \omega)$ which is the inverse of that given in Eq. (4). Thus

$$\begin{aligned}
G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega) \\
= \frac{1}{2\pi} \int_0^{2\pi} \frac{A_{i'i'}(\mathbf{k}; \omega) \exp[i(l_3 - l'_3)\theta]}{\det[D(\mathbf{k}; \omega)]} d\theta \tag{9}
\end{aligned}$$

where $\theta = k_3 a / 2$.

For every pair of indices i, i' the expression $A_{i'i'}(\mathbf{k}; \omega)$ is the algebraic complement (cofactor) of the matrix element $D_{ii'}(\mathbf{k}; \omega)$. The cofactor is defined as the determinant multiplied by $(-1)^{i+i'}$ of the 2×2 matrix which arises from the matrix $D(\mathbf{k}; \omega)$ by striking out its i th row and i' th column.

The substitution

$$z = \exp(ik_3 a / 2) = \exp(i\theta) \tag{10}$$

in Eq. (9) allows us to express the Green function $G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega)$ as a contour integral

$$G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega) = \frac{1}{2\pi i} \oint \frac{A_{i'i'}(k_{\parallel}, z, \omega) z^{l_3 - l'_3 - 1}}{\det[D(k_{\parallel}, z; \omega)]} dz. \tag{11}$$

The contour of integration in the plane of the complex variable z is the circle of the radius equal to unity and centered at $z=0$. In the latter expression, Eq. (11), the explicit z dependence has been put down in the quantities $A_{i'i'}(k_{\parallel}, z; \omega)$ and $D(k_{\parallel}, z; \omega)$. The explicit form of the matrix $H_{0,ii'}(k_{\parallel}, \Delta l_3; \omega)$ and the relation [Eq. (6)] allow one to find that the determinant $\det[D(k_{\parallel}, z; \omega)]$ is a symmetric function of the variable z , i.e., the powers z^n and z^{-n} enter this function with equal coefficients. Let us denote by M the highest power of the variable z in the function $\det[D(k_{\parallel}, z; \omega)]$. In the case of the energy matrix given in Eq. (7) $M=6$. When multiplied by z^M the determinant $\det[D(k_{\parallel}, z; \omega)]$ becomes a symmetric polynomial with respect to the variable z :

$$P(k_{\parallel}, z; \omega) = z^M \det[D(k_{\parallel}, z; \omega)]. \tag{12}$$

The integral of Eq. (11) can then be rewritten in the following form:

$$G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega) = \frac{1}{2\pi i} \oint \frac{A_{i'i'}(k_{\parallel}, z; \omega) z^{l_3 - l'_3 + M - 1}}{P(k_{\parallel}, z; \omega)} dz. \tag{13}$$

The value of the integral (13) is given by the sum of all those residues of the integrand which are contained in the unit circle: $|z|=1$. The residues correspond to the roots z_n , $n=1, \dots, 2M$ of the polynomial $P(k_{\parallel}, z; \omega)$: $P(k_{\parallel}, z_n; \omega) = 0$. Since the polynomial $P(k_{\parallel}, z; \omega)$ is symmetric and its order is $2M$, exactly M of its roots z_n , $n=1, \dots, M$ have their moduli less than one, $|z_n| < 1$, the other roots being $z_{n+M} = z_n^{-1}$. In the special case of $|z_n|=1$ both roots z_n and z_n^{-1} have their moduli equal to one. In this case a variation of the frequencies ω by a small imaginary amount makes the modulus of one of the roots greater and the modulus of the other root less than one. Consequently, in all possible cases there are M roots

z_n of the polynomials $P(k_{\parallel}, z; \omega)$ such that $|z_n| < 1$. Using these roots z_n : $|z_n| < 1$ of the polynomial $P(k_{\parallel}, z; \omega)$ one finds the following expression for the bulk Green function:

$$G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega) = \frac{1}{B} \sum_{n=1}^M \frac{A_{i'i}(k_{\parallel}, z_n; \omega) z_n^{l_3 - l'_3 + M}}{(z_n^2 - 1) \prod_{\substack{m=1 \\ (m \neq n)}}^{M-1} [(z_n - z_m)(z_n - z_m^{-1})]}, \quad (14)$$

where B is the coefficient which multiplies the highest power of the variable z in the polynomial $P(k_{\parallel}, z; \omega)$ [Eq. (12)].

The formula (14) is valid whenever the numerator of the integrand of Eq. (13) contains exclusively non-negative powers of z . Otherwise, in order to avoid multiple residues at $z=0$, one has to change the substitution in Eq. (10) into $z = \exp(-ika/2) = \exp(-i\theta)$ for all those terms $A_{i'i}(k_{\parallel}, z; \omega) z^{l_3 - l'_3 + M - 1}$ in Eq. (13) which contain negative powers of z . The resulting expression then is analogous to Eq. (14) with $A_{i'i}(z_n)$ replaced by $A_{i'i}(z_n^{-1})$ and $l_3 - l'_3$ by $l'_3 - l_3$.

The Green function [Eq. (14)] describes the reaction $u_i(k_{\parallel}, l_3; \omega)$ observed at the l_3 th atomic plane to a force spatially modulated according to the wave vector k_{\parallel} , oscillating with the frequency ω , and applied to the atomic plane number l'_3 . In the frequency region where no bulk wave can exist for the given k_{\parallel} , i.e., outside the bulk band of the lattice vibrations, all the roots z_n , $n=1, \dots, M$ entering the equation (14) have their moduli less than unity. They can be, therefore, written as $z_n = \exp[i(k_3^{(n)} + ik_3^{(n)'})a/2]$, where $k_3^{(n)}$ and $k_3^{(n)'}$ are real numbers, $k_3^{(n)' > 0$. In this case the reaction of the crystal to the applied force has a form of M waves of the amplitudes decreasing with the distance $l_3 - l'_3$ according to the corresponding damping constants $k_3^{(n)'}$. The root z_n of the greatest modulus or, equivalently, of the lowest $k_3^{(n)'}$ defines the effective range of the distortion caused by the applied force.

Within the bulk bands at least one of the roots z_n has its modulus equal to one, i.e., $z_n = \exp(ik_3^{(n)}a/2)$. This is just the case where a variation of the frequency ω by a small imaginary amount is needed to select the corresponding roots in formula (14). The quantity $k_3^{(n)}$ then is the third component of the wave vector $\mathbf{k} = (k_{\parallel}, k_3^{(n)})$ of the bulk phonon of the frequency ω . One can easily find out that whenever the modulus $|z_n|$ of a root z_n tends to unity with varying frequency the Green function (14) becomes divergent. Thus the frequencies corresponding to $|z_n| \rightarrow 1$ describe singularities of the phonon density of state. In particular, such singularities occur at the extremities of the bulk bands.

In the special case of $\omega=0$, the Green function [Eq. (14)] describes the static deviation of the structure of the crystal under external static interactions spatially modulated according to the wave vector k_{\parallel} . For all stable structures the point $\omega=0$ lies outside the bulk band so that the structural deviations decrease with the distance from the plane of application of the force. Only at $k_{\parallel}=0$, in which case the deviation of the structure consists of

mutual displacements of the whole atomic planes, the Green function as defined in Eq. (8) is divergent at $\omega=0$. In order to get rid of this divergence it is convenient to introduce local strain variables instead of the planes' displacements. The explicit expression for the Green function in these new variables has already been given in Ref. 14.

IV. GREEN FUNCTION FOR SYSTEM WITH SURFACES AND INTERFACES

Many realistic inhomogeneous systems show, in the major part of their volumes, the physical properties peculiar to bulk crystals satisfactorily described by their energy matrices analogous to Eq. (7). The surfaces and/or interfaces then introduce some perturbations limited in their spatial extent to larger or narrower surface or interface regions. Once the Green functions analogous to that of Eq. (14) are known for the constituent bulk subsystems the surface and interface response theory¹³ allows one to get the analytical expression for the Green function of the inhomogeneous system, even though the perturbations introduced by the surfaces and interfaces might be large in their numerical values.

In the present model the perturbation introduced to the energy matrix [Eq. (7)] by creating a clean [001] surface at $l_3=1$ is given by the following cleavage operator $V_0(k_{\parallel}, l_3, l'_3)$:

$$V_{0,ij}(k_{\parallel}, l_3, l'_3) = -H_{0,ij}(k_{\parallel}, l_3, l'_3; \omega)$$

for

$$l_3 = 1, 2; \quad l'_3 = -1, 0; \quad i, j = 1, 2, 3; \quad (15a)$$

$$V_{0,11}(k_{\parallel}, 1, 1) = V_{0,22}(k_{\parallel}, 1, 1) = -(\Lambda_1 + \Lambda_3)/2,$$

$$V_{0,33}(k_{\parallel}, 1, 1) = -(\Lambda_1 + \Lambda_2)/2,$$

$$V_{0,11}(k_{\parallel}, 2, 2) = V_{0,22}(k_{\parallel}, 2, 2) = -\Lambda_3/2,$$

$$V_{0,33}(k_{\parallel}, 2, 2) = -\Lambda_2/2.$$

(15b)

All the other elements of the cleavage operator vanish. The crystal is assumed to be cleaved so that the semi-infinite crystal consists of the atomic planes $l_3 = 1, 2, \dots, \infty$. The energy matrix $h_{0,ij}(k_{\parallel}, l_3, l'_3; \omega)$ of the crystal with the surface thus reads

$$h_{0,ij}(k_{\parallel}, l_3, l'_3; \omega) = H_{0,ij}(k_{\parallel}, l_3, l'_3; \omega) + V_{0,ij}(k_{\parallel}, l_3, l'_3), \quad (16)$$

where $l_3, l'_3 = 1, 2, \dots, \infty$. It should be noticed here that some elements of the cleavage operator $V_{0,ij}(k_{\parallel}, l_3, l'_3)$ [Eq. (15a)] are defined outside the range of indices $l_3, l'_3 = 1, 2, \dots, \infty$, which definition will be useful further.

The Green function $g_{0,ij}(k_{\parallel}, l_3, l'_3; \omega)$ for the crystal with the clean surface is defined by the following relation:

$$\sum_{l''_3=1}^{\infty} \sum_{i''=1}^3 g_{0,ii''}(k_{\parallel}, l_3, l''_3; \omega) h_{0,ii''}(k_{\parallel}, l'_3, l''_3; \omega) = \delta_{l_3, l'_3} \delta_{ii''}. \quad (17)$$

Its explicit expression according to the surface and interface response theory¹³ is

$$g_{0,ij}(k_{\parallel}, l_3, l'_3; \omega) = G_{0,ij}(k_{\parallel}, l_3, l'_3; \omega) - \sum_{l''_3, l'''_3=1}^2 \sum_{i', i''=1}^3 G_{0,ii'}(k_{\parallel}, l_3, l''_3; \omega) \Delta_{i'i}^{-1}(k_{\parallel}, l''_3, l'''_3; \omega) A_{0,i''j}(k_{\parallel}, l'''_3, l'_3; \omega) \quad (18)$$

where

$$A_{0,ij}(k_{\parallel}, l_3, l'_3, \omega) = \sum_{l''_3=-1}^2 \sum_{i'=1}^3 V_{0,ii'}(k_{\parallel}, l_3, l''_3) \times G_{0,i'j}(k_{\parallel}, l''_3, l'_3; \omega) \quad (19)$$

and

$$\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega) = \delta_{ij} \delta_{l_3 l'_3} + A_{0,ij}(k_{\parallel}, l_3, l'_3; \omega) \quad (20)$$

$l_3, l'_3 = 1, 2; \quad i, j = 1, 2, 3 .$

The quantities $\Delta_{ij}^{-1}(k_{\parallel}, l_3, l'_3; \omega)$ entering Eq. (18) are the elements of the matrix inverse to that defined in Eq. (20). In Eqs. (18) and (19) the summation over the atomic plane indices l''_3, l'''_3 has been extended over the range in which there exist nonvanishing matrix elements $\Delta_{ij}^{-1}(k_{\parallel}, l''_3, l'''_3; \omega)$ and $V_{0,ij}(k_{\parallel}, l_3, l''_3; \omega)$, respectively.

In the case of a system of a number of atomic adlayers deposited in epitaxy in the clean surface described above the scheme of the evaluation of the Green function is similar. The only difference is that terms $V_{\alpha,ij}(k_{\parallel}, l_3, l'_3)$ have to be added to the cleavage operator Eq. (19) in order to account for the changes of the mass and of the

force constants in the region occupied by the adatoms. Assuming that n first atomic planes of the semi-infinite crystal defined by Eqs. (15) and (16) are replaced by the planes of adatoms we have constructed the corresponding cleavage operator $V_{\alpha,ij}(k_{\parallel}, l_3, l'_3)$, $l_3, l'_3 = 1, 2, \dots, n+2$, in such a way that the force constants Λ_i , $i = 1, 2, 3$ of the substrate crystal have been replaced by the force constants Λ_i^{α} appropriate to the adsorbed atoms in the range of the indices $l_3, l'_3 = 1, 2, \dots, n-2$. Further, in the range $l_3, l'_3 = n-2, n-1, \dots, n+2$ we have replaced the constants Λ_i by those $\Lambda_i^m = (\Lambda_i + \Lambda_i^{\alpha})/2$ whenever the corresponding forces concerned interactions of the adatoms with the substrate atoms. Consequently, the cleavage operator

$$V_{ij}(k_{\parallel}, l_3, l'_3) = V_{0,ij}(k_{\parallel}, l_3, l'_3) + V_{\alpha,ij}(k_{\parallel}, l_3, l'_3)$$

which has been used in formulas (16)–(20) instead of that $V_{0,ij}(k_{\parallel}, l_3, l'_3)$ has nonzero elements for $l_3 = 1, 2, \dots, n+2$ and $l'_3 = -1, 0, \dots, n+2$. The corresponding matrix $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ has the range if its indices $i, j = 1, 2, 3$ and $l_3, l'_3 = 1, 2, \dots, n+2$ that makes its effective dimension equal to $3 \times (n+2)$. In analogy to Eq. (18) the Green function for the (001) surface with n -layer epitaxial film reads

$$g_{ij}(k_{\parallel}, l_3, l'_3; \omega) = G_{ij}(k_{\parallel}, l_3, l'_3; \omega) - \sum_{l''_3, l'''_3=1}^{2+n} \sum_{i', i''=1}^3 G_{0,ii'}(k_{\parallel}, l_3, l''_3; \omega) \Delta_{i'i}^{-1}(k_{\parallel}, l''_3, l'''_3; \omega) A_{i''j}(k_{\parallel}, l'''_3, l'_3; \omega) . \quad (21)$$

V. LOCALIZED PHONON STATES

The energies or frequencies of elementary excitations in harmonic systems are defined by singularities of the corresponding Green function. In the case of systems with surfaces and/or interfaces described by the Green function given in [Eq. (18)] or (21) one can distinguish two kinds of singularities. Those corresponding to the poles of the bulk Green function [Eq. (14)] define singularities of the phonon density of states of the bulk material. The other kind of singularities of the Green function $g_{0,ij}(k_{\parallel}, l_3, l'_3; \omega)$ for the clean surface [Eq. (18)] or of the analogous Green function $g_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ for the adsorbed thin layer [Eq. (21)] arises when the matrix Δ becomes singular.

The atomic displacements $u_i(k_{\parallel}, l_3; \omega)$ connected with these new states are all proportional to the components $e_i^m(k_{\parallel}, l_3; \omega)$, $i = 1, 2, 3$, $l_3 = 1, 2, \dots, \infty$, of the eigenvectors of the energy matrix defining the clean surface [Eq. (16)] or the adsorbed layer:

$$u_i(k_{\parallel}, l_3; \omega) \propto e_i^m(k_{\parallel}, l_3; \omega) . \quad (22)$$

Here, m labels those eigenvectors of the matrix $h_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ which are associated with the eigenvalues equal to zero. We write

$$\sum_{l'_3=1}^{\infty} \sum_{j=1}^3 h_{ij}(k_{\parallel}, l_3, l'_3; \omega) e_j^m(k_{\parallel}, l'_3; \omega) = 0 \quad (23a)$$

or

$$\sum_{l'_3=1}^{\infty} \sum_{j=1}^3 e_j^{m*}(k_{\parallel}, l_3, l'_3; \omega) h_{ji}(k_{\parallel}, l'_3, l_3; \omega) = 0 \quad (23b)$$

where the asterisk indicates complex conjugate. In what follows we shall assume that the considered energy matrix $h_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ corresponds to n adsorbed atomic planes according to the discussion following Eq. (20). To find the eigenvectors of the localized states we shall invoke the following relationship equivalent to the Dyson equation for the Green function of the perturbed system:¹³

$$\sum_{l'_3=1}^{\infty} \sum_{i''=1}^3 g_{ii''}(k_{\parallel}, l_3, l'_3; \omega) [\delta_{i''i'} \delta_{l_3 l'_3} + A_{i''i'}(k_{\parallel}, l'_3, l'_3; \omega)] = G_{0,ii'}(k_{\parallel}, l_3, l'_3; \omega). \quad (24)$$

Here all the indices l_3, l'_3, l''_3 range from 1 to ∞ only although the quantity $A_{ii''}(k_{\parallel}, l_3, l'_3; \omega)$ is different from zero also for $l'_3 < 1$ [see Eq. (19)]. The latter quantities would be, however, multiplied by the elements $g_{ii''}(k_{\parallel}, l_3, l'_3; \omega)$ with $l_3 \geq 1$ and $l''_3 < 1$ which all vanish as it follows from the definition [Eq. (17)] and from the fact that $h_{ij}(k_{\parallel}, l_3, l'_3; \omega) = 0$ unless $l_3, l'_3 \geq 1$. Still using the definition (17) and the formula (24) one can express the energy matrix $h_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ in the following form:

$$\begin{aligned} h_{ij}(k_{\parallel}, l_3, l'_3; \omega) &= \sum_{l''_3=1}^{\infty} \sum_{i''=1}^3 \bar{\Delta}_{ii''}(k_{\parallel}, l_3, l'_3; \omega) G_{s,i''j}^{-1}(k_{\parallel}, l''_3, l'_3; \omega) \\ &= \sum_{l''_3=1}^{\infty} \sum_{i''=1}^3 [\delta_{ii''} \delta_{l_3 l''_3} + A_{ii''}(k_{\parallel}, l_3, l''_3; \omega)] G_{s,i''j}^{-1}(k_{\parallel}, l''_3, l'_3; \omega), \quad l_3, l'_3 = 1, 2, \dots, \infty. \end{aligned} \quad (25)$$

Here $G_{s,ij}^{-1}(k_{\parallel}, l_3, l'_3; \omega)$ stand for the elements of the matrix inverse to the matrix $G_{0,ij}(k_{\parallel}, l_3, l'_3; \omega)$ limited to the indices $l_3, l'_3 = 1, 2, \dots, \infty$. The latter limitation of the indices makes the matrix $G_{s,ij}^{-1}(k_{\parallel}, l_3, l'_3; \omega)$ not just equal to the bulk energy matrix $H_{0,ij}(k_{\parallel}, l_3, l'_3; \omega)$. One should also notice that

$$\bar{\Delta}_{ij}(k_{\parallel}, l_3, l'_3; \omega) = \Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega) \quad (26)$$

if $l_3, l'_3 = 1, 2, \dots, n+2$ [see Eq. (20)], where n is the number of the adlayers. Taking into account that

$$\bar{\Delta}_{ij}(k_{\parallel}, l_3, l'_3; \omega) = \delta_{ij} \delta_{l_3 l'_3} \quad (27)$$

for $l'_3 = 1, 2, \dots, \infty$ and $l_3 > n+2$ one finds that the matrix $\bar{\Delta}_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ is singular whenever the matrix $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ is singular. Such being the case a class of the eigenvectors $e_i^m(k_{\parallel}, l_3; \omega)$ of the energy matrix $h_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ fulfills Eq. (23b) in such a way that

$$\sum_{l'_3=1}^{\infty} \sum_{j=1}^3 e_j^{m*}(k_{\parallel}, l_3, l'_3; \omega) \bar{\Delta}_{ji}(k_{\parallel}, l'_3, l_3; \omega) = 0. \quad (28)$$

The latter eigenvectors are the polarization vectors of the phonon states existing at the presence of the considered surface. Accidentally the matrix $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ may have more than one left eigenvector $e_i^m(k_{\parallel}, l_3; \omega)$ fulfilling Eq. (28) for a given frequency ω , in which case the corresponding surface phonon state is degenerate.

In order to practically find the eigenvectors defined in Eq. (28) advantage can be taken of a relatively limited size of the matrix $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ (in the present case $i, j = 1, 2, 3$ and $l_3, l'_3 = 1, 2, \dots, n+2$) being the left upper square block of the matrix $\bar{\Delta}_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ [see Eqs. (25), (26), and (27)]. Then the first $3 \times (n+2)$ components of the eigenvector $e_i^m(k_{\parallel}, l_3; \omega)$: $i, j = 1, 2, 3, l_3, l'_3 = 1, 2, \dots, n+2$ make up the left eigenvector corresponding to the zero eigenvalue of the matrix $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$. Such eigenvectors can be found by means of a standard singular value decomposition algorithm¹⁵ applied to the matrix $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$. The remaining components of the eigenvector defined in Eq. (28) follow from the particular form of the matrix $\bar{\Delta}_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ [see Eqs. (26) and (27)]:

$$e_i^m(k_{\parallel}, l_3; \omega) = - \sum_{l'_3=1}^{n+2} \sum_{j=1}^3 e_j^m(k_{\parallel}, l'_3; \omega) A_{ji}(k_{\parallel}, l'_3, l_3; \omega). \quad (29)$$

It should be noticed that the normalization of the polarization vectors obtained in this way is such that

$$\sum_{l'_3=1}^{n+2} \sum_{j=1}^3 |e_j^m(k_{\parallel}, l'_3; \omega)|^2 = 1 \quad (30)$$

because the usual singular value decomposition algorithms give the normalized eigenvectors.

The above method of finding the polarization vectors for the localized modes is equivalent to that elaborated by Puszkarski and Dobrzynski.¹⁶ The latter method is, however, difficult to apply when the matrix Δ [Eq. (20)] is only given in a numerical form because it requires the value of the determinant and of all the cofactors of the matrix Δ ; these quantities are not evaluated in the usual procedures for matrix inversion.

VI. DYNAMICS OF Fe(001) SURFACE WITH THIN EPITAXIAL W FILMS OF DIFFERENT THICKNESS

In order to facilitate the comparison of our results with previous works on surface phonons in Fe and W we have done the present calculations for the wave vectors k_{\parallel} lying on the dashed-line contour indicated in Fig. 1. The contour is slightly displaced from the lines of high symmetry in the two-dimensional Brillouin zone so as to demonstrate the validity of our numerical program at general wave vectors \mathbf{k}_{\parallel} . Figure 2 shows the phonon spectrum of the clean (001) surface of iron. The bold lines demarcate the bulk bands, i.e., the regions in which at least one of the roots z_n [Eqs. (12) and (14)] has its modulus equal to unity. The dashed lines inside the bulk band indicate singularities of the phonon density of states, i.e., the vanishing points of the first derivatives of the frequencies with respect to the wave-vector com-

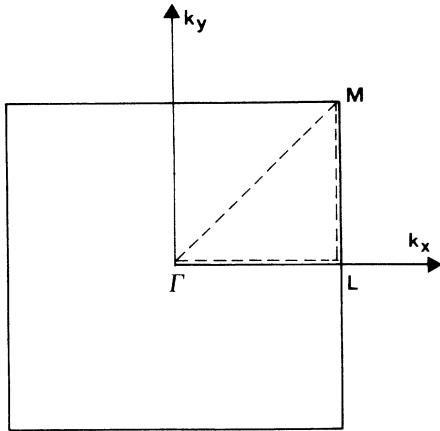


FIG. 1. Two-dimensional Brillouin zone for (001) surfaces of bcc metals with indicated contour (dashed line) on which present calculations have been done.

ponent k_3 perpendicular to the surface. The continuous fine lines outside the bulk band are the surface phonon frequencies obtained from the equation

$$\det \Delta(k_{\parallel}; \omega) = 0 \quad (31)$$

where the elements $\Delta_{ij}(k_{\parallel}, l_3, l'_3; \omega)$ of the matrix $\Delta(k_{\parallel}; \omega)$ are defined in Eq. (20). The general aspect of the curves in Fig. 2 resembles the results obtained by Castiel *et al.*⁶ and by Fasolino and Tosatti.¹⁰ Some differences, like, for example, the additional gap for $5.5 \times 10^{12} \text{ Hz} < \omega < 6.1 \times 10^{12} \text{ Hz}$ between the points L and M , come from the displacement of the actual wave vector from the high-symmetry lines. On the other hand, in the slab calculations presented in the quoted works the distinction between the bulk and surface modes is only possible on the basis of the form of the corresponding eigenvectors.

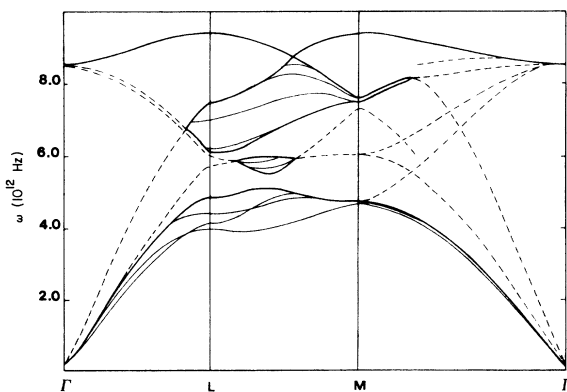


FIG. 2. Phonon spectrum of the clean Fe(001) surface obtained with present Green-function method. Heavy lines indicate limits of bulk bands. Dashed lines correspond to singularities of phonon density of states inside bulk band. Fine lines outside bulk band are dispersion curves of localized phonons. ω in units of 10^{12} Hz .

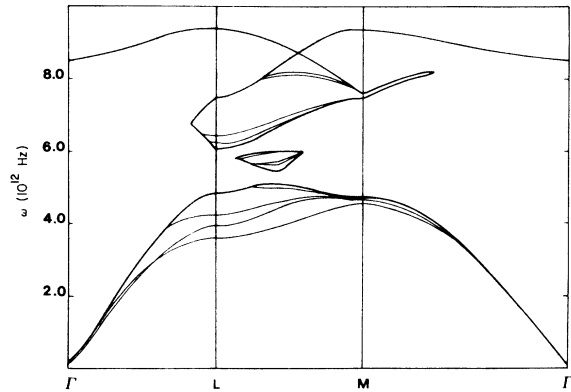


FIG. 3. Phonon spectrum of epitaxial monolayer of W on the Fe(001) surface. Meaning of lines and units same as in Fig. 2. Singularities within bulk band dropped.

In our method, which gives the exact limits of the bulk band, this distinction is always clear.

The modifications of the phonon spectrum due to one tungsten adlayer epitaxially adsorbed on the (001) surface of iron are shown in Fig. 3. The bulk singularities of the density of states have been omitted in this figure. Since the atomic mass of tungsten is greater than that of iron, the surface phonon states are shifted towards the low frequencies.

Figure 4 shows the surface phonon spectrum in the case of three atomic layers of tungsten on the same Fe(001) surface. As can be expected one observes an increase in the number of the surface phonon states and their shift towards the low frequencies.

In all these calculations we have assumed the unreconstructed structure of the free surface of tungsten that corresponds to the high-temperature structure of this surface.¹⁰ It has been also assumed that the lattice constants of the substrate Fe and of the adsorbate W are equal, which assumption may well be incorrect for sufficiently thick W films. In this latter case a modification of the force constants is expected that would result in a difference between experimental phonon spectrum and that obtained in the present work.

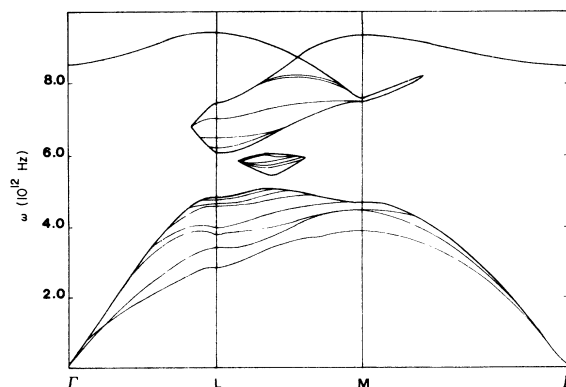


FIG. 4. Phonon spectrum of thin epitaxial W film of three atomic layers on the Fe(001) surface.

TABLE II. Relative atomic displacements $u_i(k_{\parallel}, l_3; \omega)$, $i = 1, 2, 3$ or $i = x, y, z$, $l_3 = 1, 2, \dots, 5$, corresponding to localized phonons in epitaxial thin films of $n = 0$ (clean Fe surface), $n = 1$, and $n = 3$ atomic layers of W on the Fe(001) surface $\mathbf{k}_{\parallel} = (3.0/a, 0.1/a)$. The normalization is $\sum_{l_3=1}^5 \sum_{i=1}^3 |u_i(k_{\parallel}, l_3; \omega)|^2 = 10^{10}$. Roots $z_n = |z_n| \exp[i \arg(z_n)]$ of the polynomial from Eq. (12) are given for all frequencies of localized modes. In case of complex roots z_n and z_n^* , only z_n is given.

	Frequency (10^{12} Hz)	u_x	u_y	u_z	$ z_n $	$\arg(z_n)$ (rad)
$n = 0$	3.962	3 173	88 283	-40 883	0.369	1.369
		-20 102	5 963	-6 145	0.172	0
		-3 893	-1 000	47 222	0.163	1.354
		2 249	-7 189	1 635	0.134	0
		894	-70	-440		
	4.059	9 135	-46 303	-79 239	0.389	1.372
		-33 857	-3 512	-14 412	0.170	0
		-8 309	2 414	5 702	0.167	1.350
		2 675	600	3 062	0.134	0
		1 655	-133	-462		
	4.389	59 125	2318	15 409	0.487	1.381
		12 636	-1087	66 528	0.182	1.329
		-35 567	-588	11 317	0.166	0
		-8 496	1619	11 844	0.127	0
		6 366	494	5 034		
	6.244	-33 775	699	22 207	0.953	0
		-9 039	-8674	-62 462	0.718	0
		-12 553	1612	27 723	0.500	0
		-3 841	-4926	-48 638	0.199	0
		-7 521	1693	30 232	0.128	0
	6.981				0.096	0
		69 669	38	-7 291	0.743	0
		8 674	6489	44 233	0.701	0
		43 496	-162	-2 598	0.236	0
6 137		3891	23 205	0.139	0	
	22 997	8	-488	0.114	0	
				0.086	0	
$n = 1$	3.574	146	99 480	-7029	0.309	1.362
		-4387	5 609	-825	0.176	0
		-647	-684	1389	0.151	0.369
		603	-140	307	0.143	0
		159	-15	-86		
	3.905	9 587	-8146	-92 001	0.358	1.368
		-32 548	-663	-14 815	0.172	0
		-7 967	1407	3 488	0.161	1.357
		1 607	419	2 438	0.137	0
		1 246	-69	-213		
	4.225	61 947	934	15 840	0.431	1.376
		10 779	-937	-66 131	0.174	1.340
		-32 305	-482	-9 156	0.168	0
		-6 438	1419	8 492	0.130	0
		4315	381	3 313		
	6.244	49 182	38	-9 770	0.953	0
		10 693	4246	52 204	0.718	0
		13 489	482	-11 641	0.500	0
		6 221	3779	38 194	0.199	0
		7 703	-345	-16 795	0.128	0
				0.096	0	
	6.415	-64 194	-75	6 032	0.782	0
		-8 257	-5198	-52 524	0.704	0
		-24 447	689	4 159	0.374	0
-3 585		-4929	-2 952	0.179	0	
-13 260		1065	4 598	0.125	0	
			0.093	0		

TABLE II. (Continued).

	Frequency (10^{12} Hz)	u_x	u_y	u_z	$ z_n $	$\arg(z_n)$ (rad)
$n = 3$	2.829	-196	99 666	-2960	0.244	1.356
		-2532	7 151	-297	0.136	1.389
		-237	81	319	0.181	0
		99	-74	68	0.155	0
		29	-7	-2		
	3.362	3 118	-3400	-94 273	0.285	1.329
		-28 628	-729	-10 169	0.178	0
		-3 261	1368	-11 889	0.147	0
		3 614	194	-852	0.146	1.376
		-435	123	93		
	3.828	53 508	-1920	-25 850	0.345	1.366
		-12 667	7846	75 547	0.173	0
		22 358	1498	2 967	0.159	1.360
		1 892	-1087	4 113	0.138	0
		1 675	-156	-458		
	4.019	1955	-14 899	1371	0.380	1.370
		1047	97 756	-7192	0.171	0
		-4955	11 541	-1024	0.165	1.352
		-929	-860	1447	0.134	0
		669	-189	550		
	4.580	-288	1 559	1 402	0.585	1.387
		6 118	-11 099	1 671	0.194	1.314
		3 103	96 407	-13 175	0.162	0
		-11 412	11 649	-4 292	0.123	0
		-4 073	-281	7 317		
	4.662	-1 539	925	-4 495	0.616	1.389
		41 730	3175	7 097	0.197	1.310
		18 930	-2152	-68 786	0.162	0
-37 782		-2578	-23 776	0.123	0	
-18 121		1917	17 040			
4.772	-9 226	557	-511	0.766	1.393	
	9 619	-3329	6 241	0.208	1.297	
	-44 529	-2895	-17 740	0.159	0	
	-23 974	-2038	63 601	0.120	0	
	44 712	-142	28 916			
6.244	-76 346	-783	8 462	0.953	0	
	-35 127	1879	-32 119	0.718	0	
	-27 760	-1021	-17 711	0.500	0	
	-11 048	-2163	-22 299	0.199	0	
	-87 126	-1724	-6 464	0.128	0	
			0.096	0		
6.486	-10 585	926	-29 636	0.756	0	
	78 250	-26	-8 617	0.701	0	
	8 165	2170	43 266	0.343	0	
	21 175	116	1 407	0.172	0	
	4 527	3330	19 652	0.123	0	
			0.092	0		
7.024	10 536	1627	-5 486	0.752	0	
	11 923	-786	32 183	0.703	0	
	-73 729	852	12 134	0.224	0	
	-6 505	-3915	-37 901	0.224	0	
	-39 966	13	2 406	0.113	0	
			0.086	0		

As an example of the polarization vector calculus according to the method described in Sec. V we have given in Table II the displacements $u_i(k_{\parallel}, l_3; \omega)$, $i = 1, 2, 3$ or $i = x, y, z$ for the first five atomic planes $l_2 = 1, 2, \dots, 5$ of

all the investigated systems. We have chosen the point $k_{\parallel} = (k_1, k_2) = (3.0/a, 0.1/a)$ which is close to the high-symmetry point M of the Brillouin zone from Fig. 1. In Table II we have also cited all the roots z_n of the poly-

mial from Eq. (12) which enter the bulk Green function [Eq. (14)] at the frequencies of the surface modes. As it follows from Eq. (30) and from the definition of the quantity $A_{ij}(k_{\parallel}, l'_3, l_3; \omega)$ [Eq. (19)] the roots z_n define the asymptotic behavior of the atomic displacements related with the surface modes in the region far from the surface, i.e., for $l_3 \gg 1$. Looking at the results in Table II one sees that the lowest-frequency modes of mostly sagittal polarization, i.e., $\omega = 4.059 \times 10^{12}$ Hz for the clean surface, $\omega = 3.905 \times 10^{12}$ Hz for one adsorbed layer, and $\omega = 3.362 \times 10^{12}$ Hz for three adsorbed layers, belong to the branch which has the lowest frequency in the vicinity of the Brillouin-zone center. This branch, thus, represents the Rayleigh wave. It should also be noticed that some of the modes have their greatest atomic displacements for $l_3 = 3$ or $l_3 = 4$ and not $l_3 = 1$. These are, therefore, interface rather than surface modes.

VII. DISCUSSION

The method developed in Secs. III–V allows one to obtain the surface and/or interface phonon modes in crystals in which the energy can be expressed by harmonic force-constant model with any finite range of interaction. The principal difficulty is that the roots z_n of the polynomial $P(k_{\parallel}, z; \omega)$ [Eq. (12)] have to be evaluated for every wave vector k_{\parallel} and every frequency ω . The order of this polynomial increases with increasing number of interacting neighbors so that the theory works in the best way in the systems where the interactions have their spatial range limited to several nearest neighbors. The second difficulty is the analysis of the matrix Δ [Eq. (20)]. The dimension of this matrix depends on the spatial extent of the total surface and/or interface region, i.e., the region where the force constants are different from the bulk force constants. (In our case the greatest dimension of the matrix Δ was 15 when the number of the tungsten adlayers was equal to 3). Consequently, surfaces and interfaces characterized by relatively narrow perturbed regions are the most easily treated by the present method.

As compared with the slab calculations^{6,7,10} the present method clearly separates the surface modes from the bulk phonons so that the localized character of the modes may be concluded without any insight into their polarization vectors. Moreover, the knowledge of the roots z_n gives the range of penetration of the localized modes into the bulk crystal. The polarization vectors of the surface modes can be obtained according to Eqs. (28) and (29) even if the frequencies are given with some error since the minimum eigenvalue of the matrix Δ is always easily detectable. In case of an anharmonic system the same method can be used but a renormalization due to the anharmonicity should be applied to the effective harmonic force constants.

The physical interest of the present method is that one can determine, in a schematic way, the frequencies and the corresponding atomic displacements of the surface or interface modes. Such information is useful in the planning of experiments as well as in the investigations of the real interactions in the crystals with surfaces or interfaces. In the latter case the predictions of the force-constant model should be compared with the experimental surface phonon spectra.

The example of the thin W epitaxial layers on the Fe(001) surface studied in Sec. VI is also of interest and deserves to be investigated experimentally. Such an experiment would verify our assumptions concerning the W-Fe interactions [see discussion after Eq. (20)] and reveal a possible influence of the substrate on the surface relaxation phase transition on the free W(001) surface.

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