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Crystal surface with adsorbed impurities: Phonon frequencies and polarizations

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One considers a perfect crystal with a surface on which an incomplete layer of impurities or a layer of an alloy is adsorbed. A general method allowing one to calculate the phonon spectral density given by the imaginary part of the averaged Green function over the different configurations is presented. This function is decomposed into two parts. The first one gives the shift of phonon frequencies and the frequencies and polarizations of new surface phonons. The second part accounts for the broadening of the phonon lines which is dependent upon the statistical distribution of the adsorbates. Quantitative results are given for the case of copper adatoms adsorbed on the sites of the (100) face of a copper crystal. In this paper the broadening of the phonon line is not considered and the evolution of phonon frequencies and polarizations is given in terms of the adsorbate coverage.

I. INTRODUCTION

For a long time, it has been recognized that atomic impurities in a three-dimensional crystal yield a more or less important modification of the crystal properties. In particular, those depending upon the phonon spectrum have been studied in detail. In this way, numerous methods allowing one to calculate the phonon spectral density have been proposed.[1]

After a long time spent on the study of crystals with ordered surfaces, surface physicists have oriented their works toward the study of crystals with disordered surfaces. The disorder will modify the propagation of phonons along the surface, particularly those which are localized in its vicinity.

In order to study this problem, it is first interesting to consider a perfect crystal with an ordered surface on which an incomplete layer of impurities with a given distribution is adsorbed. This has been the subject of recent works[2,3] and it will be investigated in this paper.

Qualitatively speaking, the modification of the phonon spectrum by such a layer of impurities will depend of their wavelengths. For phonons of large wavelength compared to the mean impurity or defect distance, the perturbation to their propagation will certainly be small. On the contrary, phonons of wavelength smaller than the mean defect distance will be scattered by the impurities adsorbed on the surface. The scattering process will yield a shift of the phonon frequency and a broadening of the phonon line. Furthermore, new surface phonon branches can appear, as it is the case for an ordered layer of impurities such as $p(1\times1)$, $c(2\times2)$,... structures,[4] or in vicinal surfaces where the surface unit cell contains more than one atom.[5]

The results presented at the end of this paper will illustrate on a quantitative basis these qualitative expectations. Before that we present the calculation method, which is quite general, and consider the incomplete layers of adsorbed impurities as a perturbation which involves the description of the scattering process within the framework of the T matrix.

II. MODEL AND GENERAL THEORY

Let us consider a perfect crystal with a surface. The surface crystallographic plane is composed of N^2 unit cells and in the direction normal to this plane ($\hat{\mathbf{z}}$) the crystal is supposed to be infinite. Then the cyclic boundary conditions are applied in the directions parallel to the surface.

One assumes that there is one adsorption site in each unit cell for given types of adatoms or admolecules which can be considered as adsorbed impurities. The impurity coverage θ, that is to say, the ratio of the number of occupied unit cells to their total number N^2, can vary from 0 to 1. In order to describe a given configuration of surface impurities we ascribe to each adsorption site a variable $x_{l,m}$, which can take the value 0 or 1 according to whether the site is vacant or occupied. Then, a given set of $x_{l,m}$ variables, composed of N^2 numbers 0 or 1, correspond to a well-defined configuration.

With the same set of variables $x_{l,m}$, an adsorbed layer of alloy can also be described. Two atoms of types A and B correspond, respectively, to the values 1 and 0 for the site variable. For instance, the atom mass on a site lm is then given by

$$M_{l,m}=M_A x_{l,m}+M_B(1-x_{l,m}) \tag{1}$$

and the force constant between atoms can be written in the same way. Obviously, the case of adsorbed impurities is recovered upon setting equal to zero the force constants in which a B atom is involved as well as the mass M_B.

The dynamical matrix $\tilde{D}$ of this system is an infinite square matrix which can be decomposed into an infinite set of submatrices of dimensions $3N^2\times3N^2$. Labeling the different crystallographic planes by numbers 0,1,2,..., with 0 for the impurity or alloy plane, the matrix $\tilde{D}$ becomes

$$\begin{bmatrix} \widetilde{00} & \widetilde{01} & \widetilde{02} & \cdots \\ \widetilde{10} & \widetilde{11} & \widetilde{12} & \cdots \\ \widetilde{20} & \widetilde{21} & \widetilde{22} & \cdots \\ \vdots & \vdots & \vdots & \end{bmatrix}$$

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where, for example, the terms $\widetilde{00}$ and $\widetilde{01}$ come, respectively, from the interaction between impurity or alloy atoms themselves and these atoms and atoms of the first perfect crystal plane.

The $\tilde{D}$ matrix is now decomposed into a sum of two matrices:

$$\tilde{D}=\tilde{D}_s+\tilde{V}\ , \tag{2}$$

where $\tilde{D}_s$ is the dynamical matrix of the perfect crystal and $\tilde{V}$ a perturbation matrix due to the interaction introduced by the incomplete layers of impurity or the layer of an alloy.

The number of nonvanishing $3N^2\times 3N^2$ submatrices in $\tilde{V}$ depends upon the type of interaction between the different atoms retained in the model calculation. For instance, with only central forces between nearest neighbors the nonvanishing terms are those of the $6N^2\times 6N^2$ block composed of submatrices $\widetilde{00}$, $\widetilde{01}$, $\widetilde{10}$, and $\widetilde{11}$. If one adds central forces between next nearest neighbors, one should add the $\widetilde{20}$, $\widetilde{21}$, $\widetilde{22}$, $\widetilde{02}$, and $\widetilde{12}$ submatrices.

By definition, the Green matrix for the crystal model is equal to

$$\tilde{G}^-=(\omega^2\tilde{1}-\tilde{D}_s-\tilde{V}-i\varepsilon)^{-1} \tag{3}$$

where $\tilde{1}$ stands for the unit matrix. In order to reduce the strength of the perturbation in the following perturbative development, we introduce the average of the $\tilde{V}$ matrix over the different configurations leading to the same coverage θ and denoted by $\langle\tilde{V}\rangle$. Performing the average of each term one notices that the average of the $x_{l,m}$ variable $\langle x_{l,m}\rangle$ is equal to the coverage θ, whatever the statistical distribution of atoms in the 0 plane may be. The average of the product $x_{l,m}x_{l',m'}$ is the two-body correlation function, which, with the stationarity hypothesis, depends only upon the distance between the two referred sites. $\tilde{G}$ is rewritten as

$$\tilde{G}^-=[\omega^2\tilde{1}-\tilde{D}_s-\langle\tilde{V}\rangle-(\tilde{V}-\langle\tilde{V}\rangle)-i\varepsilon]^{-1}\ , \tag{4}$$

or by defining an "average" Green function

$$\tilde{G}_a^-=[\omega^2\tilde{1}-\tilde{D}_s-\langle\tilde{V}\rangle-i\varepsilon]^{-1}\ , \tag{5}$$

$$\tilde{G}^-=\tilde{G}_a^-+\tilde{G}_a^-(\tilde{V}-\langle\tilde{V}\rangle)\tilde{G}^-\ . \tag{6}$$

This last expression can be transformed into a more convenient form

$$\tilde{G}^-=\tilde{G}_a^-+\tilde{G}_a^-\tilde{T}\tilde{G}_a^-\ , \tag{7}$$

where $\tilde{T}$ is the scattering matrix defined by the integral matrix equation

$$\tilde{T}=\tilde{V}-\langle\tilde{V}\rangle+(\tilde{V}-\langle\tilde{V}\rangle)\tilde{G}_a^-\tilde{T}\ . \tag{8}$$

This relation is formally similar to those which define the T matrix in the scattering theory by the way of the so-called distorted-wave Born approximation. The distorted Hamiltonian H_0 and the perturbation potential correspond to $\tilde{D}_s+\langle\tilde{V}\rangle$ and $\tilde{V}-\langle\tilde{V}\rangle$, respectively. In a scattering problem, we should calculated the T-matrix elements between eigenfunctions of H_0. Here we are interested in the calculation of the so-called spectral density, a function of eigenfrequency ω, proportional to the imaginary part of the Green function G^-.

From relation (8) the scattering matrix is equal to

$$\tilde{T}=[\tilde{1}-(\tilde{V}-\langle\tilde{V}\rangle)\tilde{G}_a]^{-1}(\tilde{V}-\langle\tilde{V}\rangle)\ . \tag{9}$$

With this expression one can demonstrate easily that the $\tilde{T}$ matrix has the same structure as $\tilde{V}$ with respect to the nonvanishing submatrices. Therefore, the propagator G^- between any pair of atoms labeled p and q and for the directions α,σ, that is to say, any term of $\tilde{G}^-$ [Eq. (6)], is equal to

$${}^{\alpha}_{p}G^{\sigma}_{q}(\omega)={}^{\alpha}_{p}G_{a}{}^{\sigma}_{q}(\omega)+\sum_{r,s}\sum_{\beta,\gamma}{}^{\alpha}_{p}G_{a}{}^{\beta}_{r}(\omega){}^{\beta}_{r}T^{\gamma}_{s}(\omega){}^{\gamma}_{s}G_{a}{}^{\sigma}_{q}(\omega)\ . \tag{10}$$

It is therefore equal to the sum of two terms: a direct propagator ${}^{\alpha}_{p}G_{a}{}^{\sigma}_{a}$ and an indirect one for which the propagation passes through a scattering process $({}^{\beta}_{r}T^{\gamma}_{s})$ between impurity or alloy atoms and perturbed atoms of the perfect crystal, or in general a scattering process in the perturbed layers.

This decomposition and the above consideration are also valid for the Green function $\langle G^-\rangle$ averaged over the different configuration which is given by the average of Eq. (7). As G_a^- is a constant with respect to this operation we get

$$\langle\tilde{G}^-\rangle=\tilde{G}_a^-+\tilde{G}_a^-\langle\tilde{T}\rangle\tilde{G}_a^- \tag{11}$$

and

$$\langle{}^{\alpha}_{p}G^{\sigma}_{q}\rangle={}^{\alpha}_{p}G_{a}{}^{\sigma}_{q}+\sum_{r,s}\sum_{\beta,\gamma}{}^{\alpha}_{p}G_{a}{}^{\beta}_{r}\langle{}^{\beta}_{r}T^{\gamma}_{s}\rangle{}^{\gamma}_{s}G_{a}{}^{\sigma}_{q}\ . \tag{12}$$

We can now look for the properties of the two propagators with this last equation.

The dynamical matrix which defines the Green matrix $\tilde{G}_a^-$, or the free propagator, is equal to $\tilde{D}_s+\langle\tilde{V}\rangle$. The average of the perturbation matrix yields a matrix in which the term corresponding to the interaction of any pair of atoms or atom on itself is identical to those obtained by a translation of any lattice vector. With cyclic boundary conditions, the translational invariance is satisfied as in the perfect crystal and

$${}^{\alpha}_{p}G_{a}{}^{\sigma}_{q}(\omega)=\sum_{\mathbf{K}}\exp[i\mathbf{K}\cdot(\mathbf{R}_p-\mathbf{R}_q)]{}^{\alpha}_{n_p}G_{a}{}^{\sigma}_{n_q}(\omega,\mathbf{K})\ , \tag{13}$$

where $\mathbf{K}$ is a vector of the Brillouin zone or phonon momentum parallel to the surface, and $\mathbf{R}_p$ and $\mathbf{R}_q$ are the vectors giving, respectively, the position of atoms p and q located in the crystallographic planes n_p and n_q.

On the other hand, the matrix $\tilde{D}_s+\langle\tilde{V}\rangle$ is equivalent to the dynamical matrix of the perfect crystal on the surface of which a complete layer of atoms is adsorbed. But in this layer, the atom mass on each site is equal to the average of Eq. (1)

$$M_{l,m}=M_A\theta+M_B(1-\theta) \tag{14}$$

and the central force constants are multiplied by $\langle x_{l,m}\rangle=\theta$ or $\langle x_{l,m}x_{l',m'}\rangle$.

One can thus expect that the adsorption of an averaged layer of impurities or alloy atoms will yield a shift of the surface phonon frequencies of the perfect crystal and the appearance of new surface phonons. Correspondingly, the bulk phonon density will be modified. All these effects are depicted by the imaginary part of the average Green matrix $\widetilde{G}_a^-$ and for a given **K** vector by the imaginary part of ${}^{\alpha}_{n_p}G_{a}{}^{\sigma}_{n_q}(\omega,\mathbf{K})$.

The expression of the indirect propagator can be transformed by introducing in the second term of (12) the Fourier expansion of G_a given by Eq. (13). A simple manipulation leads to

$$\sum_{\beta}\sum_{\gamma}\sum_{\mathbf{K}_1}\sum_{\mathbf{K}_2}\exp[i(\mathbf{K}_1\cdot\mathbf{R}_p-\mathbf{K}_2\cdot\mathbf{R}_q)]\sum_{n_r}{}^{\alpha}_{n_p}G_{a}{}^{\beta}_{n_r}(\omega,\mathbf{K}_1)$$
$$\times\sum_{\mathbf{R}_r}\exp[i(\mathbf{K}_2-\mathbf{K}_1)\cdot\mathbf{R}_r]$$
$$\times\sum_{n_s}{}^{\gamma}_{n_s}G_{a}{}^{\sigma}_{n_q}(\omega,\mathbf{K}_2){}^{\beta}_{n_r}FT^{\gamma}_{n_s}(\omega,\mathbf{K}_2) \quad (15)$$

with

$${}^{\beta}_{n_r}FT^{\gamma}_{n_s}(\omega,\mathbf{K}_2)=\sum_{\mathbf{R}_s}\exp[-i\mathbf{K}_2\cdot(\mathbf{R}_r-\mathbf{R}_s)]\langle{}^{\beta}_{r}T^{\gamma}_{s}(\omega)\rangle\ . \quad (16)$$

By writing expression (16), we assume that the summation does not depend upon the position of atom r in its crystallographic plane labeled n_r, or with respect to atomic positions $\mathbf{R}_r$ and $\mathbf{R}_s$, $\langle{}^{\beta}_{r}T^{\gamma}_{s}(\omega)\rangle$ is only a function of their respective distance. Upon this condition, the sum over $\mathbf{R}_r$ in (15) yields a delta function $\delta(\mathbf{K}_1-\mathbf{K}_2-\mathbf{G})$. Considering the first Brillouin zone and omitting numerical factors, this expression reduces to

$$\sum_{\mathbf{K}}\exp[i\mathbf{K}\cdot(\mathbf{R}_p-\mathbf{R}_q)]{}^{\alpha}_{n_p}\mathcal{G}^{\sigma}_{n_q}(\omega,\mathbf{K})\ , \quad (17)$$

with

$${}^{\alpha}_{n_p}\mathcal{G}^{\sigma}_{n_q}(\omega,\mathbf{K})=\sum_{\beta}\sum_{\gamma}\sum_{n_r}\sum_{n_s}{}^{\alpha}_{n_p}G_{a}{}^{\beta}_{n_r}(\omega,\mathbf{K}){}^{\beta}_{n_r}FT^{\gamma}_{n_s}(\omega,\mathbf{K})$$
$$\times{}^{\gamma}_{n_s}G_{a}{}^{\sigma}_{n_q}(\omega,\mathbf{K})\ , \quad (18)$$

where the summations over index planes n_r and n_s are extended to all planes between which the $\langle T\rangle$-matrix elements have nonzero value.

With expressions (13) and (17), the average Green matrix element (12) can be written as

$$\langle{}^{\alpha}_{p}G^{\sigma}_{q}\rangle=\sum_{\mathbf{K}}\exp[i\mathbf{K}\cdot(\mathbf{R}_p-\mathbf{R}_q)]$$
$$\times[{}^{\alpha}_{n_p}G_{a}{}^{\sigma}_{n_q}(\omega,\mathbf{K})+{}^{\alpha}_{n_p}\mathcal{G}^{\sigma}_{n_q}(\omega,\mathbf{K})]\ , \quad (19)$$

which shows that the average over the spatial distribution of impurities or alloy atoms yields an averaged Green function having the property of translational invariance. Then the quantity of interest which should be calculated is the spectral density for a given **K** vector, between planes n_p and n_q and for the two directions of phonon polarization α and σ. It is equal to

$${}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega,\mathbf{K})=\frac{2\omega}{\pi}I_m[{}^{\alpha}_{n_p}G_{a}{}^{\sigma}_{n_q}(\omega,\mathbf{K})+{}^{\alpha}_{n_p}\mathcal{G}^{\sigma}_{n_q}(\omega,\mathbf{K})]\ , \quad (20)$$

where I_m stands for the imaginary part.

As indicated above, the first term of (20) gives a contribution to the spectral density at a given **K** value, composed of the bulk phonon density and surface phonons which are represented by δ functions. Therefore, around a surface phonon frequency, on a more or less large interval of an ω value, the imaginary part of $G_a(\omega,\mathbf{K})$ is strictly equal to zero.

Let us consider now the second term of (20). It is first necessary to notice that the $\langle T(\omega)\rangle$-matrix elements are complex numbers. Their real or imaginary parts do not vanish on the whole interval of allowed ω values, except perhaps in some isolated points. Therefore, the FT function [Eq. (16)] included in the definition of $\mathcal{G}$ [Eq. (18)] should exhibit the same behavior with respect to the variable ω. Then among the four products of three terms giving a contribution to the imaginary part of $\mathcal{G}(\omega,\mathbf{K})$, three of them contain at least one imaginary part of $G_a(\omega,\mathbf{K})$, i.e., the products $I_mI_mI_m$, $I_mR_eR_e$, and $R_eR_eI_m$. The real part of $G_a(\omega,\mathbf{K})$ does not vanish over the whole interval of ω variation. Consequently, in the vicinity of a surface phonon, these products vanish and for this particular frequency they exhibit a δ function as $I_mG_a(\omega,\mathbf{K})$ does. Therefore, these three terms yield a modification of the polarization amplitude of the surface phonons and of the bulk spectral density. The remaining term, i.e., the product $R_e(G_a)I_m(TF)R_e(G_a)$, has a definite value for each frequency and consequently modifies the spectral density on all frequency values. Particularly in the vicinity of a surface phonon this term yields, for each frequency, a finite contribution and the characteristic δ-function phonon line can be destroyed. The phonon line is broadened.

This broadening due to phonon scattering by impurities or alloy atoms can be seen in another way. Using the usual iteration procedure, we get from Eq. (8) the infinite expansion of the $\widetilde{T}$ matrix. Its averaged value is then

$$\langle\widetilde{T}\rangle=\langle(\widetilde{V}-\langle\widetilde{V}\rangle)\widetilde{G}_a(\widetilde{V}-\langle\widetilde{V}\rangle)\rangle$$
$$+\langle(\widetilde{V}-\langle\widetilde{V}\rangle)\widetilde{G}_a(\widetilde{V}-\langle\widetilde{V}\rangle)\widetilde{G}_a(\widetilde{V}-\langle\widetilde{V}\rangle)\rangle+\cdots\ . \quad (21)$$

Let us consider the first term. It contains two matrices $\widetilde{V}-\langle\widetilde{V}\rangle$. Due to the averaging procedure on the product, each term of the resulting matrix can contain correlation functions such as

$$(x_{l,m}x_{l',m'}\rangle-\langle x_{l,m}\rangle\langle x_{l',m'}\rangle\ ,$$

i.e., a correlation function of position of two impurities from which its value at a very large distance has been subtracted, a distance for which the two atoms become decorrelated. Then there remains in the contribution of this first term of the $\langle\widetilde{T}\rangle$ matrix element the fluctuation of the correlation function around its large-distance value. Therefore one can expect that it will yield a broadening of the phonon line.

The second term of (21) will exhibit the correlation function of position for three atoms from which, as above, the large distance value has been subtracted. The terms of higher order contain the same type of correlation function between a larger and larger number of impurities. Each term will contribute to the broadening of the phonon line. The whole expansion contains the set of correlation functions, which is in principle necessary to describe completely the statistical distribution of impurities or alloy atoms.

To the end of this analysis, it appears that the method of calculation allows one to decompose the spectral density into two components, one giving the surface phonons lines, the other the broadening of these lines. As a first step we expose, in this paper, only the calculation of the first contribution and give some results relative to a simple case as an illustration.

III. CALCULATION OF THE DIRECT PROPAGATOR OR THE GREEN FUNCTION FOR A CRYSTAL WITH ADSORBED AVERAGE LAYER— GENERAL METHOD

We intend now to calculate the matrix $\widetilde{G}_a^-$ defined by Eq. (5). Due to the translational symmetry of the matrix $\widetilde{D}_s+\langle\widetilde{V}\rangle$ each of these terms are given by Eq. (13). Then the matrix to be calculated is $\widetilde{G}_a(\omega,\mathbf{K})$, defined by the relation

$$\widetilde{G}_a^-(\omega,\mathbf{K})=[\omega^2\widetilde{1}-\widetilde{D}_s(\mathbf{K})-\langle\widetilde{V}(\mathbf{K})\rangle-i\varepsilon]^{-1} . \tag{22}$$

The terms of this matrix ${}^{\alpha}_{n_p}G^{\sigma}_{a n_q}(\omega,\mathbf{K})$ account for the propagation of the phonon of frequency ω and momentum $\mathbf{K}$ between the two crystallographic planes labeled n_p and n_q for the directions α and σ, respectively, in the planes n_p and n_q. If N is the number of the crystallographic planes of the bare crystal the matrix, $\widetilde{G}_a^-(\omega,\mathbf{K})$ has a dimension equal to $3(N+1)\times 3(N+1)$.

We should therefore ascribe the same dimensionality to the $\widetilde{D}_s(\mathbf{K})$ and $\langle\widetilde{V}(\mathbf{K})\rangle$ matrices. Labeling the plane which contains the impurities by the subscript 0, the surface plane of the crystal by the subscript 1, etc., the $\langle\widetilde{V}(\mathbf{K})\rangle$ matrix can be decomposed in four submatrices equal to zero except the first squared block of dimension $3(n+1)\times 3(n+1)$ if n is the number of crystal planes perturbed by the adsorbed impurities. The $\widetilde{D}_s$ matrix can be decomposed in the same way, but here the nonvanishing block is the fourth one of dimension $3N\times 3N$.

In order to calculate the matrix $\widetilde{G}_a^-$ with a perturbation method, it is convenient to decompose $\widetilde{D}(\mathbf{K})+\langle\widetilde{V}(\mathbf{K})\rangle$ into two others matrices $\widetilde{D}_0(\mathbf{K})$ and $\langle v(\mathbf{K})\rangle$ such that

$$\widetilde{D}_0(\mathbf{K})=\begin{bmatrix}\widetilde{b} & 0\\ 0 & \widetilde{D}_s(K)\end{bmatrix},\quad \langle\widetilde{v}(\mathbf{K})\rangle=\langle\widetilde{V}(\mathbf{K})\rangle-\widetilde{b} ,$$

where $\widetilde{b}$ is a 3×3 diagonal matrix composed of the terms of $\langle\widetilde{V}(\mathbf{K})\rangle$, which account for the interaction of the average impurity on itself. Now one defines a Green matrix $\widetilde{G}_0^-(\mathbf{K})$ equal to

$$\widetilde{G}_0^-(\omega,\mathbf{K})=[\omega^2\widetilde{1}-\widetilde{D}_0(\mathbf{K})-i\varepsilon]^{-1} , \tag{23}$$

which introduced into expression (22) leads to the relation

$$(\widetilde{1}-\widetilde{G}_0^-\langle\widetilde{v}\rangle)\widetilde{G}_a^-=\widetilde{G}_0^- . \tag{24}$$

The Green matrices $\widetilde{G}_0^-$ and $\widetilde{G}_a^-$ are decomposed into four submatrices having the dimension of the four corresponding submatrices of $\langle\widetilde{V}(\mathbf{K})\rangle$ or $\langle v(\mathbf{K})\rangle$:

$$\widetilde{G}^-=\begin{bmatrix}\widetilde{G}_{11} & \widetilde{G}_{12}\\ \widetilde{G}_{21} & \widetilde{G}_{22}\end{bmatrix},\quad \langle\widetilde{v}\rangle=\begin{bmatrix}\widetilde{v} & 0\\ 0 & 0\end{bmatrix} .$$

In this way, relation (24) splits into four equations

$$[\widetilde{1}-\widetilde{G}_{011}^-\widetilde{v}]\widetilde{G}_{a11}^-=\widetilde{G}_{011}^- , \tag{25}$$

$$\widetilde{G}_{a21}^-=\widetilde{G}_{021}^-[\widetilde{1}+\widetilde{v}\widetilde{G}_{a11}^-] , \tag{26}$$

$$[\widetilde{1}-\widetilde{G}_{011}^-\widetilde{v}]\widetilde{G}_{a12}^-=\widetilde{G}_{012}^- , \tag{27}$$

$$\widetilde{G}_{a22}^-=\widetilde{G}_{021}^-\widetilde{v}\widetilde{G}_{a12}^-+\widetilde{G}_{022}^- . \tag{28}$$

By inspection of this set of equations one notices that (i) when Eq. (25) is solved one can get in principle the other three unknown submatrices, and (ii) the more interesting physical information is contained in $\widetilde{G}_{a11}^-$. Its terms are the Green functions describing the propagation into and between the impurity and crystal planes, those which are directly affected by the absorbed impurities. For these two reasons, it is sufficient to solve Eq. (25).

This is a kind of nonlinear equation between matrices of dimension $3(n+1)\times 3(n+1)$. One notices that this size is in general small, depends on the range of forces between atoms introduced in the harmonic model of crystal, and is independent of the number N of crystal planes.

Then Eq. (25) can be solved exactly with the method of generating coefficients of Green function. This method has been developed some years ago in order to calculate the time or frequency-dependent Green functions.[6,7] It has been used in different physical crystal configurations.[8–10] For the sake of clarity, we recall briefly the definition of the coefficients and how one can get an expansion of the Green functions, limiting our exposure to those which are frequency dependent.

Generally speaking, the spectral density to be calculated is defined by the relation

$${}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega,\mathbf{K})=2\omega\sum_{\mathbf{k},\mathbf{K}=\text{const}} b^{\alpha}_{n_p\mathbf{k}}(b^{\sigma}_{n_q\mathbf{k}})^*\delta(\omega^2-\omega_{\mathbf{k}}^2) , \tag{29}$$

where the subscripts n_p,n_q label two crystal planes and the superscripts α,σ two directions. The b coefficients are the terms of the unitary matrix which diagonalizes the dynamical matrix.

Now we define an infinite set of coefficients which are only dependent upon the momentum $\mathbf{K}$:

$${}^{\alpha}_{n_p}a^{\sigma}_{n_q,2p}(\mathbf{K})=\int_0^{\omega_m}{}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega,\mathbf{K})T_{2p}\left[\frac{\omega}{\omega_m}\right]d\omega , \tag{30}$$

where ω_m is the maximum frequency of the crystal and T_{2p} the Chebyshev polynomial of first kind and order $2p$. These polynomials are orthogonal over the interval [0,1] weighted by the factor $(1-\omega^2/\omega_m^2)^{-1/2}$. Introducing (29) into (30), one gets

$$ {}^{\alpha}_{n_p}a^{\sigma}_{n_q,2p}(\mathbf{K})=\sum_{\mathbf{k},\mathbf{K}=\text{const}} b^{\alpha}_{n_q\mathbf{k}}(b^{\sigma}_{n_q\mathbf{k}})^{*}T_{2p}\left[\frac{\omega_k}{\omega_m}\right] \tag{31} $$

and, as the b matrix is unitary,

$$ {}^{\alpha}_{n_p}a^{\sigma}_{n_q,0}={}_{n_p}\delta_{n_q\alpha}\delta_{\sigma} $$

where δ is the Kronecker symbol. In this way, the spectral density can be expanded on the basis of Chebyshev polynomials and one gets

$$ {}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega,\mathbf{K})=\frac{2}{\pi\omega_m\sqrt{1-\omega^2/\omega_m^2}} \times\left[{}_{n_p}\delta_{n_q\alpha}\delta_{\sigma}+2\sum_{p=1}^{\infty}{}^{\alpha}_{n_p}a^{\sigma}_{n_q2p}T_{2p}\left[\frac{\omega}{\omega_m}\right]\right] $$

or setting

$$ \omega=\omega_m\cos(\theta/2)\ , \tag{32} $$

$$ {}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega,\mathbf{K})=\frac{2}{\pi\omega_m\sin(\theta/2)} \times\left[{}_{n_p}\delta_{n_q\alpha}\delta_{\sigma}+2\sum_{p=1}^{\infty}{}^{\alpha}_{n_p}a^{\sigma}_{n_q2p}\cos(p\theta)\right]\ , \tag{33} $$

Now, looking for the function which is generated by the coefficients a_{2p}, one can demonstrate[6] that the Green function is given, in the complex plane, by the relation

$$ {}^{\alpha}_{n_p}G^{\sigma}_{n_q}(\omega,\mathbf{K})=\frac{4}{\omega_m^2}\frac{1}{\rho^{-1}-\rho}\left[{}_{n_p}\delta_{n_q\alpha}\delta_{\sigma}+2\sum_{p=1}^{\infty}\rho^{p}\,{}^{\alpha}_{n_p}a^{\sigma}_{n_q2p}\right]\ , \tag{34} $$

where $\rho=\lambda\exp i\theta$, $\lambda\leq 1$, and ω is a complex frequency which is equal to

$$ \omega^2=\frac{\omega_m^2}{4}(\rho+2+\rho^{-1})\ . \tag{35} $$

Starting from λ values less than 1, the limit $\lambda\rightarrow 1$ gives the usual Green function of real frequency

$$ {}^{\alpha}_{n_p}G^{-\sigma}_{\ \ n_q}(\omega,\mathbf{K}) =\frac{2i}{\omega_m^2\sin\theta}\left[{}_{n_p}\delta_{n_q\alpha}\delta_{\sigma}+2\sum_{p=1}^{\infty}\exp(ip\theta){}^{\alpha}_{n_p}a^{\sigma}_{n_q2p}\right]\ . \tag{36} $$

Taking account of the relation

$$ {}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega,\mathbf{K})=\frac{2\omega}{\pi}I_m\left[{}^{\alpha}_{n_p}G^{-\sigma}_{\ \ n_q}(\omega,\mathbf{K})\right]\ , $$

Eq. (33) is recovered, whereas the G real part is given by

$$ \mathrm{Re}\left[{}^{\alpha}_{n_p}G^{-\sigma}_{\ \ n_q}(\omega,\mathbf{K})\right]=-\frac{4}{\omega_m^2\sin\theta}\sum_{p=1}^{\infty}{}^{\alpha}_{n_p}a^{\sigma}_{n_q2p}\sin(p\theta)\ , \tag{37} $$

Obviously the Green matrices like $\tilde{G}^{-}_{011}$ and $\tilde{G}^{-}_{a11}$ [Eq. (25)] can also be expanded in the same way, the coefficient of the expansion being now, respectively, the $\tilde{a}_{2p}$ and $\tilde{A}_{2p}$ matrices. Now, using the form (34), these two different expansions are introduced into Eq. (25). Then each side of this relation becomes a polynomial with respect to the ρ variable. The identification of the terms of the same power contained, respectively, in the left- and right-hand sides yields a recurrence relation between the $\tilde{A}_{2p}$ and $\tilde{a}_{2p}$ matrices which allows one to calculate the set of the former knowing the set of the latter. The result of this operation is given in detail in Appendix A. Also exposed there is the method of calculation of $\tilde{a}_{2p}$ matrices which are obtained from the set of generating coefficient matrices of the bare crystal.

IV. MODEL FOR CALCULATION

We consider now a fcc crystal with a (100) surface. The center of each square unit cell is the locus of an adsorption site. As explained in Sec. II, an adsorbed layer is modeled by putting on each site an adsorbed atom or molecule of type A or B. A given configuration of the alloyed layer is quantitatively described by ascribing to each site a variable $x_{l,m}$ equal to 1 or 0 according to whether the site is occupied by an impurity A or B. The average value of the variable x, $\langle x_{l,m}\rangle$, is equal to the coverage θ of type-A adsorbate. In order to take account of possible relaxation the distance between impurity and surface plane is taken equal to a' (the distance between crystal planes is $a/2$).

The range of harmonic forces between atoms is limited to nearest neighbors. The size of matrices in Eq. (25) is therefore 6×6 and the recurrence relations, allowing one to calculate the generating coefficients of the unknown $\tilde{G}^{-}_{a11}$ matrix, are relations between matrices of this size. They contain as an input the $\tilde{g}_{2p}$ matrices (see Appendix A) constructed with the generating coefficients of Green functions of the (100) fcc crystal relative to the surface plane. They have been calculated previously.[7]

It remains to determine the perturbation matrix V and its average over the impurity configurations. This operation is exposed in Appendix B and the different terms of $\langle V\rangle$ are given. One should note here that the $\langle\tilde{V}\rangle$ matrix terms are independent of the distribution of the A and B species, except the three diagonal terms of the diagonal 3×3 $\tilde{b}$ matrix used to build the Green matrix $\tilde{G}^{-}_0(\omega,\mathbf{K})$ [Eq. (23)]. These three terms depend upon the probability of having couples AA, AB, BA, or BB on two nearest-neighbor sites.

In the case of an adsorbed impurity (symbolically $B=0$), these three terms become themselves independent of the impurity distribution. Then the whole matrix $\langle\tilde{V}\rangle$ and consequently the Green matrix $\tilde{G}^{-}_a(\omega,\mathbf{K})$ have this property. Therefore, the model for this calculation can be seen as if an average layer of impurities was adsorbed on the surface.

For θ equal zero, the three terms of the $\tilde{b}$ matrix are equal to respectively, the square of vibrational frequencies in the three directions of an impurity atom adsorbed on a crystal at rest and the matrix $\langle \tilde{v} \rangle = \langle \tilde{V} \rangle - \tilde{b} = 0$. Therefore, $\tilde{G}^{-}_{a11} = \tilde{G}^{-}_{011}$, and a dispersion relation is composed of that of the bare crystal and of the three constant frequencies pointed out above. This is the starting state from which the perturbation is applied.

Before looking at the results, it is important to notice that an isolated frequency, such as a surface phonon, is represented in the spectral density by a δ function. If ω_R labels this frequency, expressions (31) and (32) show that the corresponding generating coefficients are

$$ {}^{\alpha}_{n_p}a^{\sigma}_{n_q 0} = {}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K}), \quad {}^{\alpha}_{n_p}a^{\sigma}_{n_q 2p} = {}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K})\cos(p\theta_R) , $$

where ${}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K})$ is here a condensed notation for the product $b^{\alpha}_{n_p}(b^{\sigma}_{n_q})^*$. Therefore expression (33) gives

$$ {}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega_R, \mathbf{K}) = 2\omega\delta(\omega^2 - \omega_R^2)\, {}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K}) . \tag{38} $$

In a practical calculation, this yields a kind of singularity. The procedure which allows one to reduce it, to get ω_R and ${}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K})$ values and the spectral bulk density, is exposed in Appendix C.

V. RESULTS

Numerical calculation has been done for a (100) surface of a fcc crystal, on which are adsorbed atoms of the same type as those of the crystal. As previously explained, the adsorption sites are located on the center of the surface square unit cell. The harmonic forces between atoms have their range limited to nearest neighbors. Hence the model is suitable to represent copper atoms adsorbed on the (100) face of a copper crystal. Then $\mu_{l,m,0} = 1$ as well as all the reduced force constants β.

We consider the [100] direction, the $\hat{\mathbf{x}}$ axis in our notation, $\hat{\mathbf{z}}$ being normal to the surface. Due to the symmetry it is well known that waves propagating in this direction decouple into waves polarized in the sagittal plane $(\hat{\mathbf{x}}, \hat{\mathbf{z}})$ and transverse waves $(\hat{\mathbf{y}})$. The result are given for the former, which are currently detected in an experiment.

The contribution to the spectral density of a surface phonon is a δ function [Eq. (38)]. Then it can be decomposed into surface phonons and bulk phonon contribution ρ^B:

$$ {}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega_R, \mathbf{K}) = 2\omega \sum_{s} {}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K})\delta(\omega^2 - \omega_R^2) + {}^{\alpha}_{n_p}\rho^{\sigma B}_{n_q}(\omega, \mathbf{K}) . $$

The integration of this quantity over the interval of ω, $[0, \omega_m]$, should be equal to

$$ \int_0^{\omega_m} {}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}(\omega_R \mathbf{K})d\omega = \sum_{s} {}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K}) + \int_0^{\omega_m} {}^{\alpha}_{n_p}\rho^{\sigma B}_{n_q}(\omega, \mathbf{K})d\omega $$

$$ = {}_{n_p}\delta_{n_q}\,{}_{\alpha}\delta_{\sigma} , $$

as it is easily demonstrated from Eq. (33). This introduces the unitarity property.

An example of a calculated spectral density is given by Fig. 1. It is relative to the crystal surface plane on itself $(n_p = n_q = 1)$ and for two polarizations normal to the surface $(\alpha = \sigma = \hat{\mathbf{z}})$. The surface phonons are represented by vertical bars of height proportional to the coefficient ${}^{Z}_{1}B^{Z}_{1}$ of each phonon. Note that this is equivalent to integrating the quantity ρ over a small interval $2\Delta\omega$ such that $[\omega_R - \Delta\omega, \omega_R + \Delta\omega]$.

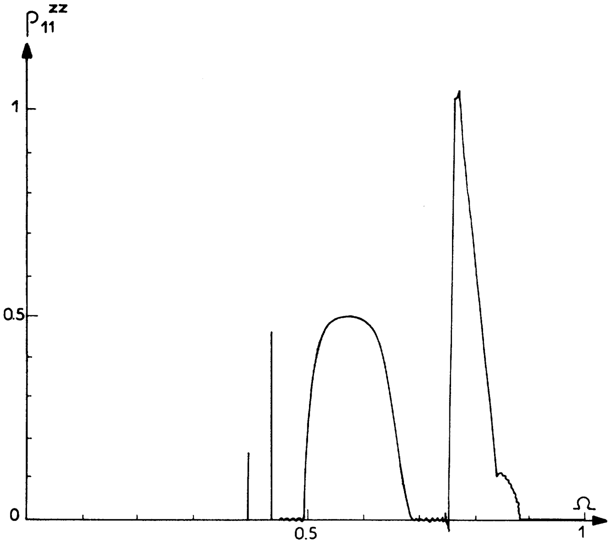

FIG. 1. Calculated spectral density in the surface plane and in the direction normal to the surface of the (100) face of a copper crystal with adsorbed copper atoms at a coverage $\theta = 0.15$. The wave vector is equal to 0.55 of the Brillouin-zone edge value in the [100] direction.

The frequency and the wave vector $\mathbf{K}$ are represented in dimensionless variables by respectively, $\Omega = \omega/\omega_m$ and $\varphi_{x,y} = K_{x,y}a/2\pi$. For the [100] direction φ_x varies from 0 to 1 and $\varphi_y = 0$.

The residual oscillations observed in the phonon bulk density, their amplitude being the greatest in the gap, are due to the finite number of calculated coefficients (in this case 600) and are analogous to a Gibbs phenomena. Their amplitude decreases as the number of calculated coefficients decreases.

Some results have been presented in a previous paper.[3] In particular the dispersion relations for different coverage values ($\theta = 0.055$ and 0.1) have been given. Here we expose the results in a different way. At a given value of the wave vector φ_x, we show the evolution of the surface phonon frequencies Ω_R and their polarization with the coverage θ. But as far as polarization is concerned, we focus our attention on the most important ones, i.e., those relative to the impurity plane $(n_p = n_q = 0)$ and the crystal plane $(n_p = n_q = 1)$ for the directions $\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$ $(\alpha = \sigma = \hat{\mathbf{x}}$ or $\hat{\mathbf{z}})$. In our notation, these are the quantities ${}^{X}_{0}B^{X}_{0}$, ${}^{Z}_{0}B^{Z}_{0}$, ${}^{X}_{1}B^{X}_{1}$, and ${}^{Z}_{1}B^{Z}_{1}$.

Note that for $\theta = 0$, there are three frequencies. As explained previously, these are the two frequencies corresponding to the vibration of an impurity atom with crystal atoms at rest, which in the case studied here are equal to $\Omega_X = 0.35$ and $\Omega_Z = 0.5$, and the crystal surface phonon frequency. The former are polarized uniquely in the impurity plane, i.e., ${}_0^XB_0^X$ and ${}_0^ZB_0^Z$ are equal to 1 for Ω_X and Ω_Z, respectively. For $\theta=1$ the spectral density of the bare crystal is of course recovered.

$\varphi_x=0.9$. The results for this value are given in Figs. 2–6. Figure 2 shows three surface phonons labeled 1–3. To these labels the conventional notations SP (sagittal parallel longitudinal) and SV (sagittal vertical) have been added, following their polarization. The subscript 00 or 11 refers the plane of their localization. Moreover, a localized mode in the gap of phonon bulk density appears. This last one is mainly polarized in the $\hat{\mathbf{x}}$ direction, in the crystal surface plane (Fig. 5) and for higher coverage in the impurity plane (Fig. 3). It corresponds, in the usual notation, to an S_6 mode.

The most important features are the three surface phonons which, as pointed out above, are generated by the three frequencies for $\theta=0$. These are $\Omega_X=0.35$, ${}_0^XB_0^X=1$; $\Omega_Z=0.5$, ${}_0^ZB_0^Z=1$; and for this wave-vector value $\Omega_r=0.496$, ${}_1^ZB_1^Z=0.989$. They evolve with the coverage until they disappear for coverage greater than 0.7 in the bulk band (2 and 3) or give again the surface phonon of the bare crystal $\Omega_R(1)$. For θ greater than 0.5, the former are mainly polarized over $\hat{\mathbf{z}}$ and $\hat{\mathbf{x}}$ directions in the surface and impurity planes (Figs. 3 and 6),

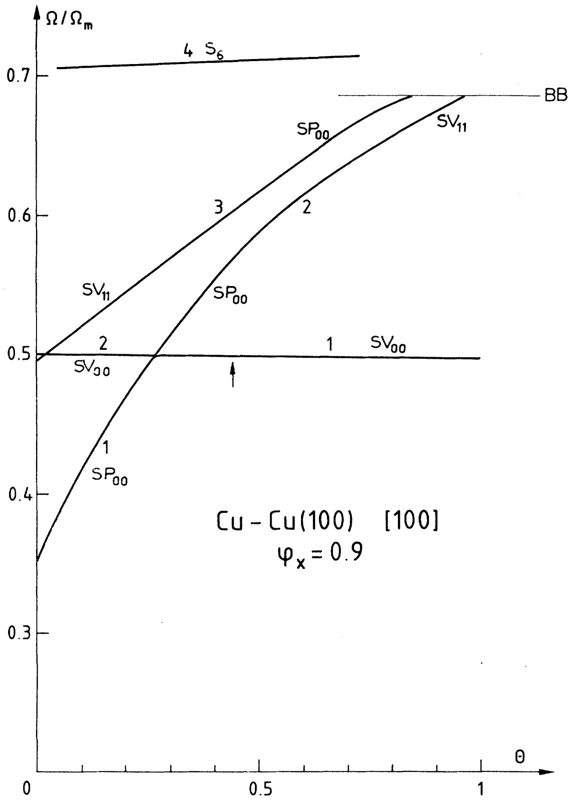

FIG. 2. Copper adatoms on a copper (100) face. Surface phonon frequencies as a function of coverage. The wave vector is equal to 0.9 of the Brillouin-zone edge value in the [100] direction. BB refers the bulk band limit, SV and SP indicate sagittal vertical and parallel polarization, respectively.

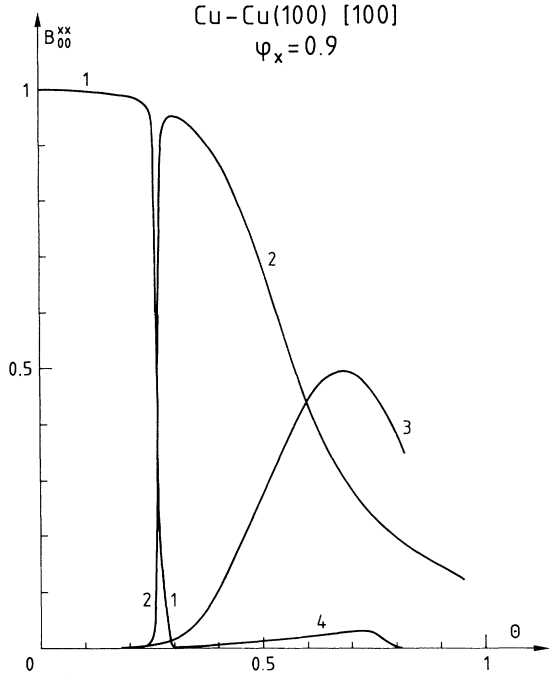

FIG. 3. Copper adatoms on a copper (100) face. Amplitude of polarization of the surface phonons in the impurity plane along the direction parallel to the surface, as a function of coverage. The wave vector is equal to 0.9 of the Brillouin-zone edge value in the [100] direction.

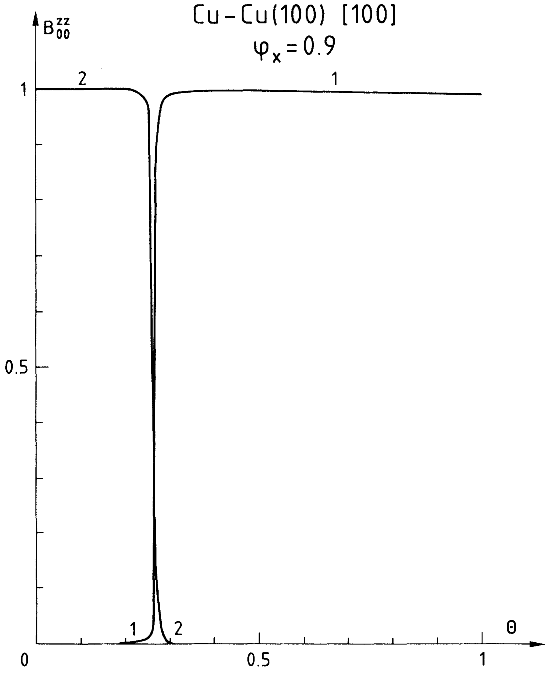

FIG. 4. Same as Fig. 3, but along the normal to the surface.

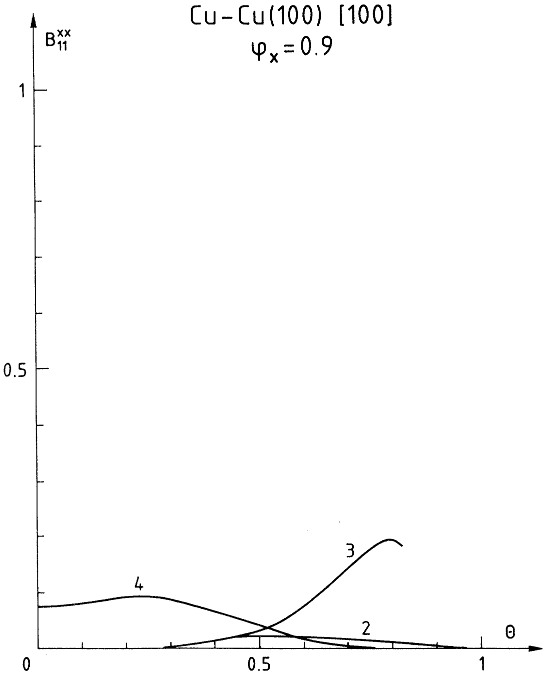

FIG. 5. Same as Fig. 3, but in the surface plane.

respectively, whereas the latter is strongly polarized along the normal in the impurity plane (Fig. 4) for θ greater than 0.4.

For small θ values, the frequency 1 (SP$_{00}$) increases until it becomes equal to the practically constant frequency 2 (SV$_{00}$). At the crossing point $\theta_c=0.266$ a gap open which in this case is very small. For θ less than θ_c, phonons 1 and 2 are strongly polarized in the impurity plane in the $\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$ directions, respectively. For θ greater than θ_c the reverse is true, yielding an exchange of polarization on a small interval of θ variations ($\Delta\theta \neq 0.1$) (Figs. 3 and 4).

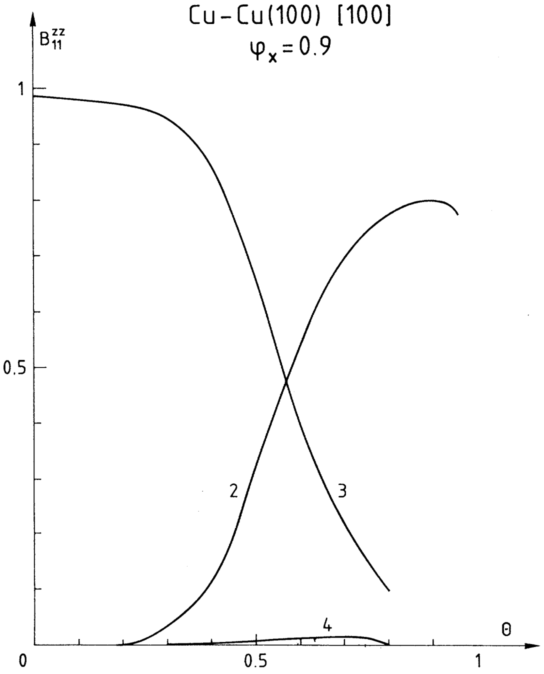

FIG. 6. Same as Fig. 3, but in the surface plane along the normal to the surface.

The same phenomenon holds for very small coverage between frequencies 2 and 3. At $\theta=0$, $\Omega_2=\Omega_R=0.496$ and ${}^{Z}_{1}B^{Z}_{1}=0.989$ (SV$_{11}$), whereas $\Omega_3=0.5$ and ${}^{Z}_{0}B^{Z}_{0}=1$ (SV$_{00}$). At this point, the frequency values are very close to each other and are polarized in the two different planes. Then their interaction depends on the coupling between these planes which at this very small coverage is very small also. Therefore, the "width" of the opened gap is so small that it is undetectable with the precision of the numerical calculation. Figures 4 and 6 show the result of polarization exchange. At θ greater than or equal to 5×10^{-2}, frequencies 2 and 3 are strongly polarized always on $\hat{\mathbf{z}}$, but on the impurity and surface plane, respectively, a situation which is the reverse of that which prevails for an infinitesimal coverage value.

$\varphi_x=0.55$. The results for this value are given in Figs. 7–11. The evolution of localized phonon frequencies with coverage is very similar to that found in the preceding case. The phonon 4 (S_6) in the gap of the bulk phonons appears in the interval of coverage values between 0.4 and 0.92. It is polarized in the two planes 0 and 1 and in the two directions $\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$. One notices that the polarization ${}^{X}_{1}B^{X}_{1}$ is important and has a maximum around $\theta=0.67$ (Fig. 10).

The evolution of the phonons 1–3 is similar to that of

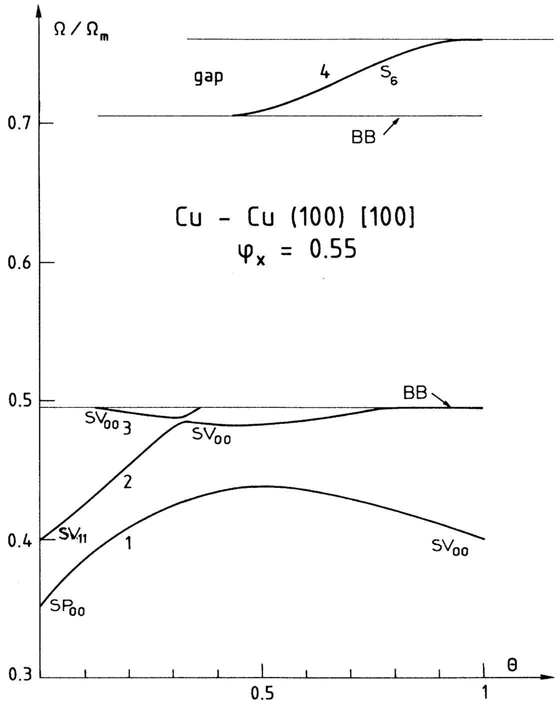

FIG. 7. Same as Fig. 2, but with the wave vector equal to 0.55.

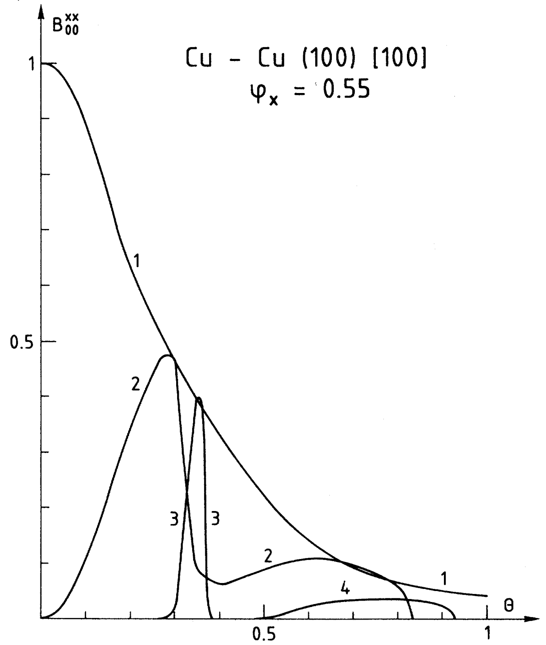

FIG. 8. Same as Fig. 3, but with the wave vector to 0.55.

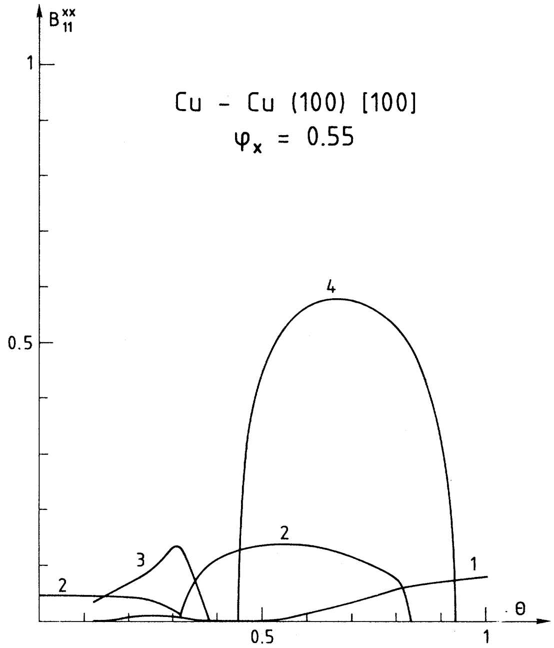

FIG. 10. Same as Fig. 5, but with the wave vector equal to 0.55.

the preceding case. The difference comes from the starting values at $\theta=0$. The $\Omega_Z=0.5$ frequency is located in the bulk band, Ω_X is unchanged, but the surface phonon of the bare surface $\Omega_R=0.401$ is also polarized mainly in the normal direction (${}^Z_1B^Z_1=0.7097, {}^X_1B^X_1=4.31\times10^{-2}$).

As θ varies, phonon 1 pushes away phonon 2, which encounters phonon 3 emerging from the bulk band. At the encounter point ($\theta=0.3$) a gap is opened and there is an exchange of polarization, in particular in the impurity plane along the direction normal to the surface (Fig. 9). During this evolution, phonon 2 disappears into the bulk at $\theta=0.82$, whereas phonon 1 gets progressively and con-

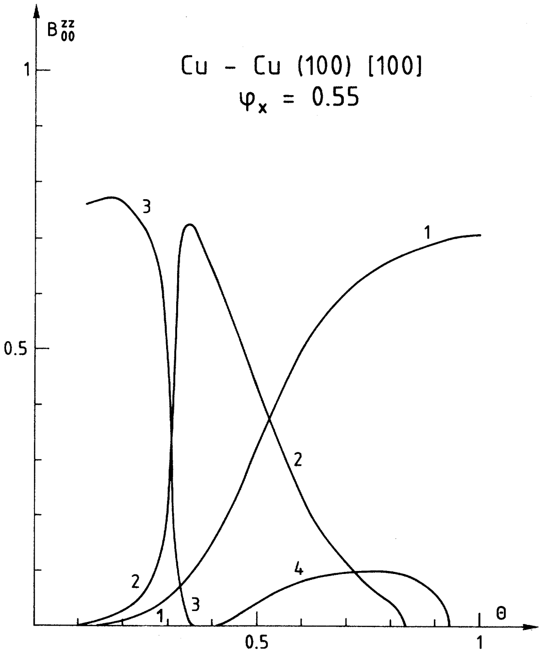

FIG. 9. Same as Fig. 4, but with the wave vector equal to 0.55.

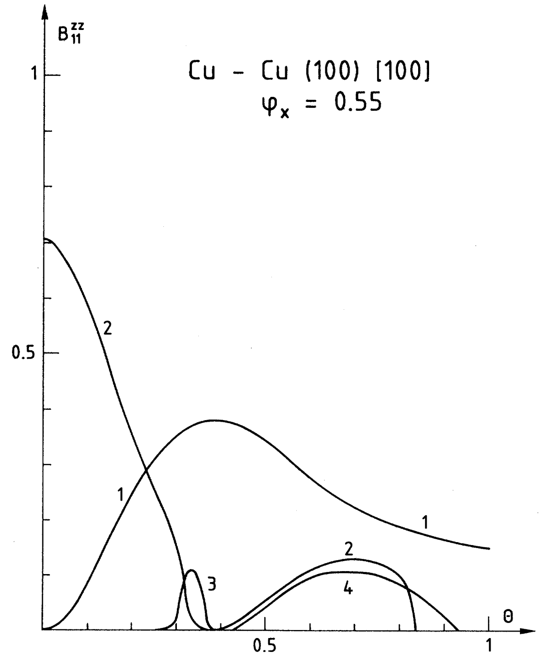

FIG. 11. Same as Fig. 6, but with the wave vector equal to 0.55.

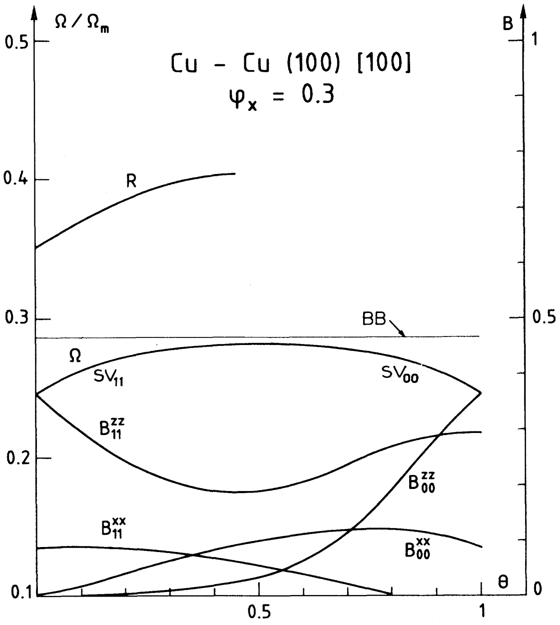

FIG. 12. Copper adatoms on a copper (100) face. Surface phonon frequency and amplitude of polarization as a function of the coverage. Curve labeled *R* gives the frequency of a resonance in bulk band. The wave vector is equal to 0.3 of the Brillouin-zone edge value in the [100] direction. BB refers the bulk band limit, SV and SP indicate sagittal vertical and parallel polarization, respectively.

tinuously the characteristic properties of the surface phonon of the bare crystal at $\theta=1$.

$\varphi_x=0.3$. For this wave-vector value, the frequencies Ω_X and Ω_Z at $\theta=0$ are inside the bulk band. The surface phonon is characterized by $\Omega_R=0.246$, ${}^X_1B^X_1=8.72\times10^{-2}$, ${}^Z_1B^Z_1=0.368$. The evolution of this frequency and its polarizations in the two planes and two directions are given in Fig. 12. All these quantities vary continuously without any noticeable features. However, the frequency $\Omega_X=0.35$ at $\theta=0$ gives rise to a resonance located in bulk band at a frequency which increases with coverage, but disappears as soon as this value is greater than 0.5 At low coverage it appears as a peak in the spectral density in the impurity and crystal planes, respectively, along the $\hat{\mathbf{x}}$ and $\hat{\mathbf{z}}$ directions. As the coverage increases, this resonance peak is detectable in the polarization relative to the two planes and two directions.

VI. MEASUREMENTS

Experimentalists are able to detect surface phonons and to measure their frequencies. In a measurement these phonons appear as isolated peaks over a more or less intense background. A peak intensity is proportional to the cross section of the single phonon exchanged between the incident particle and the surface.

Different theories indicate that the cross sections of the measured phonon is proportional to its polarization amplitude normal to the surface ${}^zB^z$ to which a contribution of the amplitude of polarization parallel to this surface ${}^xB^x$ is added. To our knowledge there is no reliable theory in the case studied here, i.e., a surface with adsorbed impurities. Nevertheless, we can expect that the preceding conclusions will be true provided that the polarization amplitude in the impurity and crystal planes are multiplied respectively by θ^2 and $(1-\theta)^2$. With this qualitative rule, it is possible to anticipate the results of measurements.

$\varphi_x=0.9$. Due to its polarization along $\hat{\mathbf{z}}$ in the surface plane (Fig. 6) and along $\hat{\mathbf{x}}$ in the impurity plane (Fig. 3), frequency 3 should be detected up to a coverage approximately equal to 0.6. For θ less than 0.3, its value is given by the linear relation

$$\Omega_3=0.496+0.24\theta\ ,$$

a relation which can characterize the presence of an adsorbed impurity on the surface.

The frequency 1 should be measured in the interval of θ [0.4,1] because it is then strongly polarized along $\hat{\mathbf{z}}$ in the impurity plane (Fig. 4). For coverage less than 0.4, the possibility of detection is doubtful. But if it is, one should observe the exchange of polarization between frequencies 1 and 2. This will yield an increase of the peak width for the coverage corresponding to the small gap between these frequencies.

$\varphi_x=0.55$. Frequency 1 could be measured from coverage 0.2, 0.3, up to 1, due its polarization along the normal in the impurity and crystal planes (Figs. 9 and 11). For the same reason frequency 2 seems to be detectable in the whole interval of coverage where it appears. However, it is closed to the bulk band frequency for θ greater than 0.25 and then possibly cannot be readily separated from the bulk phonon contribution in a measurement. If this is the case, the exchange of polarization with frequency 3 cannot be seen and this last frequency will not be detected too.

$\varphi_x=0.3$. The surface phonon can be surely detected in the whole interval of coverage variation except perhaps when its frequency is closed to the bulk band limit as explained above. But the most important point here is to characterize without ambiguity in the measurement the presence of the resonance which appears even at very small coverage.

VII. CONCLUSIONS

We have considered in this paper a perfect crystal on the surface of which is adsorbed an incomplete layer of impurities or a layer of alloy. A theoretical approach, similar to that used in the case of a three-dimensional disordered crystal,[1] is proposed, allowing one to calculate the average Green functions and therefore the phonon spectral density. These functions are decomposed into two terms giving, respectively, the new surface phonon frequencies and their broadening.

The first term, which corresponds to virtual-crystal approximation, has been calculated in the case of copper atoms adsorbed on the (100) face of this metal. For coverage less than approximately 0.5, new surface phonons appear and their frequencies evolve with adatom coverage. At a higher value of this quantity the whole system can be seen as a crystal with vacancies on the surface. For small coverage in vacancies, there is only one surface phonon of frequency and polarization close to that of the surface phonon of the perfect surface. The strong modification to the dynamic of surface with impurity atoms is then due to adatoms.

The present results can be tested in an experiment and could help to characterize the presence of adatoms on the surface, as it is the case in surface roughening. Then surface phonon measurements can be used to separate the effect of roughening of the onset of strong anharmonicity. In this last case, the dispersion relation of surface phonons should remain approximately that of the perfect surface.

ACKNOWLEDGMENTS

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APPENDIX A

The Green matrix $\tilde{G}_0^-(\Omega,K)$ [Eq. (23)] is equal to

$$\begin{bmatrix} (\Omega^2-b-i\varepsilon)^{-1} & 0 \\ 0 & \tilde{G}_s^- \end{bmatrix} , \tag{A1}$$

where the matrix $(\Omega^2-b-i\varepsilon)$ is a 3×3 diagonal matrix and $\tilde{G}_s^-$ is the Green matrix of the bare crystal. Then, $\tilde{G}_{011}^-$ in Eq. (25) is similar to $\tilde{G}_0^-$, except that the $\tilde{G}_s^-$ block is reduced to a $3n\times3n$ block with n the number of the crystal planes directly affected by the impurities. In this notation Ω is a dimensionless frequency as it is usual in this type of calculation. Equation (25) can be rewritten

$$\tilde{G}_{a11}^- - \begin{bmatrix} (\Omega^2-b-i\varepsilon)^{-1} & 0 \\ 0 & \tilde{G}_{s11}^- \end{bmatrix} \tilde{v}\tilde{G}_{a11}^- = \begin{bmatrix} (\Omega^2-b-i\varepsilon)^{-1} & 0 \\ 0 & \tilde{G}_{s11}^- \end{bmatrix} . \tag{A2}$$

This matrix equation is first multiplied on the left-hand side by the matrix

$$\begin{bmatrix} \Omega^2-b-i\varepsilon & 0 \\ 0 & \rho^{-1} \end{bmatrix} ,$$

in which the two diagonal block are diagonal matrices. Then the $\tilde{G}^-$ matrices are replaced by their expansion (Eq. (34)], which can be written

$$\tilde{G}_{a11}^- = \frac{4}{\Omega_m^2}\frac{\rho}{1-\rho^2}\left[\tilde{1}+2\sum_{p=1}^{\infty}\rho^p\tilde{A}_{2p}\right]$$

or

$$\tilde{G}_{s11}^- = \frac{4}{\Omega_m^2}\frac{\rho}{1-\rho^2}\left[\tilde{1}+2\sum_{p=1}^{\infty}\rho^p\tilde{a}_{2p}\right] .$$

Afterwards one multiplies each member by the number $(\Omega_m^2/4)(1-\rho^2)^2$ in order to suppress the denominators $(1-\rho^2)^{-1}$. Using the relation (35), each member is transformed into a polynomial with respect to the ρ variable. Identification of the terms of the same power yields the recurrence relations. In order to give their expressions in compact form, we define the matrices:

$$\tilde{g}_{2p} = \begin{bmatrix} \tilde{0} & \tilde{0} \\ \tilde{0} & \tilde{a}_{2p} \end{bmatrix} \quad \text{with } \tilde{g}_0 = \begin{bmatrix} \tilde{0} & \tilde{0} \\ \tilde{0} & \tilde{1} \end{bmatrix} ,$$

$$\tilde{B} = \begin{bmatrix} b-\tilde{\Omega}_{m/2}^2 & \tilde{0} \\ \tilde{0} & \tilde{0} \end{bmatrix} , \quad \tilde{1}_s = \begin{bmatrix} \tilde{1} & \tilde{0} \\ \tilde{0} & \tilde{0} \end{bmatrix} ,$$

where the first blocks $\tilde{0}$, $\tilde{0}$, $b-\tilde{\Omega}_{m/2}^2$, and $\tilde{1}$ are a 3×3 diagonal matrix. Then

$$\tilde{A}_0=\tilde{1}, \quad \tilde{A}_2=\frac{2}{\Omega_m^2}[\tilde{v}+\tilde{B}+\tilde{g}_2] ,$$

$$\tilde{A}_4=\frac{4}{\Omega_m^2}[(\tilde{v}+\tilde{B})\tilde{A}_2+\tilde{g}_2\tilde{v}]+\tilde{g}_4-\tilde{1}_s ,$$

$$\tilde{A}_6=\frac{4}{\Omega_m^2}[(\tilde{v}+\tilde{B})\tilde{A}_4+2\tilde{g}_2\tilde{v}\tilde{A}_2+(\tilde{g}_4-\tfrac{1}{2}\tilde{1}_s)\tilde{v}-\tfrac{1}{2}\tilde{B}]+\tilde{g}_6-\tilde{g}_2+\tilde{g}_0\tilde{A}_2 ,$$

$$\tilde{A}_8=\frac{4}{\Omega_m^2}[(\tilde{v}-\tilde{B})\tilde{A}_6+2\tilde{g}_2\tilde{v}\tilde{A}_4+2(\tilde{g}_4-\tfrac{1}{2}\tilde{1}_s)\tilde{v}\tilde{A}_2-\tilde{B}\tilde{A}_2+\tilde{g}_6\tilde{v}]+\tilde{g}_8-\tilde{g}_4+\tilde{g}_0\tilde{A}_4 ,$$

$$\tilde{A}_{2n}=\frac{4}{\Omega_m^2}\left[(\tilde{v}+\tilde{B})\tilde{A}_{2n-2}+2\tilde{g}_2\tilde{v}\tilde{A}_{2n-4}+2(\tilde{g}_4-\tfrac{1}{2}\tilde{1}_s)\tilde{v}\tilde{A}_{2n-6}-\tilde{B}\tilde{A}_{2n-6}+\sum_{p=3}^{n-2}\tilde{g}_{2p}\tilde{v}\tilde{A}_{2n-2p-2}+\tfrac{1}{2}\tilde{g}_{2n-2}\tilde{v}\right]$$
$$+\tilde{g}_{2n}-\tilde{g}_{2n-4}+\tilde{g}_0\tilde{A}_{2n-4}+\tilde{1}_s\tilde{A}_{2n-8} .$$

The generating coefficient matrices $\tilde{a}_{2p}$ are those of the bare crystal with a surface. A general method of calculation has been exposed in Refs. 6 and 7. They are those of an infinite crystal with a surface.

APPENDIX B

In order to determine the V matrix element, one writes the equation of motion of the atoms with atomic displacement u proportional to $\exp(i\omega t)$. As usual the mass, force constant, and frequency are transformed into dimensionless quantities, using atom crystal mass M and the nearest-neighbor force constant between crystal atoms α, as scaling quantities. Then the equations are written with the dimensionless frequency $\Omega=\omega(M/\alpha)^{1/2}$, the force constant ratio $\beta_{A,B}=\alpha_{A,B}/\alpha$ between the impurity and atom of the crystal surface, $\beta_{AA,AB,BB}=\alpha_{AA,AB,BB}/\alpha$ between impurity atoms, $\mu_{l,m,0}=\mu_A x_{l,m,0}+\mu_B(1-x_{l,m,0})$, $\mu_{A,B}=M_{A,B}/M$ for the impurity atom, and $\mu_{l,m,1}=1$ for a crystal surface atom. This difference in the μ value yields a V matrix which is not Hermitian. For instance, two symmetric terms with respect to the diagonal can be written

$$ {}_{l,m,0}^{Z}V_{l+1,m,1}^{Z}=-d_c\beta^{01}_{l,m,0}/\mu_{l,m,0} \,, $$

$$ {}_{l+1,m,1}^{Z}V_{l,m,0}^{Z}=-\beta^{01}_{l,m,0}d_c \,, $$

with

$$ \beta^{01}_{l,m,0}=\beta_A x_{l,m,0}+\beta_B(1-x_{l,m,0}) $$

and

$$ d_c=\frac{4a'^2}{a^2+4a'^2} \,. $$

In order to recover the symmetry, one proceeds to a unitary transform $\tilde{\gamma}^{-1}\tilde{V}\tilde{\gamma}$, where γ is a diagonal matrix of terms $(\mu_{l,m,0})^{-1/2}$. All the matrix elements between atoms belonging to planes 0 and 1 are then expressed in functions of the quantity

$$ \delta^{01}=\frac{\beta^{01}_{l,m,0}}{\sqrt{\mu_{l,m,0}}} \,. $$

This operation is equivalent to a change of basis for the displacements $u_{l,m,0}$ which become $u_{l,m,0}\sqrt{\mu_{l,m,0}}$ and are unchanged for the others.

Now we proceed to the average of $\tilde{\gamma}^{-1}\tilde{V}\tilde{\gamma}$. Due to the symmetry of translation, any displacement can be written $\exp(i\mathbf{K}\cdot\mathbf{R}_{l,m}b_k^{\sigma})$, and the matrix reduces to a 6×6 matrix called $\langle\tilde{V}\rangle$ in the text. Its nonvanishing terms are

$$ {}_{0}^{x}V_{0}^{x}={}_{0}^{y}V_{0}^{y}=2d_s\langle\delta^0\rangle+2\langle\delta^{00}\rangle(1-C_xC_y)={}^{x}b^{x}={}^{y}b^{y} \,, $$

$$ {}_{0}^{Z}V_{0}^{Z}=4\langle\delta^0\rangle d_c={}^{Z}b^{Z} \,, $$

$$ {}_{1}^{x}V_{1}^{x}={}_{1}^{y}V_{1}^{y}=2d_s\langle\beta^{01}\rangle, \quad {}_{1}^{Z}V_{1}^{Z}=4d_c\langle\beta^{01}\rangle \,, $$

$$ {}_{0}^{x}V_{0}^{y}={}_{0}^{y}V_{0}^{x}=2\langle\delta^{00}\rangle S_xS_y \,, $$

$$ {}_{0}^{x}V_{1}^{x}={}_{1}^{x}V_{0}^{x}=-2\langle\delta^{01}\rangle d_sC_x \,, $$

$$ {}_{0}^{y}V_{1}^{y}={}_{1}^{y}V_{0}^{y}=-2\langle\delta^{01}\rangle d_sC_y \,, $$

$$ {}_{0}^{x}V_{1}^{Z}={}_{1}^{Z}V_{0}^{x\,*}=-2i\langle\delta^{01}\rangle d_{Sc}S_x={}_{0}^{Z}V_{1}^{x}={}_{1}^{x}V_{0}^{Z\,*} \,, $$

$$ {}_{0}^{y}V_{1}^{Z}={}_{1}^{Z}V_{0}^{y\,*}=-2i\langle\delta^{01}\rangle d_{Sc}S_y={}_{0}^{Z}V_{1}^{y}={}_{1}^{y}V_{0}^{Z\,*} \,, $$

$$ {}_{0}^{Z}V_{1}^{Z}={}_{1}^{Z}V_{0}^{Z}=-2\langle\delta^{01}\rangle d_c(C_x+C_y) \,, $$

with

$$ d_{Sc}=\frac{2aa'}{a^2+4a'^2}, \quad d_s=\frac{a^2}{a^2+4a'^2} \,, $$

$$ C_x=\cos(\pi\varphi_x)\; S_x=\sin(\pi\varphi_x) \,, $$

$$ K_x\frac{a}{2}=\pi\varphi_x \,, $$

and the equivalent definition for the y direction

$$ \delta^0=\frac{\beta^{01}_{l,m,0}}{\mu_{l,m,0}} \,, $$

$$ \delta^{00}=[x_{l,m,0}x_{l+1,m+1,0}(\beta_{AA}-2\beta_{AB}+\beta_{BB}) + (\beta_{AB}-\beta_{BB})(x_{lm0}+x_{l+1,m+1,0})+\beta_{BB}]/\mu_{l,m,0} \,. $$

The average values of β^{01}, δ^0, and δ^{01} do not depend upon the distribution of the A and B species, as in the case of an alloyed layer

$$ \langle\beta^{01}\rangle=\beta_A\theta+\beta_B(1-\theta) \,, $$

$$ \langle\delta^{01}\rangle=\frac{\beta_A}{\sqrt{\mu_A}}\theta+\frac{\beta_B}{\sqrt{\mu_B}}(1-\theta) \,, $$

$$ \langle\delta^{0}\rangle=\frac{\beta_A}{\mu_A}\theta+\frac{\beta_B}{\mu_B}(1-\theta) \,, $$

or on the distribution of an impurity ($\beta_B=\mu_B=0$)

$$ \langle\beta^{01}\rangle=\beta_A\theta, \quad \langle\delta^{01}\rangle=\frac{\beta_A}{\sqrt{\mu_A}}\theta, \quad \langle\delta^{0}\rangle=\frac{\beta_A}{\mu_A} \,. $$

But the average of δ^{00} depends upon the A and B species distribution because it contains the product of two nearest-neighbors variable x. For a random distribution, it is equal to

$$ \langle\delta^{00}\rangle=\theta^2\frac{\beta_{AA}}{\mu_A}+(1-\theta)^2\frac{\beta_{BB}}{\mu_B} + \theta(1-\theta)\beta_{AB}\left[\frac{1}{\mu_A}+\frac{1}{\mu_B}\right] \,. $$

The case of adsorbed impurities is singular. δ^{00} reduces to

$$ \delta^{00}=\frac{\beta_{AA}x_{l,m,0}}{\mu_A x_{l,m,0}}x_{l+1,m+1,0} \quad (\beta_{AB}=\beta_{BB}=0) $$

and its average does not depend upon the impurity distribution

$$ \langle\delta^{00}\rangle=\frac{\beta_{AA}}{\mu_A}\theta \,. $$

APPENDIX C

Each generating coefficients can be decomposed in a sum of partial coefficients relative to surface phonons and bulk phonons contribution:

$$ {}^{\alpha}_{n_p}A^{\sigma}_{n_q 2p}(\mathbf{K}) = \sum_{s} {}^{\alpha}_{n_p}B^{\sigma}_{n_q}(\mathbf{K})\cos(p\theta_R) + {}^{\alpha}_{n_p}A^{\sigma\,b}_{n_q\,2p}(\mathbf{K}) , \quad \text{(C1)} $$

where s is the number of surface phonons at the given $\mathbf{K}$ value. In a numerical calculation, the number of coefficients ${}^{\alpha}_{n_p}A^{\sigma}_{n_q 2p}(\mathbf{K})$ calculated is limited to a number, say P. Then a surface phonon gives a contribution to the spectral density equal to

$$ \frac{2}{\pi\omega_m \sin(\theta/2)} {}^{\alpha}_{n_p}B^{\sigma}_{n_q} \left[1 + 2\sum_{1}^{P} \cos\langle p\theta_R\rangle \cos p\theta \right] = \frac{2}{\pi\omega_m \sin(\theta/2)} {}^{\alpha}_{n_p}B^{\sigma}_{n_q} \times \frac{\cos[(P+1)\theta_R]\cos P\theta - \cos[(P+1)\theta]\cos P\theta_R}{\cos\theta_R - \cos\theta} , \quad \text{(C2)} $$

which has a maximum value for $\theta=\theta_R$ equal to

$$ \frac{2}{\pi\omega_m \sin(\theta_R/2)} {}^{\alpha}_{n_p}B^{\sigma}_{n_q} \left[P + \frac{\cos(P\theta_R)\sin[(P+1)\theta_R]}{\sin\theta_r} \right] , \quad \text{(C3)} $$

roughly speaking proportional to P.

This yields, in the spectral density graph, a peak surrounded by oscillations of large amplitudes (see, for instance, Ref. 10). So the approximate value of $\omega_R(\theta_R)$ can be identified: for $\theta=\theta_R$ a maximum proportional to P should appear at the same position in the different spectral density calculated ${}^{\alpha}_{n_p}\rho^{\sigma}_{n_q}$ (for instance, $n_p=n_q$, $\alpha=\sigma$, $\alpha=x$, y, or z). Then from expression (C3), an approximate value of each ${}^{\alpha}_{n_p}B^{\sigma}_{n_q}$ can be obtained.

These are the starting values for a least-squares adjustment where one compares the exact ρ value and the value given by the sum of surface phonon contribution. One assumes that the contribution of bulk phonons vanishes. This is true if the adjustment is realized for ω values chosen on each side of the ω_R values and far from small $\Delta\omega$, and if the number P is sufficiently large. With the exact ω_R and B values known, expression (C1) gives the generating coefficients relative to the contribution of bulk phonons.

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