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Local vibrations in real crystals with combined defects

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The conditions of formation and the main characteristics of local vibrations due to the presence of light impurities Al, Mg, and Mn in the bulk and on the close-packed [111] surface of the fcc crystal lattice of silver are investigated. The influence of surface roughness is analyzed. Analytical approximations are obtained which describe the frequency and intensity of the local vibrations at the impurity atom and its nearest neighborhood to high accuracy. The proposed analytical approximations provide a practical way of determining the parameters of the defect structure and the interatomic interactions from the experimentally determined characteristics of the local vibrations. © 2008 American Institute of Physics. [DOI: 10.1063/1.2834262]

INTRODUCTION

Local vibrations, which are discrete vibrational levels lying outside the bands of the quasi-continuous spectrum of a crystal containing lighter or more strongly coupled impurity atoms, have been known for more than sixty years.^{1–3} The amplitudes of these vibrations fall off rapidly with distance from the defect. At distances from the impurity atom much greater than the characteristic radius of the interatomic interaction in the lattice, the fall-off can be considered exponential. Since that time, these local vibrations (LVs) have been investigated both theoretically and experimentally (see, e.g., Refs. 1–15). The results obtained in this field of research have been set forth in monographs on crystal lattice dynamics (Refs. 16–20 and others).

Local vibrations are determined as well-defined resonance levels by optical methods, by the method of point-contact spectroscopy, and in scattering experiments with neutrons, helium nuclei, etc. However, they are practically never used as a source of information about the defect structure and force interactions in real crystals, although such information can be obtained from an analysis of the main characteristics of the LVs. One of the main reasons for this is the difficulty of carrying out an effective comparison of the theory with experiment. Calculation of the frequencies and intensities and investigation of the conditions of formation and the character of the damping of LVs near a defect by conventional methods meet with great computational difficulties. Therefore, such calculations have been done only for extremely simplified models, which give only a qualitative description of LVs in real systems, or on the basis of numerical simulations. In the latter case one can make a quantitative comparison with experiment, but it is extremely difficult to extract information about the interatomic interaction and defect structure of the lattice from an analysis of the characteristics of the LVs.

Progress in the description of LVs has been furthered significantly by the development of the Jacobian, or \mathcal{J} matrix method (Refs. 21–23; see also Ref. 24). Rapid convergence of the local frequencies in the basis adopted in that method has been shown, and a simple numerical algorithm for its

implementation has been proposed.²⁵ The Jacobian matrix method has opened up possibilities for calculating the characteristics of LVs due to combined defects. The first numerical analysis of the influence of a surface on LVs due to point defects was given in Ref. 26. However, for obtaining information about the parameters of the defects and the host lattice from experimentally measured characteristics of the LVs it is extremely desirable to have analytical expressions relating the given characteristics with the desired parameters. Such expressions for frequencies lying outside the bands of the continuous spectrum were obtained in Ref. 27. The analytical approximation of Ref. 27 is based on the rapid convergence of Green functions in the basis adopted in the Jacobian matrix method for frequencies lying outside the quasi-continuous spectrum.

The present paper is devoted to investigation of LVs due to the presence of a combined defect — an impurity plus the surface of the sample — and to investigate the influence of surface roughness on these characteristics. Calculations are carried out on the basis of the analytical approach of Ref. 27. It is shown that measurements of the characteristics of LVs can be used to obtain information about the force interactions in crystals containing an impurity.

ANALYTICAL DESCRIPTION OF THE CHARACTERISTICS OF LOCAL VIBRATIONS

The analytical approach²⁷ that we have adopted for describing the frequencies and other characteristics of LVs makes use of the basis adopted in the \mathcal{J} -matrix method.^{21–24} That basis, $\{\vec{h}_n\}_{n=0}^{\infty}$, is obtained by orthonormalization of the sequence

$$\{\hat{\mathcal{L}}^n \vec{h}_0\}_{n=0}^{\infty} = \vec{h}_0, \hat{\mathcal{L}} \vec{h}_0, \hat{\mathcal{L}}^2 \vec{h}_0, \dots, \hat{\mathcal{L}}^n \vec{h}_0, \dots, \quad (1)$$

where $\hat{\mathcal{L}} \equiv \hat{\mathcal{L}}(\mathbf{r}, \mathbf{r}') = \hat{\Phi}(\mathbf{r}, \mathbf{r}') / \sqrt{m(\mathbf{r})m(\mathbf{r}'')}$ is an operator describing the lattice vibrations, $\hat{\Phi}(\mathbf{r}, \mathbf{r}')$ is the matrix of force constants^{16–20} describing the interaction of the atoms in positions \mathbf{r} and \mathbf{r}' , and $m(\mathbf{r})$ and $m(\mathbf{r}')$ are the masses of those atoms. The equation of the crystal lattice vibrations can be written as $(\hat{\mathcal{L}} - \omega^2 \hat{\mathcal{T}})\vec{\psi} = 0$, where ω is the eigenfrequency of

the vibrations, and $\hat{\mathcal{I}}$ is the unit operator. The operator $\hat{\mathcal{L}}$ operates in the $3N$ -dimensional space H of displacements of the lattice atoms (N is the number of atoms in the system). The vectors of this space, e.g., an eigenvector $\vec{\psi} \in H$ or basis vectors $\vec{h}_n \in H$ (we use an arrow above a symbol to distinguish it from the usual three-dimensional vectors, which are shown in boldface type).

The rapid convergence of the Green function in the basis $\{\vec{h}_n\}_{n=0}^{\infty}$ for any frequency interval is evidence of localization of the corresponding vibrations.

The basis $\{\vec{h}_n\}_{n=0}^{\infty}$ is defined by the choice of generating vector \vec{h}_0 and selects from the space of displacements H a certain subspace $H^{(h_0)}$, which is invariant with respect to the operator $\hat{\mathcal{L}}$, which is a linear shell stretched onto the basis $\{\vec{h}_n\}_{n=0}^{\infty}$. If the generating vectors are transformed via irreducible representations of the symmetry group of the system, then the subspace generated by them will be orthogonal, and in each of them only one local vibration can arise. The operator induced by the operator $\hat{\mathcal{L}}$ in each of these subspaces, in the basis $\{\vec{h}_n\}_{n=0}^{\infty}$, is described in the form of a tridiagonal \mathcal{J} matrix $\hat{\mathcal{L}} = \mathcal{L}_{mn} = a_n \delta_{mn} + b_n (\delta_{m,n+1} + \delta_{m+1,n})$, which has a simple spectrum. The nondegeneracy of the spectrum of operators induced by the operator $\hat{\mathcal{L}}$ in each of the subspaces $H^{(h_0)}$ allows one to obtain rather simple analytical approximations for the local Green functions of the system $\mathcal{G}(\omega^2)$. In other words, the matrix elements $\mathcal{G}_{00}(\omega^2)$ of the operator $\hat{\mathcal{G}}(\omega^2) = (\omega^2 \hat{\mathcal{I}} - \hat{\mathcal{L}})^{-1}$ can be approximated by an analytical function (Refs. 23 and 24; see also Ref. 27). If the band of the quasi-continuous spectrum is singly connected, $\omega \in [0; \omega_m]$, the matrix elements a_n and b_n obey the following relations:

$$\lim_{n \rightarrow \infty} a_n = 2 \lim_{n \rightarrow \infty} b_n = \frac{\omega_m^2}{2}, \quad (2)$$

and this, in particular, ensures the presence of square-root singularities of the spectral densities at the edges of the quasi-continuous spectrum. The analytical approximation, normalized to unity by the spectral density $\rho(\omega^2) = \pi^{-1} \text{Im } \mathcal{G}(\omega^2)$, is the so-called ‘‘regular’’ or ‘‘elliptical’’ distribution of the squares of frequencies often used in approximate calculations (see, e.g., Ref. 19), modulated by a certain polynomial of degree $2n$.

The analytical approximation of the real and imaginary parts of the Green function cannot be exact in the band of the continuous spectrum, where neither its real nor its imaginary part is an analytical function. However, outside the band of the continuous spectrum the local Green function (LGF) is an analytical function that converges very rapidly with increasing n . As was shown in Ref. 27, the analytical approximations for $n=1$, $\mathcal{G}_{(1)}(\omega^2)$, and for large n , $\mathcal{G}_{(n \gg 1)}(\omega^2)$, coincide to high accuracy. In the next Section we shall illustrate this for the example of the LGF of silver atoms located both in the bulk and on the surface of the sample. Therefore, using the LGF $\mathcal{G}_{(1)}(\omega^2)$, one can obtain a completely satisfactory description of the characteristics of the local vibrations. Their frequencies are solutions of the Lifshits equation,^{1-4,6} which can be written in the form

$$\mathcal{G}(\omega^2) \approx \mathcal{G}_{(1)}(\omega^2) = \mathcal{S}(\omega^2, \hat{\Lambda}); \quad \omega > \omega_m. \quad (3)$$

The function $\mathcal{S}(\omega^2, \hat{\Lambda})$ describes the influence of the defect and depends on the corresponding parameters of the perturbation operator $\hat{\Lambda}$. In the case of a degenerate regular perturbation^{1-4,6} one can always obtain an exact expression for this function. Thus for an isotopic impurity of substitution

$$\mathcal{S}(\omega^2, \hat{\Lambda}) \equiv \mathcal{S}(\omega^2, \varepsilon) = -\frac{1}{\omega^2 \varepsilon}, \quad (4)$$

where $\varepsilon \equiv (\tilde{m} - m)/m$ is the mass defect of the impurity, \tilde{m} is the mass of the impurity, and m is the mass of an atom of the host lattice. We note that one can practically always obtain uncomplicated analytical expressions for the first matrix elements a_0 and b_0 of the \mathcal{J} matrix and, hence, for the function $\mathcal{G}_{(1)}(\lambda)$.

In many cases a constructive alternative to solution of the Lifshits equation can be taken to find directly the poles of the LGF of the perturbed system $\tilde{\mathcal{G}}(\omega^2) = (\vec{h}_0, [\omega^2 \hat{\mathcal{I}} - \hat{\mathcal{L}}_0 - \hat{\Lambda}]^{-1} \vec{h}_0)$ with the use of the \mathcal{J} matrix of the perturbed operator $\hat{\mathcal{L}} = \hat{\mathcal{L}}_0 + \hat{\Lambda}$. This method is also convenient for determining the local vibrations due to a nondegenerate perturbation operator. If such a perturbation does not affect the width of the continuous spectrum or, hence, the limiting values of the \mathcal{J} matrix, then it can be considered ‘‘asymptotically degenerate.’’

The poles of the Green function ω_d^2 determine discrete frequencies, in particular, the local frequencies ω_l , and the residues at the poles, $\mu_0^{(d)} \equiv \text{res}_{\omega=\omega_d} \mathcal{G}_{00}(\omega^2)$, and the intensities, which characterize the value of the amplitude of the oscillations at discrete frequencies in the subspace of a certain vector \vec{h}_0 . The temperature dependence of the mean-square displacement of the impurity atom $\langle \vec{u}_i^2(T) \rangle$ has the form

$$\langle \vec{u}_i^2(T) \rangle = \frac{\hbar}{2\tilde{m}} \left[\int_0^{\omega_m^2} \frac{\rho(z)}{\sqrt{z}} \coth\left(\frac{\hbar\sqrt{z}}{2kT}\right) dz + \frac{\mu_0^{(l)}}{\omega_l} \coth\left(\frac{\hbar\omega_l}{2kT}\right) \right]. \quad (5)$$

It was shown in Ref. 27 that the square of the frequency of a local vibration is equal to

$$\omega^2(\eta, \zeta) = \frac{\omega_m^2}{4\zeta(1+\eta)} \left\{ 2\zeta - \eta - \sqrt{-\zeta + \frac{(\eta-\zeta)^2}{1+\zeta}} \right\}, \quad (6)$$

where the parameters η and ζ characterize the deviation of the matrix elements a_0 and b_0 from the limiting values (2):

$$a_0 = \frac{\omega_m^2}{2}(1+\eta); \quad b_0 = \frac{\omega_m^2}{4\sqrt{1+\zeta}}; \quad \eta, \zeta \in [-1, +\infty). \quad (7)$$

A local vibration exists for

$$\left\{ \begin{array}{l} \zeta < -\frac{3}{4}; \\ \eta \in [-1, +\infty); \end{array} \right. \left\{ \begin{array}{l} \zeta > -\frac{3}{4}; \\ \eta < \eta^*(\zeta) \equiv -\frac{1+2\zeta}{3+4\zeta}. \end{array} \right. \quad (8)$$

If conditions (8) are satisfied and a local vibration exists, its intensity will have the form

$$\mu_0 = \frac{\eta + (1+2\zeta) \sqrt{-\zeta + \frac{(\eta-\zeta)^2}{1+\zeta}}}{2\zeta \sqrt{-\zeta + \frac{(\eta-\zeta)^2}{1+\zeta}}}. \quad (9)$$

Substitution of Eq. (6) into the Lifshits equation (3) shows that $\omega_l(\eta, \zeta)$ satisfies this equation when conditions (8) are met.

After determining the functions $\eta(\varepsilon)$ and $\zeta(\varepsilon)$ for specific crystallographic structures containing various defect configurations and substituting them into Eqs. (6), (8), and (9), one can obtain the dependence of the conditions for formation and the dynamical characteristics of the local vibrations on the parameters characterizing the defect or configuration of defects.

LOCAL VIBRATIONS DUE TO A SUBSTITUTIONAL IMPURITY FOUND IN THE BULK AND NEAR AN ATOMICALLY SMOOTH SURFACE

In the description of the interatomic interaction in the fcc crystal lattices of certain metals such as Ag, Cu, and Al and solidified rare gases Ar, Kr, and Xe, one can limit consideration to the interaction of nearest neighbors.^{19,28} The corresponding matrices of force constants have the form²⁹

$$\Phi_{ik} \left(\mathbf{r}, \mathbf{r} + \left[\frac{a}{2}; \frac{a}{2}; 0 \right] \right) = - \begin{pmatrix} \alpha & \gamma & 0 \\ \gamma & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}. \quad (10)$$

For the other nearest neighbors, the coordinates of which are specified by a vector $\mathbf{\Delta} \neq 0$, the matrices of force constants $\Phi_{ik}(\mathbf{r}, \mathbf{r} + \mathbf{\Delta})$ are obtained from Eq. (10) with the aid of the symmetry operations of the point group O_h . The condition of translational invariance implies that the self-effect matrix has the form

$$\Phi_{ik}(\mathbf{r}, \mathbf{r}) = - \sum_{\mathbf{\Delta}} \Phi_{ik}(\mathbf{r}, \mathbf{r} + \mathbf{\Delta}) = (8\alpha + 4\beta) \delta_{ik}. \quad (11)$$

For a sufficiently large sample of an ideal crystal the LGFs of the bulk atoms are identical for all displacement directions and coincide with the total Green function

$$\mathcal{G}_{(n)}(\omega^2) = \lim_{N \rightarrow \infty} (3N)^{-1} \sum_{i=1}^3 \sum_{n=0}^{N-1} (\vec{h}_n^{(i)}, \hat{\mathcal{G}}_n^{(i)}).$$

As we see in Fig. 1, the real parts of the Green function $\mathcal{G}_{(n)}(\omega) \equiv 2\omega \mathcal{G}_{(n)}(\omega^2)$, and the corresponding spectral densities $\nu(\omega) = \pi^{-1} \text{Im } \mathcal{G}(\omega)$ of the fcc crystal lattice of silver for $n=1$ and $n=76$ differ noticeably for $\omega \in [0, \omega_m]$. However, for $\omega > \omega_m$, except for a very narrow region near the boundaries of the band of the continuous spectrum, the curves corresponding to the real part of the Green function practically coincide. The force constants of Ag were determined in Ref. 30: $\alpha \approx 1.3432$, $\beta \approx -0.2994$, and $\gamma \approx 1.5162$ (10^5 dyn/cm).

In the same figure we show examples of the graphical solution of the Lifshits equation (3) for the cases of light isolated substitutional impurities of Al, Mg, and Mn in silver. Such impurities can be considered as isotopic to extremely high accuracy. As a parameter characterizing the deviation from isotopicity one can take the relative difference of the volume of the substitutional impurity, equal to -0.09 for Al, 0.07 for Mg, and 0.001 for Mn in Ag.¹⁹ Curves 3–5 of this same figure correspond to the functions $\mathcal{S}(\omega, \varepsilon) = -2/(\omega\varepsilon)$, where $\varepsilon = -0.7499$ for Al (curve 3), $\varepsilon = -0.7747$ for Mg (curve 4), and $\varepsilon = -0.4907$ for Mn (curve 5). The values of the corresponding local frequencies ω at which these curves intersect the curves $\mathcal{G}_{(76)}(\omega)$ and $\mathcal{G}_{(1)}(\omega)$ coincide to an accuracy as good as $\sim 10^{-4}$. In the “isotopic approximation” we have adopted, the impurities mentioned above in Ag generate LVs with frequencies $\omega'_l \approx 7.7518$ THz for Al, $\omega'_l \approx 8.1172$ THz for Mg, and $\omega'_l = 5.8986$ THz for Mn (here $\omega' \equiv \omega/2\pi$).

To investigate the deviation from isotopicity of an impurity in a host lattice one can refine the interaction constants of the impurity and lattice using the frequencies and intensities of the LVs, expressed with the aid of Eqs. (6) and (9), in which we set

$$\left\{ \begin{array}{l} \eta(\varepsilon, \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) = \frac{\varepsilon - 1}{2} + \frac{\tilde{\gamma}(1 + \varepsilon)}{2\tilde{\alpha} + \tilde{\beta}}; \\ \zeta(\varepsilon, \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) = \frac{-4(\tilde{\alpha} - \tilde{\gamma})^2 + \tilde{\beta}(4\tilde{\alpha} + 4\tilde{\gamma} - 3\tilde{\beta}) + \varepsilon[2(\tilde{\alpha} + \tilde{\gamma}) + \tilde{\beta}]^2}{4[2(\tilde{\alpha}^2 + \tilde{\gamma}^2) + \tilde{\beta}^2]}, \end{array} \right. \quad (12)$$

where the force constants with tildes describe the interaction of an impurity with the atoms of the host lattice. The substitution of (12) into (6) and (9) leads to extremely awkward expressions that will not be written out here.

We consider the close-packed [111] surface of the fcc silver crystal. Here the change of the force interaction be-

tween the surface atoms themselves can be neglected. For Ag the stress in the crystal lattice, which for the interaction of nearest neighbors can be characterized by the values of the deviations $(\alpha - \gamma)/\gamma$ and β/γ , is small, and that was the reason we chose this crystal for our studies. It can be assumed to rather good accuracy that the relaxation of the stress oc-

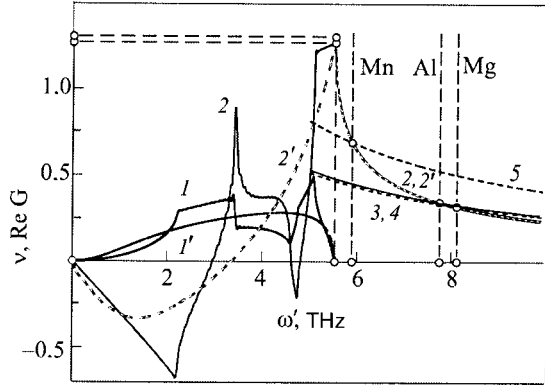


FIG. 1. Spectral densities (curves 1 and 1') and the real parts of the Green functions of the fcc crystal lattice of silver (curves 2 and 2'). The solid curves 1 and 2 correspond to $n=76$, and the dashed curves 1' and 2' to $n=1$. A graphical solution of the Lifshits equation for a local vibration due to light isotopic impurities is shown: the function $S(\omega, \varepsilon)$ for Al (curve 3), for Mg (curve 4), and for Mn (curve 5).

curs in the first coordination sphere of the surface atoms, and we assume that the interaction of the surface atoms (S) with the subsurface layer (US) is a central one,

$$\Phi_{ik}^{(S)}(\mathbf{r}^{(S)}, \mathbf{r}^{(S)} + \mathbf{\Delta}^{(US)}) = \alpha_0 \cdot \frac{\Delta_i^{(US)} \Delta_k^{(US)}}{|\Delta^{(US)}|^2},$$

and we neglect the change of the interaction between the remaining atoms.

The local spectral density and real parts of the LGFs of the surface atoms for displacements along and normal to the surface are presented in Fig. 2, where we have used the same notation as in Fig. 1. The values of the parameter $\alpha_0 = 1.0 \times 10^5$ and 1.8×10^5 dyn/cm correspond approximately to the limiting values of this parameter. The approximation of complete stress relaxation in the first coordination sphere of the surface atoms should hold in the interval of α_0 values considered. Near the frequencies of the local vibrations due to Al and Mg impurities, the real parts of $\mathcal{G}_{(n)}(\omega)$ for $n=1$ and $n=76$ coincide to high accuracy, and, just as for atoms found in the bulk of the crystal, the conditions of formation and the characteristics of the LVs can be described in the framework of approximations (6), (8), and (9). For the heavier manganese impurity the frequency of the LV due to vibrations of the impurity atom along the surface for $\alpha_0 = 10^5$ dyn/cm is close to ω_m . The values of ω_l calculated according to Eq. (6) with the aid of the \mathcal{J} matrix of rank $n=76$ differ by $\sim 1\%$.

The deviations η and ζ of the first elements of the \mathcal{J} matrix from the limiting values (2) have the following form: for displacements of a surface atom along the normal to the surface

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{4\gamma - 2\alpha_0 + \varepsilon[2(\alpha + \gamma) + \beta]}{2(\alpha + \alpha_0 - \gamma) + \beta}; \\ \zeta(\varepsilon, \alpha_0) = \frac{16\alpha\gamma + 4\beta(\alpha + \gamma) - \beta^2 - 8\alpha_0^2 + \varepsilon[2(\alpha + \gamma) + \beta]^2}{2[2(\alpha - \gamma)^2 + \beta^2 + 4\alpha_0^2]}; \end{cases} \quad (13)$$

and for displacements of this atom along the surface

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{2\gamma - \alpha_0 + 2\varepsilon[2(\alpha + \gamma) + \beta]}{4\alpha + 2\beta + 2\gamma + \alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{4(\alpha\beta + \alpha\gamma + \beta\gamma) - \beta^2 - 2\alpha_0^2 + \varepsilon[2(\alpha + \gamma) + \beta]^2}{2[(\alpha + \gamma)^2 + \alpha^2 + \beta^2 + \gamma^2 + \alpha_0^2]}; \end{cases} \quad (14)$$

for displacements of a subsurface atom along the normal to the surface

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{-2\alpha - \beta + 6\gamma - 4\alpha_0 + 2\varepsilon[2(\alpha + \gamma) + \beta]}{6\alpha + 3\beta - 2\gamma + 4\alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{4(\alpha\beta + \alpha\gamma) + 6\beta\gamma - 2(\alpha^2 + \beta^2 + \gamma^2 + 4\alpha_0^2) + \varepsilon[2(\alpha + \gamma) + \beta]^2}{2(\alpha - \gamma)^2 + 4\alpha^2 + 3\beta^2 + 4\gamma^2 + 8\alpha_0^2}; \end{cases} \quad (15)$$

and for its displacement along the surface

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{-2\alpha - \beta + 3\gamma - \alpha_0 + 2\varepsilon[2(\alpha + \gamma) + \beta]}{6\alpha + 3\beta + \gamma + \alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{2(2\alpha\beta + 3\alpha\gamma + 2\beta\gamma) - 2(\alpha^2 + \beta^2 + \gamma^2 + \alpha_0^2) + \varepsilon[2(\alpha + \gamma) + \beta]^2}{2(\alpha - \gamma)^2 + (\alpha + \gamma)^2 + 5(\alpha^2 + \gamma^2) + 3\beta^2 + 2\alpha_0^2}. \end{cases} \quad (16)$$

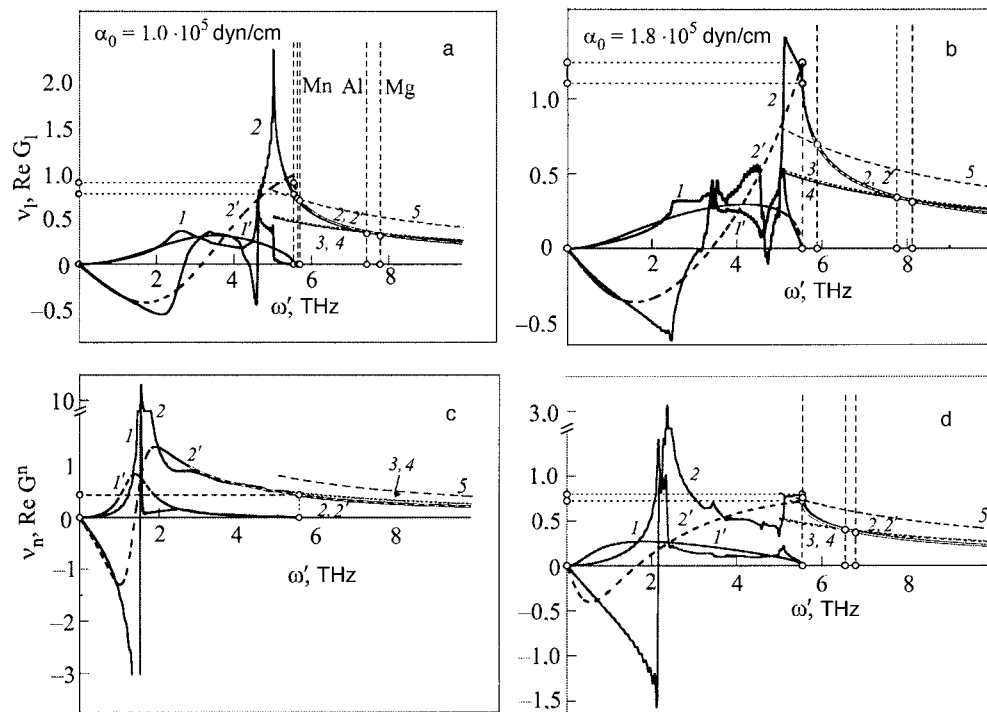


FIG. 2. Real parts of the local Green functions of surface atoms and the corresponding spectral densities $\nu(\omega) = \pi^{-1} \text{Im } \mathcal{G}(\omega)$ for displacements along and normal to the [111] Ag surface. The notation is the same as in Fig. 1.

By substituting these expressions into Eq. (8), one can determine the values of the defect parameters α_0 and ε for which LVs exist. The points $(\alpha_0; \varepsilon)$ at which LVs exist lie above the corresponding curves shown in Fig. 3. The vertical lines on the figure indicate the values of the mass defect of aluminum, magnesium, and manganese and also the value $\varepsilon^* \approx -0.2771$, which is the threshold mass defect for the formation of LVs in the bulk of Ag. The horizontal straight lines correspond to the values of the force constants α and γ for silver and the limiting values of the parameter α_0 .

Impurities of Al and Mg in Ag, treated here as isotopic (Fig. 3), can give rise to LVs in all four cases considered (displacements of an impurity atom found in the surface and subsurface layers in the directions along the surface and per-

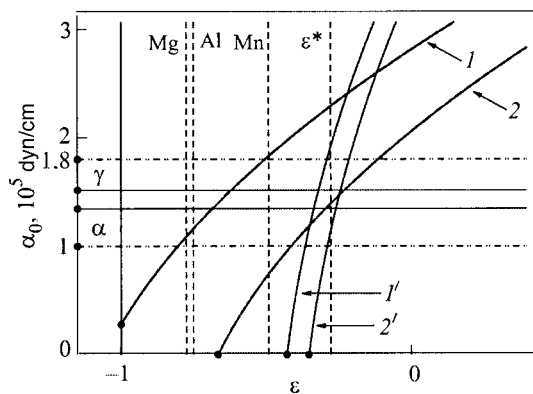


FIG. 3. Existence regions of local vibrations for different displacements of an impurity lying on the surface and in the subsurface layer. The values of the parameters α_0 and the mass defect ε at which the local vibrations form lie above the respective curves. Curves 1 and 1' correspond to surface atoms and curves 2 and 2' correspond to subsurface atoms; 1 and 2 are for displacement of the impurity normal to the surface; 1' and 2' to displacement along the surface.

pendicular to it). Only for displacements of an impurity on the surface in the direction normal to it is the threshold value α_0^* somewhat in excess of 10^5 dyn/cm. An Mn impurity is approximately twice as heavy as Al or Mg. If such an impurity is found at the surface, then in the interval of α_0 values from 1.0×10^5 to 1.8×10^5 dyn/cm it forms LVs only on account of displacements along the surface.

For all the cases considered, Fig. 4 shows the dependence of the LV frequencies ω'_l / ω'_m ($\omega'_m \approx 5.5367$ THz)³⁰ on the parameter α_0 , their intensities at the impurity atom, μ_0 , and on its first coordination sphere, μ_1 , for impurities whose mass defects correspond to Al, Mg, and Mn. Also shown in the figure are lines representing the calculations according to formulas (6) and (9) with the values from (13)–(16) substituted in. The symbols correspond to calculations of the poles of the functions $\tilde{\mathcal{G}}_{(76)}(\omega, \alpha_0, \varepsilon)$ and the residues at those poles. The good agreement of the data of both calculations indicates the real possibility of recovering the parameters of the lattice and defect from experimental measurements of the frequencies and other characteristics of the local vibrations.

INFLUENCE OF SURFACE ROUGHNESS ON THE CHARACTERISTICS OF THE LOCAL VIBRATIONS

If the surface is not atomically smooth but has some roughness, the frequency spectrum of an impurity found near roughness will differ from the spectrum of an impurity on the atomically smooth surface or in the bulk of the crystal. The differences can be substantial. Accordingly, both the conditions of formation and the characteristics of the LVs vary.

In the framework of the model considered in this study, the change of the force constants of an atom at the edge of a “crater” on the surface of the crystal can be described exactly in the same way as the change of the force interaction upon

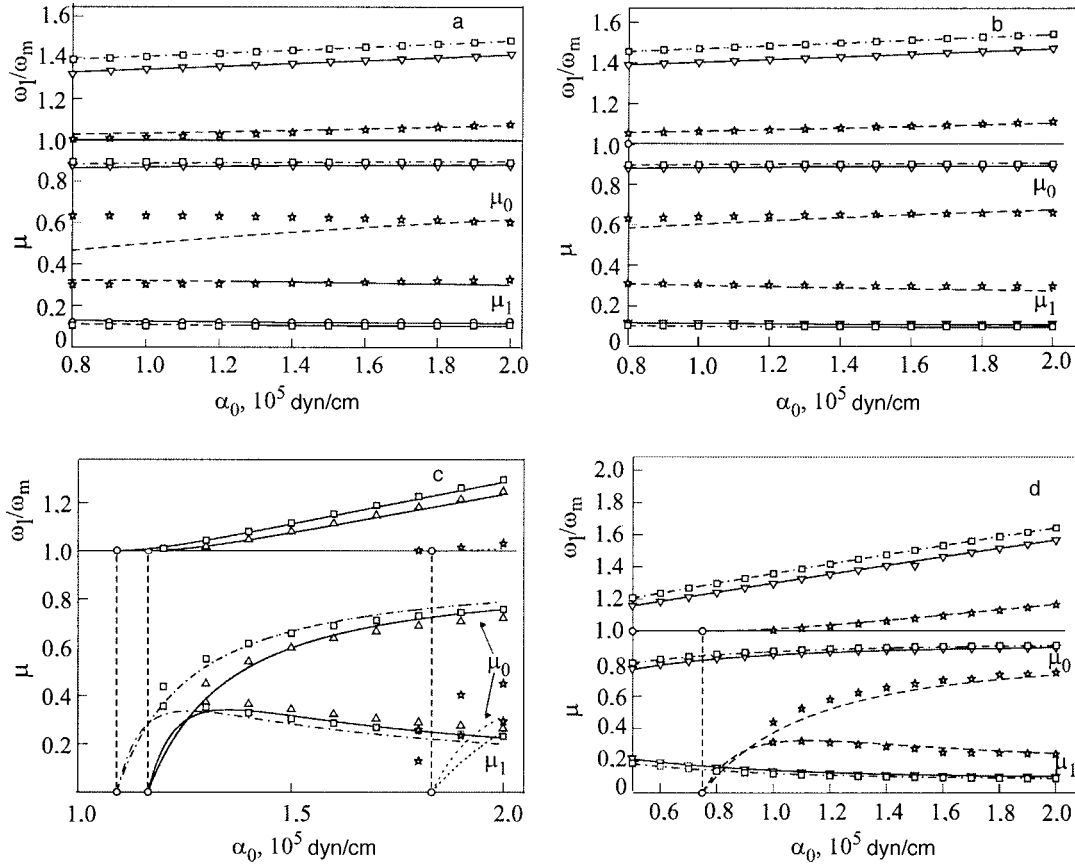


FIG. 4. Dependence of the frequencies and intensities of local vibrations on the parameter α_0 for Al (solid curves), Mn (dashed curves), and Mg (dot-and-dash curves). Local vibrations are generated by displacements of the surface atom along the [111] surface (a) and normal to the surface (b). Analogous displacements of a subsurface atom (c) and (d), respectively. The symbols are the characteristics calculated according to a \mathcal{J} matrix of rank $n=76$: Al (Δ), Mg (\square), Mn (\star); the analytical approximation is shown by the solid curves.

the formation of a surface. We shall assume that if some atom with radius vector \mathbf{r} is missing nearest neighbors at radius vectors $\mathbf{r} + \Delta^{(p)}$, then the interaction with atoms found at the points $\mathbf{r} - \Delta^{(p)}$ is central, $\Phi_{ik}(\mathbf{r} - \Delta^{(p)}) = \alpha_0 \Delta_i^{(p)} \Delta_k^{(p)} / \Delta^2$, and the interaction with the remaining atoms (10) does not change.

The possibility of describing to high accuracy the conditions of formation and the characteristics of LVs with the aid of the approximate formulas (6), (8), and (9) means that the given quantities are determined almost entirely by the first two moments of the spectral density.²⁷ Since the first two moments of the spectral density generated by the displacement of an isotopic impurity are influenced only by atoms that interact directly with it,²¹ a substantial difference in the behavior of the characteristics of the LVs from those considered in the preceding paragraph should be expected only for impurities located at the edge of some “crater” on the sur-

face. The size of the “crater” does not affect the first two moments of the spectral density, and it suffices to consider only the following configurations:

- an impurity found on the surface is missing one of the nearest neighbors lying on the surface;
- an impurity is located at the edge of a “crater,” i.e., it is missing two nearest neighbors on the surface which in turn are nearest neighbors of each other;
- an impurity located at the vertex of a “crater” and is missing three or four nearest neighbors lying on the surface.

For the first configuration, upon a displacement of the impurity in the direction normal to the surface (\mathbf{n}) the values of η and ζ are equal to

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta)(1 + 3\varepsilon) + 2\gamma(5 + 3\varepsilon) - 6\alpha_0}{2(2\alpha + 3\alpha_0 + \beta - 2\gamma)}; \\ \zeta(\varepsilon, \alpha_0) = \frac{4\alpha^2 - 72\alpha_0^2 + 52\alpha\beta - 11\beta^2 + 136\alpha\gamma + 20\beta\gamma + 4\gamma^2 + 9(2\alpha + \beta + 2\gamma)^2\varepsilon}{4[8\alpha^2 + 18\alpha_0^2 + 5\beta^2 + 4\beta\gamma + 8\gamma^2 - 4\alpha(\beta + 4\gamma)]}; \end{cases} \quad (17)$$

for the displacement of the impurity in the plane of the surface in the direction of the vacancy (\mathbf{l})

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{2\alpha(1+2\varepsilon) + 2\beta\varepsilon + 4\gamma(1+\varepsilon) - 3\alpha_0}{2\alpha + 3\alpha_0 + 2\beta}; \\ \zeta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)^2(1+\varepsilon) - 2(\alpha^2 + 3\alpha_0^2 + \beta^2 + \gamma^2)}{2(\alpha^2 + 3\alpha_0^2 + \beta^2 + \gamma^2)}; \end{cases} \quad (18)$$

for displacements of the impurity in the plane of the surface in the direction perpendicular to the direction to the vacancy (τ)

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{2\alpha - 3\alpha_0 + 4(\beta + \gamma) + 6(2\alpha + \beta + 2\gamma)\varepsilon}{10\alpha + 3\alpha_0 + 2\beta + 8\gamma}; \\ \zeta(\varepsilon, \alpha_0) = \frac{-2\alpha^2 - 18\alpha_0^2 + 52\alpha\beta - 5\beta^2 + 40\alpha\gamma + 20\beta\gamma - 2\gamma^2 + 9(2\alpha + \beta + 2\gamma)^2\varepsilon}{2[19\alpha^2 + 9\alpha_0^2 - 8\alpha\beta + 7\beta^2 + 8\gamma(2\alpha + \beta) + 19\gamma^2]}. \end{cases} \quad (19)$$

The dependence on α_0 of the frequency of the LV and also the intensities at the impurity itself and at its nearest neighbors, calculated according to formulas (6) and (9) for an isotopic impurity of aluminum, are presented in Fig. 5a. We see that in this case one isotopic impurity generates three local vibrations, the conditions of formation and characteristics of which are substantially different.

If the impurity is located at the edge of a “crater” on the surface, then for a displacement along this edge (l)

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{\alpha + \beta + \gamma + (2\alpha + \beta + 2\gamma)\varepsilon - \alpha_0}{\alpha + \gamma + \alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)^2(1+\varepsilon) - 2[(2\alpha_0^2 + (\alpha + \gamma)^2)]}{2[2\alpha_0^2 + (\alpha + \gamma)^2]}. \end{cases} \quad (20)$$

for a displacement of the impurity in the direction of the normal to the surface (\mathbf{n})

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)(2 + 3\varepsilon) + 4\gamma - 6\alpha_0}{2\alpha + \beta - 2\gamma + 6\alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{16\alpha^2 - 72\alpha_0^2 + 52\alpha\beta - 5\beta^2 + 112\alpha\gamma + 20\beta\gamma + 16\gamma^2 + 9(2\alpha + \beta + 2\gamma)^2\varepsilon}{2[10\alpha^2 + 36\alpha_0^2 + 7\beta^2 + 8\beta\gamma + 10\gamma^2 - 4\alpha(2\beta + 5\gamma)]}. \end{cases} \quad (21)$$

and for a displacement of the impurity in the plane of the layer in the direction perpendicular to the edge (τ)

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{5\alpha + \beta + 7\gamma + 3(2\alpha + \beta + 2\gamma)\varepsilon - 6\alpha_0}{\alpha + 2\beta - \gamma + 6\alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{22\alpha^2 + 52\alpha\beta - 1\beta^2 + 100\alpha\gamma + 20\beta\gamma + 22\gamma^2 + 9(2\alpha + \beta + 2\gamma)^2\varepsilon - 72\alpha_0^2}{2[7\alpha^2 + 10\beta^2 - 2\alpha(4\beta + 7\gamma) + 8\beta\gamma + 7\gamma^2 + 36\alpha_0^2]}. \end{cases} \quad (22)$$

The corresponding curves of the characteristics of the LVs for an Al impurity are shown in Fig. 5b. For the case l the threshold of formation of a local vibration is substantially lower, and the local frequencies and degree of localization of the vibrations is significantly higher than for the cases \mathbf{n} and τ . The curves for \mathbf{n} and τ practically coincide. Moreover, the local frequencies in the direction l are noticeably smaller than for the analogous vibrations in the previous configuration. This provides every justification for assuming that the LVs due to a light impurity on a rough surface can be reliably identified, making it possible to determine the defect structure and force interactions from experimental data.

For an impurity located at the vertex of a “crater,” there are two possible cases. If the edges forming this vertex cross at an obtuse angle (three nearest neighbors located alongside are missing), for all directions of displacement of the impurity the parameters η and ζ coincide:

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)(1 + \varepsilon) - 2\alpha_0}{2\alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)^2(1 + \varepsilon) - 8\alpha_0^2}{8\alpha_0^2}. \end{cases} \quad (23)$$

In this case all the characteristics of the LVs coincide for all directions also (see curves l in Fig. 5c).

In the second case the vertex is formed by edges that intersect at an acute angle, i.e., an impurity found on the surface is missing four nearest-neighbor surface atoms. Here the values of the parameters η and ζ for displacements of the impurity along the normal to the surface and along the bisector of the angle between the edges remain the same as in the previous case. And for a displacement of the impurity in the direction τ perpendicular to these two directions, the parameters η and ζ are equal to

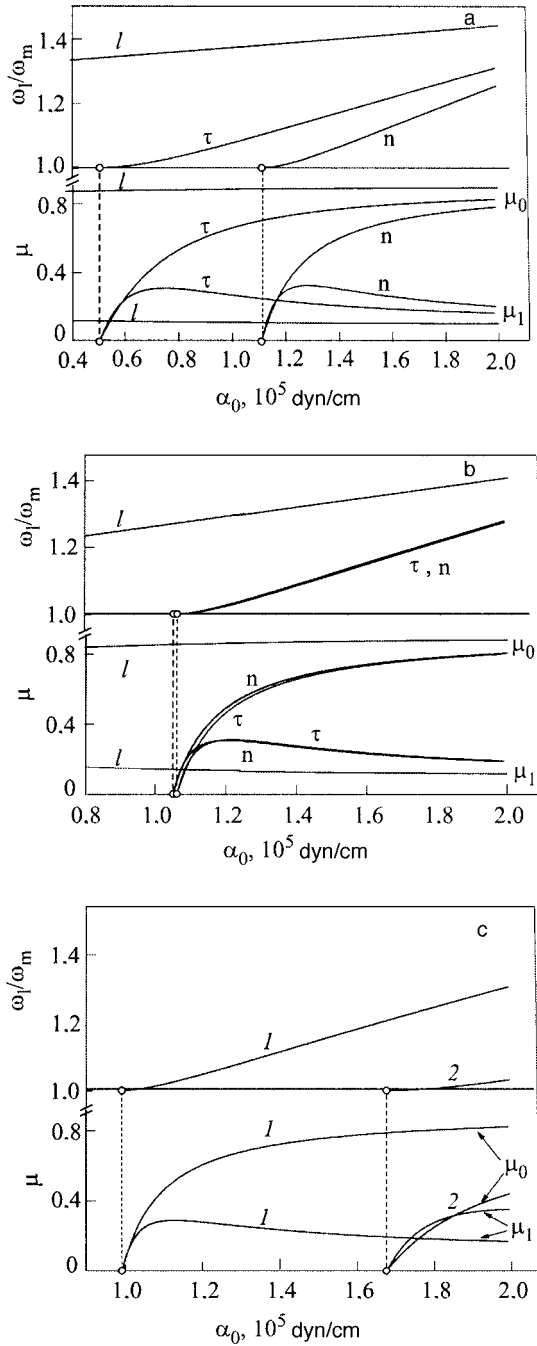


FIG. 5. Characteristics of the local vibrations of an impurity located on a rough surface.

$$\begin{cases} \eta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)(1 + \varepsilon) - \alpha_0}{\alpha_0}; \\ \zeta(\varepsilon, \alpha_0) = \frac{(2\alpha + \beta + 2\gamma)^2(1 + \varepsilon) - 4\alpha_0^2}{4\alpha_0^2}. \end{cases} \quad (24)$$

Vibrations in this direction have very low frequencies, in agreement with the results of Refs. 31 and 32. The characteristics of such LVs are given by curves 2 in Fig. 5c. We note that in this case the formation of LVs is hindered.

It should be noted that for displacements of the impurity along the normal to the surface, with a decrease of the number of surface atoms that are nearest neighbors with an impurity the threshold values α_0^* decrease, and the frequencies and degree of localization of the LVs increase (Fig. 4c and

Fig. 5). This is explained by the fact that for silver, the force constant β that determines the restoring force exerted on the atom by the other surface atoms is negative.

CONCLUSION

In this paper we have shown that the method of constructing analytical approximations for the main characteristics of local vibrations, proposed in Ref. 27, can be employed successfully for calculating the frequencies and intensities of the LVs due to complex defects, in particular, impurities located near an atomically smooth or a rough surface. The analytical approximations obtained enable one quite easily to extract information about the parameters of the host crystal and its defect structure from experimental data on the frequencies and other characteristics of the LVs. In an analogous way one can obtain analytical approximations for LVs due to impurities near other boundaries of the sample, e.g., surfaces of different orientation, various edges and vertices, which are their intersections, and also, when the LVs are generated by impurities found next to vacancies, as takes place in solutions of hydrogen and deuterium in palladium.³³

Our assumption of complete stress relaxation on the first coordination sphere of surface atoms is completely justified for the [111] surface of silver, considered here. This is due to the low stress of the crystal lattice. The same model of the surface can be used, although with somewhat lower accuracy, in the case of copper and gold.

For more highly stressed lattices, such as aluminum, and also for planes that are not close-packed, the relaxation can be more complicated and involve a greater number of coordination spheres. One can arrive at an analogous problem when considering substantially nonisotopic impurities, the force interaction of which with atoms of the host lattice differs significantly from the interaction in the lattice. However, in these cases also it is possible to use the proposed analytical approximation to obtain the characteristics of LVs whose frequencies are sufficiently well split off from the upper boundaries of the spectrum of the host lattice. The large number of additional parameters and the extraordinary awkwardness of the expressions obtained for such systems makes it possible to calculate the characteristics of LVs and to recover from them the parameters characterizing the defect structure only by making use of the corresponding experimental data. Therefore, one of our goals in this paper is to call the attention of experimenters to measurement of the main characteristics of local vibrations as an important source of information about the interatomic interactions in real crystals and the relaxation of the force interactions at the boundary of the sample.

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