

Effect of Boundary Surfaces on Localized Mode Frequencies of a Crystal Containing a Mass Defect

M. ASHKIN

Westinghouse Research Laboratories, Beulah Road, Churchill Borough, Pittsburgh, Pennsylvania

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The vibrational frequencies of the localized modes due to a mass defect in a simple cubic lattice with boundary surfaces have been studied. The perfect crystal is treated in the harmonic approximation with nearest- and next-nearest-neighbor central-force interactions between atoms. The most general problem is solved formally, and a detailed treatment is presented for the case of a very small mass of the defect atom compared to that of the host atom. The detailed calculations are performed in the case where a condition is imposed on the force constants of the crystal which leads to elastic isotropy in the long-wavelength limit. A pair of boundary surfaces is created mathematically by setting to zero all interatomic forces which cross a given plane. It is found that two of the three localized modes caused by the defect are degenerate. The nondegenerate mode corresponds to motion of the impurity atom normal to the surface, and the degenerate ones correspond to motions in two perpendicular directions parallel to the surface. For a light defect in the crystal surface and a ratio of its mass to the host atom's mass of $\frac{1}{2}$, the frequency of the nondegenerate mode is 71% of the bulk value, i.e., the frequency of a localized mode corresponding to the same defect in the absence of a free surface; the frequency of the degenerate modes is 91% of the bulk value. The localized-mode vibrational frequency when the defect atom is in the first layer below the surface differs from the bulk value by less than 0.02% of the latter value.

INTRODUCTION

IN a real crystal the presence of a boundary surface influences the physical properties of the atoms of the crystal, especially those in the vicinity of the surface. Many examples of surface effects have been studied. Since we will deal with a problem in lattice dynamics, we cite a few examples in this latter area. At low temperatures the lattice specific heat has a contribution proportional to T^2 , where T is the absolute temperature, which can be interpreted as due to the vibrations of the surface atoms.¹ From the diffraction of low-energy electrons by the surface of nickel crystals, MacRae and Germer² concluded that the surface atoms have a larger vibrational amplitude in a direction normal to the surface than the amplitude of the atoms in the interior of the crystal. Various authors³ have studied the Mössbauer effect for a crystal with a surface and have found a strong dependence of the mean-square amplitude and second-order Doppler shift on the position of the resonant nucleus relative to the surface.

This paper presents a calculation of the vibrational frequencies of the localized modes that result when a light mass defect is in the surface of a simple cubic Bravais crystal. The perfect crystal is treated in the harmonic approximation. Explicit calculations of the local mode frequencies are performed for the model with nearest and next-nearest-neighbor central-force interaction between atoms. The force constants of the crystal have been chosen in such a way that it elastically isotropic in the long-wavelength limit. These

explicit calculations are valid only for light defect atoms with a mass ratio $M'/M \ll \frac{1}{4}$, where M' and M are the masses of the defect and host atoms, respectively. This restriction is due to the method of calculation which involves an expansion in inverse powers of the ratio of the eigenfrequency to the maximum frequency of the perfect bulk crystal. The over-all treatment is, however, more general, and a formal solution of the most general problem is given.

A quantitative understanding of the differences between the localized mode frequencies when the defect atom is in the surface of the crystal and when the defect is in the interior of a crystal can be gained by recognizing how the environment of the defect atom differs in the two cases. There are two main features.

An atom in the surface has fewer neighbors than one in the bulk of the crystal, and therefore the total interaction of a surface atom with its neighbors is weaker than the total interaction of a bulk atom with its neighbors. As a consequence of one of Rayleigh's theorems,^{4,5} the localized mode frequencies due to a surface defect are smaller than those due to a bulk defect. The second difference is the degree of degeneracy of the modes. For a simple cubic Bravais crystal, in the absence of a free surface, the localized modes which arise when a light mass defect is present are triply degenerate.⁵ This degeneracy is partially removed when the defect atom is in the surface of a simple cubic Bravais crystal. The presence of the surface lowers the basic crystal symmetry from cubic to tetragonal about an axis normal to the surface; the triply degenerate modes are replaced by two degenerate modes and one

¹ M. Dupuis, R. Mazo, and L. Onsager, *J. Chem. Phys.* **33**, 1452 (1960).

² A. U. MacRae and L. H. Germer, *Phys. Rev. Letters* **8**, 489 (1962).

³ R. F. Wallis and D. C. Gazis, *Phys. Rev.* **128**, 106 (1962); M. Rich, *Phys. Letters* **4**, 153 (1963); A. Corciovei and A. Berinde, *J. Phys. Radium* **24**, 89 (1963); A. A. Maradudin and J. Melngailis, *Phys. Rev.* **133**, A1168 (1964).

⁴ Lord Rayleigh, *Theory of Sound* (Dover Publications, Inc., New York, 1945), Vol. I.

⁵ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963).

nondegenerate mode. The results for the models treated show these qualitative features.

FORMULATION

We follow Lifschitz⁶ in viewing a boundary surface of a crystal as an extended defect in an infinite crystal. A pair of boundary surfaces is thus created by removing the set of interactions which cross some given plane of the infinite crystal.

An eigenvalue equation for the frequency of the localized modes that occur when a mass defect is present in a crystal with a pair of boundary surfaces is obtained by taking the perfect crystal with boundary surfaces as the unperturbed crystal and considering the mass defect as a perturbation. The potential energy in the harmonic approximation of the perfect crystal without a surface can be written

$$\Phi = \frac{1}{2} \sum_{l'l''\alpha\beta} \Phi_{\alpha\beta}^{(0)}(l'l'') u_{\alpha}(l) u_{\beta}(l''), \quad (1)$$

where $l = (l_1, l_2, l_3)$ is a set of integers which label the position of an atom relative to some origin, $u_{\alpha}(l)$ is the α -Cartesian component of the displacement of the l th atom from equilibrium, and the energy of the static crystal is omitted. This expression for the potential energy holds also for a crystal with a defect when a change in force constants is neglected. The effects of force constant changes will not be considered. The force on the atom at the l th site of the infinite crystal is

$$F_{\alpha}(l) = \partial\Phi/\partial u_{\alpha}(l) = - \sum_{l'\beta} \Phi_{\alpha\beta}^{(0)}(ll') u_{\beta}(l'). \quad (2)$$

A pair of surfaces whose atoms lie in one of the planes $l_3 = l_z = 0$, and 1, is created by removing the forces that cross the space between these two planes. The case of nearest- and next-nearest-neighbor force interactions between atoms will be treated. When these forces are subtracted from the original force on an atom of the unbounded crystal, the force on an atom of the crystal with a pair of surfaces becomes

$$F_{\alpha}(l) = - \sum_{l'\beta} \Phi_{\alpha\beta}^{(0)}(ll') u_{\beta}(l') + \delta_{l_z,0} \sum_{l'\beta} \delta_{l_z',1} \Phi_{\alpha\beta}^{(0)}(ll') u_{\beta}(l') + \delta_{l_z,1} \sum_{l'\beta} \delta_{l_z',0} \Phi_{\alpha\beta}^{(0)}(ll') u_{\beta}(l'), \quad (3)$$

where $\delta_{a,b} = 1$, if $a = b$, and is zero otherwise. The sum over l' in Eq. (3) and similar sums in the equations to follow include nearest and next-nearest neighbors only. The expression for the potential energy of a crystal with the kind of surface created, which follows from Eq. (3), can be written

$$\Phi' = \sum_{l'l''\alpha\beta} \Phi_{\alpha\beta}(ll'') u_{\alpha}(l) u_{\beta}(l''), \quad (4)$$

with the expansion coefficient $\Phi_{\alpha\beta}(ll'')$ given, in terms of the coefficient for the unperturbed crystal, by

$$\Phi_{\alpha\beta}(ll'') = \Phi_{\alpha\beta}^{(0)}(ll'') + \delta\Phi_{\alpha\beta}(ll'') \quad (\text{for } l \neq l''), \quad (5)$$

$$\Phi_{\alpha\beta}(ll'') = - \sum_{l', l'' \neq l} \Phi_{\alpha\beta}(ll'),$$

where

$$\delta\Phi_{\alpha\beta}(ll'') = - (\delta_{l_z,0} \delta_{l_z',1} + \delta_{l_z,1} \delta_{l_z',0}) \Phi_{\alpha\beta}^{(0)}(ll'') \quad (\text{for } l \neq l''),$$

$$\delta\Phi_{\alpha\beta}(ll'') = - \sum_{l', l'' \neq l} \delta\Phi_{\alpha\beta}(ll'). \quad (6)$$

The potential energy of a crystal with a mass defect when force-constant changes are neglected is the same as when the defect is not present, but the kinetic energy is changed by the presence of the defect. If a single defect atom of mass M' is substituted for a host atom of mass M at the l_0 th site, the kinetic energy of the crystal becomes

$$\text{K.E.} = \frac{1}{2} \sum_{l'\alpha} M \dot{u}_{\alpha}^2(l') - (1 - M'/M) \frac{1}{2} M \sum_{\alpha} \dot{u}_{\alpha}^2(l_0). \quad (7)$$

Since we choose the mass defect as the perturbation, the time-independent equations of motion for the system of a mass defect at $l = l_0$ and a pair of free surfaces at $l_3 = 0$ and 1 in an harmonic crystal will be written

$$\sum_{l'\beta} L_{\alpha\beta}(ll'; \omega^2) u_{\beta}(l') = \sum_{l'\beta} \delta L_{\alpha\beta}(ll'; \omega^2) u_{\beta}(l'), \quad (8)$$

or in a matrix form

$$\mathbf{L}(\omega^2) \mathbf{u} = \delta \mathbf{L} \mathbf{u}, \quad (9)$$

where

$$L_{\alpha\beta}(ll'; \omega^2) = \omega^2 M \delta_{l,l'} \delta_{\alpha,\beta} - \Phi_{\alpha\beta}(ll') \quad (10)$$

$$= (\omega^2 M \mathbf{1} - \Phi)_{ll' \alpha\beta}. \quad (10')$$

and the perturbation $\delta \mathbf{L}$ is

$$\delta L_{\alpha\beta}(ll'; \omega^2) = \omega^2 M \epsilon \delta_{l,l_0} \delta_{l',l_0} \delta_{\alpha\beta}. \quad (11)$$

In these expressions $\Phi_{\alpha\beta}(ll')$ is given by Eq. (5) and $\epsilon = 1 - (M'/M)$.

We obtain an eigenvalue equation for the vibrational frequencies of the localized modes with the help of $G_{\alpha\beta}(ll'; \omega^2)$, the Green's function for the crystal with a surface, defined by the equation

$$\sum_{l'', \beta'} L_{\alpha\beta'}(ll'') G_{\beta'\gamma}(l''l'; \omega^2) = \delta_{\alpha\beta} \delta_{ll'} \quad (12)$$

or in a matrix form

$$\mathbf{L} \mathbf{G} = \mathbf{1}. \quad (13)$$

With the use of G , we can rewrite Eq. (8) as

$$\sum_{l', \beta} [\delta_{\alpha\beta} \delta_{ll'} - \sum_{l'', \gamma} G_{\alpha\gamma}(ll''; \omega^2) \delta L_{\gamma\beta}(l''l')] u_{\beta}(l') = 0, \quad (14)$$

[⁶ I. M. Lifschitz, Nuovo Cimento Suppl. 3, 716 (1956).

which leads to the eigenvalue equation

$$\det[\mathbf{1} - \mathbf{G}(\omega^2)\delta\mathbf{L}(\omega^2)] = 0. \quad (15)$$

For a fixed value of l , labeling the defect atom $\mathbf{1} - \mathbf{G}\delta\mathbf{L}$ is a 3×3 matrix in the Cartesian indices x , y , and z .

In the present representation, for a simple cubic Bravais lattice, the 3×3 matrix $\mathbf{1} - \mathbf{G}\delta\mathbf{L}$ is diagonal; the xx and yy elements are equal to each other, but, in general, they are not equal to the zz element. These properties follow from the invariance of the crystal when its atoms are reflected in the xz and yz planes, and the tetragonal symmetry about the z axis of the crystal with a pair of boundary surfaces normal to the z axis. The determinantal equation, Eq. (15), can thus be replaced by the pair of equations

$$\begin{aligned} 1 &= \epsilon M \omega^2 G_{xx}(l; \omega^2), \\ 1 &= \epsilon M \omega^2 G_{zz}(l; \omega^2), \end{aligned} \quad (16)$$

where l now labels the defect site.

BASIC APPROXIMATIONS

In a bulk crystal (crystal with no surface) the presence of a defect with mass lighter than that of the host atom gives rise to a localized mode with a frequency greater than the maximum frequency of the perfect crystal. The presence of a surface depresses the localized mode frequencies, at least when the defect atom is in the vicinity of the surface. However, for small enough mass ratio the depressed frequencies will be much greater than ω_L . It is this case we now study.

The Green's function $G_{\alpha\beta}(l'; \omega^2)$, as the inverse of \mathbf{L} defined by Eq. (10), can be written

$$\begin{aligned} G_{\alpha\beta}(l'; \omega^2) &= \{[\omega^2 M \mathbf{1} - \Phi]^{-1}\}_{l' \alpha \beta} \\ &= (1/\omega^2) \{M^{-1/2} [\mathbf{1} - \omega^{-2} M^{-1/2} \Phi M^{-1/2}]^{-1} M^{-1/2}\}_{l' \alpha \beta}, \end{aligned} \quad (17)$$

or, since all masses are the same in the unperturbed crystal as it has been defined, Eq. (17) can be rewritten

$$M \omega^2 G_{\alpha\beta}(l'; \omega^2) = \{[\mathbf{1} - \omega^{-2} \mathbf{D}]^{-1}\}_{l' \alpha \beta}, \quad (18)$$

where

$$[\mathbf{D}]_{l' \alpha \beta} = (1/M) \Phi_{\alpha\beta}(l'). \quad (19)$$

The dynamical matrix \mathbf{D} is proportional to the ω_L^2 , the square of the maximum frequency of the perfect crystal, and since we are considering the case where $\omega^2 \gg \omega_L^2$, $M \omega^2 G$ will be evaluated by expanding it in powers of ω^{-2} . The expansion of the diagonal part of $[\mathbf{1} - \omega^{-2} \mathbf{D}]^{-1}$,

$$\{[\mathbf{1} - \omega^{-2} \mathbf{D}]^{-1}\}_{l' \alpha \alpha} = 1 + \sum_{n=1}^{\infty} [\mathbf{D}^n]_{l' \alpha \alpha} \omega^{-2n} \quad (20)$$

can be partially resummed to give

$$\{[\mathbf{1} - \omega^{-2} \mathbf{D}]^{-1}\}_{l' \alpha \alpha} = [1 - D_\alpha(l, \omega^2)]^{-1}. \quad (21)$$

$D_\alpha(l, \omega^2)$ is defined by the series

$$D_\alpha(l, \omega^2) = \sum_{n=1}^{\infty} a_n(\alpha, l) \omega^{-2n}, \quad (22)$$

where the first three coefficients are

$$a_1(\alpha, l) = [\mathbf{D}]_{l' \alpha \alpha}, \quad (23)$$

$$a_2(\alpha, l) = \sum_{\substack{l', l'' \neq l \\ \beta, \beta' \neq \alpha}} [\mathbf{D}]_{l' \alpha \beta} [\mathbf{D}]_{l'' \beta' \alpha}, \quad (24)$$

$$a_3(\alpha, l) = \sum_{\substack{l', l'' \neq l \\ l''', l'''' \neq l \\ \beta, \beta' \neq \alpha \\ \gamma, \gamma' \neq \alpha}} [\mathbf{D}]_{l' \alpha \beta} [\mathbf{D}]_{l'' \beta' \gamma} [\mathbf{D}]_{l''' \gamma' \alpha}. \quad (25)$$

The remaining expansion coefficients in Eq. (22) are defined in an analogous way; for $a_n(\alpha, l)$, as in Eqs. (24) and (25), no summation variable can equal l or α . For the eigenvalue problem, only $G_{\alpha\alpha}(l'; \omega^2)$ with $l=l'$ is required.

When the form for $G_{\alpha\alpha}(l'; \omega^2)$ given by Eq. (21) is used in Eq. (16), we find

$$M'/M \equiv \lambda = D_\alpha(l, \omega^2), \quad (26)$$

where $\alpha = x$ and z , and l labels the site of the defect atom. $D_\alpha(l, \omega^2)$ is defined in Eq. (22) by a power series in inverse power of ω^2 . Substitution of this series in Eq. (26) and the solution of the resulting equation for ω^2 gives the following expression for the localized mode frequencies:

$$[\omega(\alpha, l)]^2 = \frac{a_1(\alpha, l)}{\lambda} + \frac{a_2(\alpha, l)}{a_1(\alpha, l)} + \frac{\lambda a_3(\alpha, l)}{[a_1(\alpha, l)]^2} + O(\lambda^2). \quad (27)$$

In Eq. (27), $\omega(\alpha, l)$ denotes the vibrational frequency of the localized mode in which the impurity nucleus is at the l th site and vibrates in the direction of the α axis of the Cartesian coordinate system. The square of the eigenfrequencies is obtained to order λ , which is sufficient to distinguish a defect atom one layer away from the surface atoms from one in the bulk of the material.

DETAILS OF CALCULATION

The atomic force constants for central forces are

$$\begin{aligned} \Phi_{\alpha\beta}^{(0)}(l') &= -[X_\alpha(l-l') X_\beta(l-l') / |\mathbf{X}(l-l')|^2] \\ &\quad \times \phi''(|\mathbf{X}(l-l')|). \end{aligned} \quad (28)$$

$\mathbf{X}(l-l')$ is the distance between the atoms at the l th and l' th site and is defined by

$$\mathbf{X}(l-l') = (l_1 - l'_1) a_0 \hat{i}_1 + (l_2 - l'_2) a_0 \hat{i}_2 + (l_3 - l'_3) a_0 \hat{i}_3, \quad (29)$$

where a_0 is the lattice parameter, and $\hat{i}_1, \hat{i}_2, \hat{i}_3$ the unit vectors of the Cartesian coordinate system coincide in their directions with the primitive lattice vectors of the simple cubic lattice. ϕ is the potential function describing the interaction between pairs of atoms and is a

function only of the magnitude of their separation. ϕ'' denotes the second derivative of this function. If the force constants of the crystal satisfy the condition

$$\phi''(a_0) = \phi''(a_0\sqrt{2}), \quad (30)$$

then the crystal is elastically isotropic in the long-wavelength limit. This condition will be imposed for simplicity. For the crystal model considered, the maximum frequency ω_L of the perfect crystal is

$$\omega_L = [12\phi''(a_0)/M]^{1/2}. \quad (31)$$

For $a_1(\alpha, l)$, using Eqs. (5), (6), and the equations of the present section, we find

$$a_1(\alpha, l) = \begin{cases} (6 - \delta_s)\omega_L^2/12 & \text{for } \alpha = x \text{ and } y \\ (6 - 3\delta_s)\omega_L^2/12 & \text{for } \alpha = z, \end{cases} \quad (32)$$

where

$$\delta_s = \delta_{l_z, 0} + \delta_{l_z, 1}, \quad (33)$$

which equals one, if the defect atom is in the surface and is zero otherwise. If we let

$$A = \sum_{\substack{l', l'' \neq l \\ \beta, \beta \neq \alpha}} \Phi_{\alpha\beta}^{(0)}(l'l')\Phi_{\beta\alpha}^{(0)}(l'l''), \quad (34)$$

$$B_\alpha = \sum_{\substack{l', l'' \neq l \\ \beta, \beta \neq \alpha}} \delta\Phi_{\alpha\beta}(l'l')\delta\Phi_{\beta\alpha}(l'l''), \quad (35)$$

$$C_\alpha = \sum_{\substack{l', l'' \neq l \\ \beta, \beta \neq \alpha}} \delta\Phi_{\alpha\beta}(l'l')\Phi_{\beta\alpha}^{(0)}(l'l''), \quad (36)$$

then

$$a_2(\alpha, l) = A + B_\alpha + 2C_\alpha. \quad (37)$$

We find easily that

$$A = (1/M^2) \sum'_{l, \beta, \beta \neq \alpha} \hat{l}_\alpha \hat{l}_\beta \hat{l}_\alpha [\phi''(a_0|l|)]^2 \\ = 2(\omega_L^2/12)^2 \quad (38)$$

and that

$$B_\alpha = -C_\alpha = \delta_s \sum'_{\hat{l}, \beta, \beta \neq \alpha} \hat{l}_\alpha \hat{l}_\beta \hat{l}_\alpha [\phi''(a_0|l|)/M]^2 \\ = \begin{cases} \frac{1}{2}\delta_s(\omega_L^2/12)^2 & \text{for } \alpha = x \text{ and } y \\ \delta_s(\omega_L^2/12)^2 & \text{for } \alpha = z. \end{cases} \quad (39)$$

The prime on the summation symbol in Eq. (38) denotes that the term with $l' = 0$ is to be excluded. The quantities $|l|$ and \hat{l}_α are defined by

$$|l| = (l_1^2 + l_2^2 + l_3^2)^{1/2}, \quad (40)$$

$$\hat{l}_\alpha = l_\alpha/|l|. \quad (41)$$

In Eq. (39) and the equations to follow, \hat{l} , l' , etc., denote the set of five triplets: $(0, 0, -1)$, $(1/\sqrt{2})$ $(\pm 1, 0, -1)$, and $(1/\sqrt{2})$ $(0, \pm 1, -1)$.

We write $a_3(\alpha, l)$ in the following way:

$$a_3(\alpha, l) = (1/M^3)(E + F_\alpha + 2H_\alpha + J_\alpha + 2P_\alpha + Q_\alpha), \quad (42)$$

where

$$E = \sum \Phi_{\alpha\beta}^{(0)}(l'l')\Phi_{\beta\gamma}^{(0)}(l'l'')\Phi_{\gamma\alpha}^{(0)}(l'l'''), \\ F_\alpha = \sum \delta\Phi_{\alpha\beta}(l'l')\delta\Phi_{\beta\gamma}(l'l'')\delta\Phi_{\gamma\alpha}(l'l'''), \\ H_\alpha = \sum \Phi_{\alpha\beta}^{(0)}(l'l')\delta\Phi_{\beta\gamma}(l'l'')\delta\Phi_{\gamma\alpha}(l'l'''), \\ J_\alpha = \sum \Phi_{\alpha\beta}^{(0)}(l'l')\delta\Phi_{\beta\gamma}(l'l'')\Phi_{\gamma\alpha}^{(0)}(l'l'''), \\ P_\alpha = \sum \Phi_{\alpha\beta}^{(0)}(l'l')\Phi_{\beta\gamma}^{(0)}(l'l'')\delta\Phi_{\gamma\alpha}(l'l'''), \\ Q_\alpha = \sum \delta\Phi_{\alpha\beta}(l'l')\Phi_{\beta\gamma}^{(0)}(l'l'')\delta\Phi_{\gamma\alpha}(l'l'''). \quad (43)$$

The summations in Eqs. (43) are the same as those in Eq. (25). We find that

$$H_\alpha = -F_\alpha, \\ P_\alpha = -Q_\alpha. \quad (44)$$

The various terms of Eq. (42) are obtained in a straightforward manner and we record only the details for a part of J_α , the only term of a_3 which explicitly depends on $l_z = -1$ or 2 , the labels of the atoms one layer away from the surface.

This part of J_α , which we denote as J'_α , is

$$J'_\alpha(l) = R_\alpha(l) + T_\alpha(l), \quad (45)$$

where

$$R_\alpha(l) = -\phi''(a_0) \sum'_{l', \beta} \Phi_{\alpha\beta}^{(0)}(l'l')\Phi_{\beta\alpha}^{(0)}(l'l'') \\ \times [1 + 2\delta_{\beta, z}]\delta_{l_z - l'_z, 0}, \\ T_\alpha(l) = -\phi''(a_0) \sum'_{l', \beta} \Phi_{\alpha\beta}^{(0)}(l'l')\Phi_{\beta\alpha}^{(0)}(l'l'') \\ \times [1 + 2\delta_{\beta, z}]\delta_{l_z - l'_z, 1}. \quad (46)$$

Since $\Phi_{\alpha\beta}^{(0)}(l')$ vanishes unless $l'_z = 0$, or ± 1 , $R_\alpha(l)$ likewise vanishes unless $l_z = 0$, or ± 1 . For $l_z = -1$,

$$R_x(l_z = -1) = [\phi''(a_0)]^2 \sum_{\hat{l}} (\hat{l}_x)^2 [(\hat{l}_y)^2 + 3(\hat{l}_z)^2] \\ = (\frac{3}{2})[\phi''(a_0)]^2, \quad (47)$$

$$R_z(l_z = -1) = [\phi''(a_0)]^2 \sum_{\hat{l}} (\hat{l}_z)^2 [(\hat{l}_y)^2 + (\hat{l}_x)^2] \\ = [\phi''(a_0)]^2. \quad (48)$$

In a similar way, we find that $T_\alpha(l)$ vanishes unless $l_z = 0, 1$, or 2 and that $T_\alpha(l_z = 2) = R_\alpha(l_z = -1)$.

The results of these calculations are:

$$a_1(x, l) = (6 - 1\delta_s)(\omega_L^2/12), \\ a_1(z, l) = (6 - 3\delta_s)(\omega_L^2/12), \\ a_2(x, l) = (2 - \frac{1}{2}\delta_s)(\omega_L^2/12)^2, \\ a_2(z, l) = (2 - 1\delta_s)(\omega_L^2/12)^2, \\ a_3(x, l_z = 0, 1) = 7(\omega_L^2/12)^3, \\ a_3(z, l_z = 0, 1) = 6(\omega_L^2/12)^3, \\ a_3(x, l_z = -1, 2) = (21/2)(\omega_L^2/12)^3, \\ a_3(z, l_z = -1, 2) = 11(\omega_L^2/12)^3,$$

for $l_z \neq 0, \pm 1, 2$;

$$a_3(x, l) = a_3(z, l) = 12(\omega_L^2/12)^3. \quad (49)$$

RESULTS AND DISCUSSION

When the expressions for $a_n(\alpha, l)$ given by Eqs. (49) are substituted in Eq. (27), we obtain the following values of the eigenfrequencies of the localized modes which are correct to first order in the ratio of the mass of the defect atom M' to the mass of the host atom M ($\lambda = M'/M$):

(1) For $l_z \neq 0, \pm 1, 2$ (defect atom in the bulk of the crystal),

$$\begin{aligned} \left[\frac{\omega(x, l)}{\omega_L} \right]^2 &= \left[\frac{\omega(y, l)}{\omega_L} \right]^2 = \left[\frac{\omega(z, l)}{\omega_L} \right]^2 \\ &= \frac{1}{2\lambda} + \frac{1}{36} + \frac{\lambda}{36} \\ &\equiv \left(\frac{\omega_B}{\omega_L} \right)^2. \end{aligned} \quad (50)$$

(2) For $l_z = 0$, and 1 (defect atom in the surface),

$$\left[\frac{\omega(x, 0)}{\omega_L} \right]^2 = \left[\frac{\omega(x, 1)}{\omega_L} \right]^2 = \frac{5}{12\lambda} + \frac{1}{40} + \left(\frac{21}{25} \right) \frac{\lambda}{36}, \quad (51)$$

$$\left[\frac{\omega(z, 1)}{\omega_L} \right]^2 = \left[\frac{\omega(z, 1)}{\omega_L} \right]^2 = \frac{1}{4\lambda} + \frac{1}{36} + \frac{2\lambda}{36}. \quad (52)$$

(3) For $l_z = -1$ and 2 (defect atom one layer in from the surface),

$$\left[\frac{\omega(x, 0)}{\omega_L} \right]^2 = \left[\frac{\omega(x, 1)}{\omega_L} \right]^2 = \frac{1}{2\lambda} + \frac{1}{36} + \left(\frac{7}{8} \right) \left(\frac{\lambda}{36} \right), \quad (53)$$

$$\left[\frac{\omega(z, 0)}{\omega_L} \right]^2 = \left[\frac{\omega(z, 1)}{\omega_L} \right]^2 = \frac{1}{2\lambda} + \frac{1}{36} + \left(\frac{11}{12} \right) \left(\frac{\lambda}{36} \right). \quad (54)$$

Equations (65) and (67) are supplemented by

$$\omega(y, l) = \omega(x, l), \quad (55)$$

since the modes corresponding to motions in two perpendicular directions parallel to the surface are degenerate. The results contained in Eqs. (50) through (54) are valid when $[\omega(\alpha, l)/\omega_B]^2 \gg 1$, which is satisfied when $\lambda = M'/M \ll \frac{1}{4}$.

For the present model, the effect of the surface is

TABLE I. The square of the vibrational frequencies of the localized modes for the different defect site locations indicated and for the mass ratio $\lambda = M'/M = \frac{1}{5}$. ω_B is the vibrational frequency when the defect is in the bulk of the crystal.

l_z of defect site	$[\omega(x, l)/\omega_B]^2$	$[\omega(z, l)/\omega_B]^2$
0 and 1	0.8341	0.5088
-1 and 2	0.9997	0.9998
$l_z \neq 0, \pm 1, 2$	1.0000	1.0000

most pronounced when the defect atom is at the surface ($l_z = 0, 1$), in which case

$$[\omega(z, 0)/\omega_B]^2 \simeq \frac{1}{2} \quad \text{and} \quad [\omega(x, 0)/\omega_B]^2 \simeq \frac{5}{6}.$$

We thus see that for this situation the presence of a surface reduces the value of the vibrational frequency of the localized mode corresponding to motion normal to the surface to roughly 0.7 the value of the frequency when the defect is in the bulk of the crystal. Table I lists values of $[\omega(\alpha, l)/\omega_B]^2$ for $\lambda = \frac{1}{5}$. This appreciable frequency change may possibly be detected by optical absorption experiments. The use of polarized light may allow one to distinguish modes corresponding to motions parallel to the surface from the mode corresponding to motions normal to the surface. A possible candidate for these experiments is the system of Al substituted in Au which has a mass ratio $\lambda \simeq 0.14$.

The results of the present model show that the localized mode frequencies are only slightly influenced by the surface when the defect atom is even one layer in from the surface. This rapid approach of the value of $[\omega(\alpha, l)/\omega_B]^2$ to that of the bulk when the defect has diffused away from the surface is shown in Table I for $\lambda = \frac{1}{5}$. This result is due to the short-range nature of the forces considered. If the range of the forces was increased, then the properties of atoms located off the surface would, of course, be influenced to a greater extent by the presence of a crystal boundary surface.

In applying the present considerations to a physical situation, besides the obvious change from simple cubic to the correct bulk-crystal structure, account would have to be taken, along with other things, of the following: force constant changes, anharmonic forces, and distortion of the ideal plane surface, or, what amounts to the same thing, a change from the basic periodic structure of the bulk to the periodic structure present at the surface.

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