Lattice Relaxations near a Vacancy or Interstitial in Aluminum*

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The method of lattice statics is applied to calculate the lattice relaxations in the vicinity of a vacancy or an interstitial defect in aluminum. A least-squares fit to the phonon specturm obtained by Stedmann and Nilsson was used, in conjunction with the elastic constants as constraints, to derive the dynamical matrix including up to eighth-neighbor interactions. The interionic interaction was obtained by using Harrison's model pseudopotential, with parameters adjusted to give a best fit with the phonon data. For a vacancy, the relaxations are found to be 2% (of the lattice constant) or smaller. For the nominal interstitial, the first neighbors are found to relax by 17% and the rest of the neighbors by 3% or less.

I. INTRODUCTION

Lattice defects in the form of vacancies and interstitials play an important role in the properties of metals. In particular, the annealing process depends on the mobility of defects and the formation energies; the mechanical and electrical properties depend on the formation and migration energies through the dependence of cluster formations and of defect concentrations on these energies.

The changes in interatomic interactions in the vicinity of a defect cause the atoms of the lattice to readjust their positions, giving rise to the lattice relaxation. In some cases this relaxation can be rather large and must be taken into account in any meaningful studies of the defect. Most of the previous work on interstitials and vacancies in metals have used the semidiscrete approach[1] to the atomic displacements in which one divides the crystal into two regions: region I, consisting of the defect and a few close neighbors, and region II, consisting of the rest of the crystal. The atoms in region I are treated as discrete, and the atoms in region II as a continuum. Due to the complexity and number of equations to be handled, only a few neighbors have usually been included in region I. This unrealistic approximation and the difficulty in obtaining a satisfactory matching of the unconstrained displacements in region I to the constrained displacements in region II make the method of lattice statics, proposed by Kenzaki,[2] a better choice.

The lattice statics method enables the calculation of the actual displacements of all atoms from their Fourier transforms. The lattice equilibrium equations are solved in reciprocal space and transformed back to the real space by summing over the allowed wave vectors in the first Brillouin zone. This allows the reduction of $3N\times3N$ array of linear equations (for a "supercell" with the defect and containing N unit cells) which determine the direct space displacements to N 3×3 arrays, one for each Fourier amplitude. Section II gives a short review of this method and the generalization to integration instead of summation of discrete wave vectors to avoid having an artificial periodicity of a "superlattice" imposed on the lattice relaxations.

Section III deals with the dynamical matrix and its evaluation using the phonon spectrum, while in Secs. IV and V the actual relaxations in the vicinity of a vacancy and an interstitial atom, respectively, are considered. In the latter case, an explicit form of the interionic interactions is required. The evaluation of such an interaction based on pseudopotentials is also discussed in Sec. V. Relaxations around a vacancy or an interstitial are computed using both the empirical force constants (phonon fit for up to eighth-neighbor interactions) and the semiempirical approach (pseudopotential fitted to pnonon spectrum).

II. REVIEW OF LATTICE STATICS METHOD

In this section the method of lattice statics as proposed by Kenzaki[2] and later used extensively by Hardy and his co-workers[3–5] is briefly reviewed.

A defect introduced into a crystal will interact with the host lattice atoms by means of an effective pairwise potential. Taking the defect itself as the origin of the coordinate system, the position of the lth atom of the host lattice will be given by a vector $(\vec{r}^{\,l}+\vec{\xi}^{\,l})$, where $\vec{r}^{\,l}$ is the position vector for this atom in the perfect lattice and $\vec{\xi}^{\,l}$ is the displacement caused by the presence of the defect.

The potential energy of the distorted lattice can be written

$$U=U_0-\sum_{l,\alpha}F_\alpha(\vec{r}^{\,l})\xi_\alpha^l+\frac{1}{2}\sum_{l,l'}\sum_{\alpha,\beta}A_{\alpha\beta}(l,l')\xi_\alpha^l\xi_\beta^{l'}\,, \quad (1)$$

where U_0 is the potential energy of the perfect lattice (undistorted), $\vec{F}(\vec{r}^{\,l})$ is the force on the lth atom due to the defect; α, β run from 1 to 3 and refer to the Cartesian components and

$$A_{\alpha\beta}(l,l')=\left(\frac{\partial^2U}{\partial r_\alpha^l\,\partial r_\beta^{l'}}\right)_0 \quad (2)$$

gives the force-constant matrix for the perfect lattice (the subscript 0 indicates that the derivatives are evaluated in the undistorted configuration). These quantities are symmetric in their indices, according to their definition, and depend only on the difference of position vectors $(\vec{r}^{\,l} - \vec{r}^{\,l'})$,

$$A_{\alpha\beta}(l, l') = A_{\beta\alpha}(l', l) \ . \tag{3}$$

The equilibrium value of the displacements can be obtained by minimizing U with respect to the displacements which imply

$$\frac{\partial U}{\partial \xi_\alpha^l} = 0 \ , \tag{4}$$

which becomes

$$F_\alpha(\vec{r}^{\,l}) = \sum_{l',\beta} A_{\alpha\beta}(l, l')\, \xi_\beta^{l'} \ . \tag{5}$$

Equations (5) are the fundamental equations of the problem and are linear because all terms beyond the second degree in the Taylor expansion of the potential energy in Eq. (1) have been neglected.

In order to perform the actual calculations, however, the displacements are expanded in terms of the normal coordinates, i.e.,

$$\vec{\xi}^{\,l} = \frac{1}{N} \sum_{\vec{q}} \vec{Q}(\vec{q})\, e^{i\vec{q}\cdot\vec{r}^{\,l}} \ , \tag{6}$$

where N is the number of atoms in the supercell containing the defect and $\vec{q}$ are the wave vectors in the first Brillouin zone (at a later stage in the computations, we let $N \to \infty$ and convert discrete sums over $\vec{q}$ to a Brillouin-zone integration); $\vec{Q}(\vec{q})$, the normal coordinates, are, in general, complex and must satisfy

$$\vec{Q}(-\vec{q}) = \vec{Q}^*(\vec{q}) \tag{7}$$

to ensure that the displacements are real.

Defining the Fourier transforms of other quantities in a similar fashion as Eq. (6) we have

$$F_\alpha(\vec{q}) = \sum_l F_\alpha(\vec{r}^{\,l})\, e^{-i\vec{q}\cdot\vec{r}^{\,l}} \ , \tag{8a}$$

$$V_{\alpha\beta}(\vec{q}) = \sum_{(l-l')} A_{\alpha\beta}(l, l')\, e^{-i\vec{q}\cdot(\vec{r}^{\,l'} - \vec{r}^{\,l})} \ , \tag{8b}$$

where in (8b) we take a Fourier transform with respect to $(\vec{r}^{\,l'} - \vec{r}^{\,l})$. $V_{\alpha\beta}(\vec{q})$ can be rearranged [since $A_{\alpha\beta}(ll')$ depend only on $\vec{r}^{\,l} - \vec{r}^{\,l'}$] to give

$$V_{\alpha\beta}(\vec{q}) = \sum_{l'} A_{\alpha\beta}(0, l')\, e^{-i\vec{q}\cdot\vec{r}^{\,l'}} \ . \tag{8c}$$

Equations (5) now become

$$F_\alpha(\vec{q}) = \sum_\beta V_{\alpha\beta}(-\vec{q})\, Q_\beta(\vec{q}) \ , \tag{9}$$

where we have used the fact that $\vec{q}$ lies within the first Brillouin zone. In matrix form Eq. (9) is

$$F(\vec{q}) = V(-\vec{q})\, Q(\vec{q}) \tag{9a}$$

and can be inverted to give

$$Q(\vec{q}) = [V(-\vec{q})]^{-1} F(\vec{q}) \ . \tag{9b}$$

Invariance of the potential energy under rigid translations gives the conditions on the dynamical matrix

$$V_{\alpha\beta}(\vec{q} = 0) = 0 \ , \tag{10a}$$

and on forces and displacements,

$$F_\alpha(\vec{q} = 0) = 0, \tag{10b}$$

$$Q_\alpha(\vec{q} = 0) = 0 \tag{10c}$$

for all values of α and β.

Inserting (9b) in (6) we finally get

$$\xi_\alpha^l = \frac{1}{N} \sum_{\vec{q},\beta} [V(-q)]^{-1}_{\alpha\beta}\, F_\beta(\vec{q})\, e^{i\vec{q}\cdot\vec{r}^{\,l}} \ . \tag{11}$$

Thus the displacement of any atom may be obtained from (11) once the dynamical matrix and the Fourier transform of the forces exerted by the defect are known, without relaxing the whole lattice explicitly.

As pointed out by Boyer and Hardy,[5] relation (11) gives displacements that have the periodicity of the superlattice where a unit supercell contains N atoms, and fails to give the continuum results for the isotropic lattice. This can be overcome by letting the volume of periodicity become infinite, i.e.,

$$\frac{1}{N} \sum_{\vec{q}} \to \frac{\Omega}{(2\pi)^3} \int_{BZ} d\vec{q} \ , \tag{12}$$

where Ω is the volume per atom ($2a^3$ for aluminum, where $2a$ is the lattice constant) and the integration is over the first Brillouin zone (BZ). However, since the integrations must be performed numerically in most problems, any choice of $\vec{q}$ vectors on a regularly spaced basis will bring back the problem of supercell periodicity. Fortunately, this can be avoided by performing integrations by the Gaussian quadrature method after first changing the integration to a cube (c) inscribing the first BZ and using the fact

$$\int_{BZ} f(\vec{q})\, d^3q = \tfrac{1}{2} \int_c f(\vec{q})\, d^3q \ , \tag{13}$$

where $f(\vec{q})$ is any function with the periodicity of the reciprocal lattice.

Due to the singularity in V^{-1} at the corners and the origin of the integration volume, we need a denser sample in both of these regions. Thus using x_i and w_i as the abcissas and weights for a Gaussian quadrature with n positive roots, we have

$$\frac{1}{N} \sum_{\vec{q}} f(\vec{q}) = \frac{1}{8} \sum_{i,j,k} f(x_i', x_j', x_k') w_i' w_j' w_k' \ , \tag{14}$$

where i, j and k are summed from $-2n$ to $2n$ (excluding zero) and

$$x_i' = \frac{\pi}{2a} \times \begin{cases} (1-x_i), & |i| \le n \\ 1+x_{i-n}, & i > n \\ 1+x_{i+n}, & i < -n \end{cases} \tag{14a}$$

$$w_i' = \tfrac{1}{2} \times \begin{cases} w_i, & |i| \le n \\ w_{i-n}, & i > n \\ w_{i+n}, & i < -n \,. \end{cases} \tag{14b}$$

However, the symmetry of the problem can be used to reduce the actual number of terms to be evaluated for the sum in (14).

III. DYNAMICAL MATRIX

One of the basic necessities of this calculation is the dynamical matrix defined by Eqs. (8c) and (2). Various attempts have been made[3,5-8] at evaluating this quantity in terms of central as well as noncentral forces.

We will assume the central-force model for the pairwise interactions, i.e.,

$$V(|\vec{r}+\vec{\delta}|) = V(r) + \frac{\partial V(r)}{\partial r}\frac{\vec{\delta}\cdot\vec{r}}{r} + \frac{1}{2}\frac{\partial V(r)}{\partial r}\frac{(\vec{\delta}\times\vec{r})^2}{r^3} + \frac{1}{2}\frac{\partial^2 V(r)}{\partial r^2}\frac{(\vec{\delta}\cdot\vec{r})^2}{r^2} + \cdots, \tag{15}$$

which gives

$$A_{\alpha\beta}(0, l') = \tfrac{1}{2}\alpha_{2l'}\left(\frac{\gamma_\alpha^{l'}\gamma_\beta^{l'}}{|\vec{r}^{\,l'}|^2} - \delta_{\alpha\beta}\right) - \tfrac{1}{2}\alpha_{2l'-1}\frac{\gamma_\alpha^{l'}\gamma_\beta^{l'}}{|\vec{r}^{\,l'}|^2}\,, \tag{16}$$

where

$$\alpha_{2l} = 2\,\frac{1}{r}\,\frac{\partial V(r)}{\partial r}\bigg|_{r=|\vec{r}^{\,l}|} \tag{16a}$$

and

$$\alpha_{2l-1} = 2\,\frac{\partial^2 V(r)}{\partial r^2}\bigg|_{r=|\vec{r}^{\,l}|}\,, \tag{16b}$$

subject to the condition (10a). This gives us

$$V_{\alpha\beta}(\vec{q}) = \sum_l \frac{n_l}{48}\sum_{\gamma=1}^{48} e^{-i\vec{q}\cdot\gamma\vec{r}^{\,l,0}}\left[\tfrac{1}{2}(\alpha_{2l}-\alpha_{2l-1})\times\frac{(\gamma\vec{r}^{\,l,0})_\alpha(\gamma\vec{r}^{\,l,0})_\beta}{|\vec{r}^{\,l,0}|^2} - \frac{1}{2}\alpha_{2l}\delta_{\alpha\beta}\right] + \sum_l \frac{n_l}{6}(2\alpha_{2l}+\alpha_{2l-1})\delta_{\alpha\beta}\,, \tag{17}$$

where $\vec{r}^{\,l,0}$ is some vector chosen out of the star of $\vec{r}^{\,l}$, the atoms in the lth neighbor set consisting of n_l atoms (for convenience we choose $r_x^{l,0} \ge r_y^{l,0} \ge r_z^{l,0} \ge 0$) and γ's run over the 48 operators of the cubic group. Performing the summations explicitly in (17) we have (for interactions up to eighth neighbors)

$$\begin{aligned} V_{11}(\vec{q}) = {} & 2\alpha_1 + 4\alpha_2 - (\alpha_1+\alpha_2)(\cos q_2a + \cos q_3a)\cos q_1a - 2\alpha_2\cos q_2a\cos q_3a \\ & + \alpha_3 + 2\alpha_4 - \alpha_3\cos 2q_1a - \alpha_4(\cos 2q_2a + \cos 2q_3a) + 4(\alpha_5+2\alpha_6) - \tfrac{2}{3}(\alpha_5+5\alpha_6) \\ & \times(\cos 2q_2a\cos q_3a + \cos q_2a\cos 2q_3a)\cos q_1a - \tfrac{4}{3}(2\alpha_5+\alpha_6) \\ & \times\cos 2q_1a\cos q_2a\cos q_3a + 2\alpha_7 + 2\alpha_8(2 - \cos 2q_2a\cos 2q_3a) - (\alpha_7+\alpha_8) \\ & \times(\cos 2q_2a + \cos 2q_3a)\cos 2q_1a + 4(\alpha_9+2\alpha_{10}) - \tfrac{1}{5}(9\alpha_9+\alpha_{10}) \\ & \times(\cos q_2a + \cos q_3a)\cos 3q_1a - \tfrac{1}{5}(\alpha_9+9\alpha_{10})(\cos 3q_2a + \cos 3q_3a)\cos q_1a \\ & - 2\alpha_{10}(\cos 3q_2a\cos q_3a + \cos q_2a\cos 3q_3a) + \tfrac{4}{3}(\alpha_{11}+2\alpha_{12}) - \tfrac{4}{3}(\alpha_{11}+2\alpha_{12}) \\ & \times\cos 2q_1a\cos 2q_2a\cos 2q_3a + 8(\alpha_{13}+2\alpha_{14}) - \tfrac{2}{7}(9\alpha_{13}+5\alpha_{14}) \\ & \times(\cos 2q_2a\cos q_3a + \cos q_2a\cos 2q_3a)\cos 3q_1a - \tfrac{4}{7}(2\alpha_{13}+5\alpha_{14}) \\ & \times(\cos 3q_2a\cos q_3a + \cos q_2a\cos 3q_3a)\cos 2q_1a - \tfrac{2}{7}(\alpha_{13}+13\alpha_{14}) \\ & \times(\cos 2q_2a\cos 3q_3a + \cos 3q_2a\cos 2q_3a)\cos q_1a + (\alpha_{15}+2\alpha_{16}) \\ & - \alpha_{15}\cos 4q_1a - \alpha_{16}(\cos 4q_2a + \cos 4q_3a), \end{aligned} \tag{18a}$$

$$\begin{aligned} V_{12}(\vec{q}) = {} & (\alpha_1-\alpha_2)\sin q_1a\sin q_2a + \tfrac{2}{3}(\alpha_5-\alpha_6) \\ & \times[\sin q_1a\sin q_2a\cos 2q_3a + 2(\sin 2q_1a\sin q_2a + \sin q_1a \\ & \times\sin 2q_2a)\cos q_3a] + (\alpha_7-\alpha_8)\sin 2q_1a\sin 2q_2a + \tfrac{3}{5}(\alpha_9-\alpha_{10}) \\ & \times[\sin 3q_1a\sin q_2a + \sin q_1a\sin 3q_2a] + \tfrac{4}{3}(\alpha_{11}-\alpha_{12})\sin 2q_1a\sin 2q_2a \\ & \times\cos 2q_3a + \tfrac{4}{7}(\alpha_{13}-\alpha_{14})[(\sin q_1a\sin 2q_2a + \sin 2q_1a\sin q_2a)\cos 3q_3a \\ & + \tfrac{3}{2}(\sin 3q_1a\sin q_2a + \sin q_1a\sin 3q_2a)\cos 2q_3a + 3(\sin 3q_1a \\ & \times\sin 2q_2a + \sin 2q_1a\sin 3q_2a)\cos q_3a], \end{aligned} \tag{18b}$$

and the symmetry relations

$$V_{22}(q_1, q_2, q_3) = V_{11}(q_2, q_3, q_1),$$
$$V_{33}(q_1, q_2, q_3) = V_{11}(q_3, q_1, q_2),$$
$$V_{13}(q_1, q_2, q_3) = V_{12}(q_3, q_1, q_2), \quad (18c)$$
$$V_{23}(q_1, q_2, q_3) = V_{12}(q_2, q_3, q_1),$$
$$V_{23} = V_{32}, \quad V_{12} = V_{21}, \quad V_{13} = V_{31}.$$

To obtain $V(\vec{q})$ for any vector $\vec{q}$ in the Brillouin zone in terms of the value for $\vec{q}$ in the irreducible subzone ($q_x \geq q_y \geq q_z \geq 0$ with $q_x + q_y + q_z \leq 3\pi/2a$), we have the matrix form

$$V(\gamma\vec{q}) = U(\gamma)\, V(\vec{q})\, U^{\dagger}(\gamma), \quad (19)$$

where $U(\gamma)$ is the matrix representation of the cubic group operator γ.

The force constants α_1 to α_{16} are evaluated using the dispersion curves for phonons given by the matrix equation

$$V(\vec{q})\,\epsilon(\vec{q}) = m\omega^2(\vec{q})\epsilon(\vec{q}), \quad (20)$$

where $\omega(\vec{q})$ is the frequency of a phonon of momentum $\vec{q}$ and polarization $\vec{\epsilon}(\vec{q})$, and m is the mass of the atoms in the lattice. Relations (20) can be rewritten

$$m\omega^2(\vec{q}) = \sum_{\alpha,\beta} \epsilon_\alpha(\vec{q}) V_{\alpha\beta}(\vec{q}) \epsilon_\beta(\vec{q}) \Big/ \Big(\sum_\alpha \epsilon_\alpha^2(\vec{q}) \Big). \quad (21)$$

In the limit $\vec{q} \to 0$, we compare the coefficients of $q_\alpha q_\beta$ in the expansion of $V_{\alpha\beta}$ with the corresponding coefficients in the elastic equations to obtain the elastic constants in terms of the force constants, i.e.,

$$C_{44} = \tfrac{1}{2}(\alpha_1 + 3\alpha_2) + 2\alpha_4 + 3\alpha_5 + 9\alpha_6 + 2(\alpha_7 + 3\alpha_8) + \tfrac{9}{5}\alpha_9 + \tfrac{91}{5}\alpha_{10} + \tfrac{8}{3}(\alpha_{11} + 2\alpha_{12}) + 14(\alpha_{13} + 3\alpha_{14}) + 8\alpha_{16}, \quad (22a)$$

$$C_{12} + C_{44} = (\alpha_1 - \alpha_2) + 6(\alpha_5 - \alpha_6) + 4(\alpha_7 - \alpha_8) + \tfrac{18}{5}(\alpha_9 - \alpha_{10}) + \tfrac{16}{3}(\alpha_{11} - \alpha_{12}) + 28(\alpha_{13} - \alpha_{14}), \quad (22b)$$

and

$$C_{11} - C_{44} = \tfrac{1}{2}(\alpha_1 - \alpha_2) + 2(\alpha_3 - \alpha_4) + 3(\alpha_5 - \alpha_6) + 2(\alpha_7 - \alpha_8) + \tfrac{73}{5}(\alpha_9 - \alpha_{10}) + 14(\alpha_{13} - \alpha_{14}) + 8(\alpha_{15} - \alpha_{16}). \quad (22c)$$

A least-squares fit to the phonon spectrum obtained by Stedmann and Nilsson[9] at 80 °K (taken from plots given by Gilat and Nicklow[8]), with Eqs. (22) as constraints, was used to obtain the empirical force constants α_i ($i = 1$–16). The results are shown in Table I for both the anisotropic aluminum and the isotropic aluminum (using $C_{11} = C_{12} + 2C_{44}$) so that the relaxation results can later be compared with the relation $\vec{\xi}(\vec{r}) \propto \vec{r}/r^3$ valid for an isotropic elastic medium.

Our values of the force constants are compared in Table I with the "corresponding" values obtained by Boyer and Hardy[5] (using only up to fifth-neighbor interactions) as well as the results of Gilat and Nicklow.[8] Also shown are the force constants from a pseudopotential approach (described in Sec. V), which we refer to as the semiempirical force constants.

The reproducibility of the phonon spectrum is shown in Figs. 1–3 for the three principal directions [100], [110], and [111] as a plot of $m\omega^2$ against q. Results from both the empirical and semiempirical (pseudopotential) approach are compared with the experimental data as well as those from the Boyer and Hardy[5] (BH) force constants. The present calculation gives a much better fit than the results of Boyer and Hardy and should lead to improved relaxation values than previously available. The pseudopotential method does not give the proper elastic constants and will be expected to fail in the long-range effects (such as for relaxations reasonably far from the defect).

We have found that the force constants are extremely sensitive to the phonon frequencies used for the least-squares fit. All three cases discussed above (empirical, pseudopotential, and BH) reproduce the phonon curves within a reasonable accuracy but have widely different values for the force constants.

IV. RELAXATIONS FOR A VACANCY

Once the dynamical matrix is evaluated, the calculation of the lattice relaxation still needs the defect potential. In the case of a vacancy, this can be obtained from the force constants, which give the magnitude of the forces at lattice points up to eighth neighbors of the vacancy. From symmetry considerations, we know that the forces on the first, second, fourth, sixth and eighth neighbors due to the vacancy are radial. Since the force constants for the third, fifth, and seventh neighbors are small, we assume the forces on these neighbors to be radial also. Then we find

$$F_1(\vec{q}) = i\{2\sqrt{2} f_1 \sin q_1 a(\cos q_2 a + \cos q_3 a) + 2f_2 \sin 2q_1 a + \tfrac{4}{3}\sqrt{6} f_3[2\sin 2q_1 a \cos q_2 a \cos q_3 a + (\cos 2q_2 a \cos q_3 a + \cos q_2 a \cos 2q_3 a) \times \sin q_1 a] + 2\sqrt{2} f_4(\cos 2q_2 a + \cos 2q_3 a)\sin 2q_1 a + \tfrac{2}{5}\sqrt{10} f_5[3(\cos q_2 a + \cos q_3 a)\sin 3q_1 a + (\cos 3q_2 a + \cos 3q_3 a)\sin q_1 a] + \tfrac{8}{3}\sqrt{3} f_6 \sin 2q_1 a \cos 2q_2 a \cos 2q_3 a + \tfrac{4}{7}\sqrt{14} f_7$$

$$\times[3(\cos 2q_2a\cos q_3a+\cos q_2a\cos 2q_3a)\sin 3q_1a+2\sin 2q_1a$$
$$\times(\cos 3q_2a\cos q_3a+\cos q_2a\cos 3q_3a)+(\cos 3q_2a\cos 2q_3a$$
$$+\cos 2q_2a\cos 3q_3a)\sin q_1a]+2f_8\sin 4q_1a\} \quad (23a)$$

and

$$F_2(q_1, q_2, q_3)=F_1(q_2, q_3, q_1)\ , \quad (23b)$$

$$F_3(q_1, q_2, q_3)=F_1(q_3, q_1, q_2)\ , \quad (23c)$$

where f_l is the magnitude of the radial force on the lth-neighbor atoms. For any vector $\vec{q}$ in the Brillouin zone we have [similar to relation (19) for V matrix]

$$F(\gamma\vec{q})=U(\gamma)F(\vec{q})\ . \quad (24)$$

However, the forces to be used in Eq. (11) have to be evaluated at the relaxed positions, i.e., f_l will be given by

$$f_l=\left.\frac{\partial V(r)}{\partial r}\right|_{r=|\vec{r}^l+\vec{\xi}^l|}\ . \quad (25)$$

The sign of the term on the right-hand side is positive since this is the force on the neighbors due to the absence of one atom. From (25) we obtain one set of equations connecting f_l and ξ_r^l (the radial displacement under assumed radial forces on all eight sets of neighbors):

$$f_l=\tfrac{1}{2}\alpha_{2l}|\vec{r}^l|+\tfrac{1}{2}\alpha_{2l-1}|\vec{\xi}_r^l|,\quad l=1, 2, \ldots, 8. \quad (26)$$

The other set of equations is obtained from (11) under the radial displacement assumption giving a total of 16 equations in the 16 unknowns f_l and ξ_r^l for $l=1$–8. These equations are solved simultaneously and then the displacements of the lattice are obtained by relation (11) for both isotropic and anisotropic aluminum.

The results are shown in Fig. 4 for the isotropic aluminum in the three directions ⟨100⟩, ⟨110⟩, and ⟨111⟩ and are compared with the corresponding results obtained by Boyer and Hardy. We have plotted $(1/a)[\xi(l_1, l_2, l_3)](l_1^2+l_2^2+l_3^2)$ against l for points $a(l, 0, 0)$, $a(l, l, 0)$, and $a(l, l, l)$. The continuum value is obtained much faster in our results than those of Boyer and Hardy. A negative sign indicates the displacement is towards the origin (defect).

For the anisotropic aluminum, the relaxations are shown in Table II for neighbors at lattice sites $a(l_1, l_2, l_3)$ for points $l_1^2+l_2^2+l_3^2\leq 66$. The first neighbors show the largest displacement (2.5% of the unit a).

V. INTERSTITIAL DEFECT

The location of an interstitial atom for aluminum is not known experimentally. The lattice relaxation and the formation energy will depend on the choice of its position. For symmetry reasons, we have chosen the interstitial atom at the body center of the aluminum unit cell, the nominal interstitial. However, the present calculation can be easily ex-

TABLE I. Values of the force constants defined by Eqs. (16a) and (16b) for eight neighbors in units of dyn/cm. Results of the present empirical fit are compared with the semiempirical pseudopotential approach and previous results of Boyer and Hardy (BH) and those of Gilat and Nicklow.

	Isotropic		Anisotropic		Gilat and	Pseudopotential
	Present work	BH	Present work	BH	Nicklow (80 °K)	case $\beta=47.5$, $r_c=0.2765$
α_1	42891	43008	42927	43232	43102	42912
α_2	−2617	−3627	−2536	−3403	−2674	−3121
α_3	5331	3268	5427	1919	4904	5808
α_4	−1097	−457	−1398	217	−1058	−346
α_5	−1950	−151	−1956	−779	−1840	−1870
α_6	140	510	123	−118	−68	89
α_7	916	−1196	1042	−1533	442	569
α_8	456	1116	509	778	642	−70
α_9	775	175	829	692	980	423
α_{10}	155	−666	269	−149	396	34
α_{11}	−927		−786		−152	−693
α_{12}	488		571		502	3
α_{13}	44		−20		−68	186
α_{14}	−205		−253		−236	−21
α_{15}	−828		−1315		−1068	384
α_{16}	−37		−37		−232	7

tended to other choices of the interstitial location.

With this choice, the first five neighbors are (in units of a) at (1, 0, 0), (1, 1, 1), (2, 1, 0), (2, 2, 1), (3, 0, 0) and at the positions in the star of these vectors, (the body center is now being used as the origin). The last two are at the same distance from the defect and will have the same force exerted in the absence of relaxation (central-force approximation). However, since the two sets of atoms may relax differently, we will allow these to be two separate sets of neighbors (one can call them neighbors $4a$ and $4b$).

Due to symmetry considerations, the forces on the first, second, and fifth (or $4b$) neighbors will be radial. The forces on the first neighbors can be expected to be quite large compared to the others, so an approximation of taking the forces on all five neighbor sets to be radial is justifiable. Using $\mathfrak{F}_l$ for the magnitude of the force at the lth neighbor, we get [equivalent to Eq. (23) for vacancy]

$$F_1(\vec{q}) = i\{2\mathfrak{F}_1 \sin q_1 a + \tfrac{8}{3}\sqrt{3}\,\mathfrak{F}_2 \sin q_1 a \cos q_2 a \cos q_3 a + \tfrac{4}{5}\sqrt{5}\,\mathfrak{F}_3[2(\cos q_2 a + \cos q_3 a)\sin 2q_1 a + (\cos 2q_2 a + \cos 2q_3 a)\sin q_1 a] + \tfrac{8}{3}\mathfrak{F}_4[2(\cos 2q_2 a \cos q_3 a + \cos q_2 a \cos 2q_3 a)\sin 2q_1 a + (\cos 2q_2 a \cos 2q_3 a)\sin q_1 a] + 2\mathfrak{F}_5 \sin 3q_1 a\}\ , \quad (27)$$

and the same symmetry relations (23b), (23c), and (24) as in the case of the vacancy.

In the case of the vacancy, we expanded the forces f_l at the relaxed positions in terms of their values (and the derivatives) at the unrelaxed positions which were available from the dynamical matrix. However, in the present case, the unrelaxed positions are not the regular lattice sites (in terms of the new origin) and thus we require some knowledge of interionic forces at distances other than the nearest-neighbor distances.

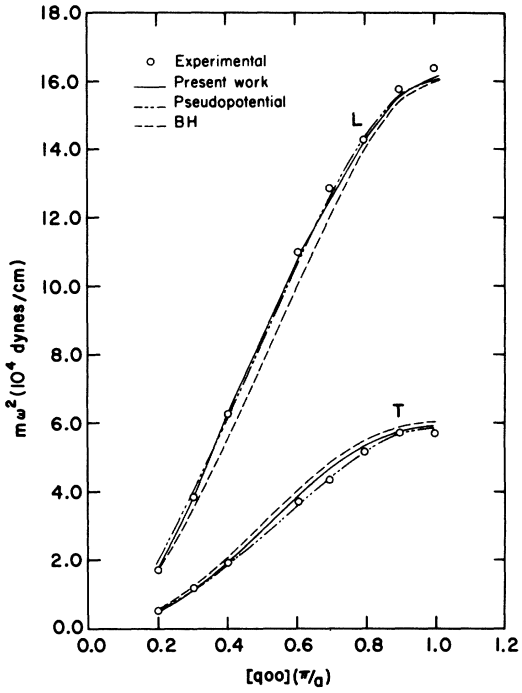

FIG. 1. Values of $m\omega^2$ for phonons along [100] direction. The present empirical fit is compared with experimental data of Stedmann and Nilsson along with pseudopotential curves and those from Boyer and Hardy force constants.

A. Interionic Forces

Previous work on a similar problem[4] (interstitial Cu atom in Cu) used the Born-Mayer potential for the pairwise interaction and obtained the values of forces $\mathfrak{F}_l$ by differentiation of that function. In view of the oscillatory behavior of the force constants evaluated from phonon-fitting studies, such a potential is seen to be a very crude approximation. The interpolation of the force constants for distances other than regular neighbor distances may be acceptable for second and further neighbors of the interstitial, but extrapolation of the force constants to first neighbor, distance a, using values that are available at $\sqrt{2}a$ and larger distances cannot be relied upon due to the very large values of the second derivatives.

Numerous studies have been made[10–14] of the interionic potential in aluminum based on various forms of pseudopotentials and the screening factors. The interionic potential $V(r)$ is written as a sum of two terms, one the direct Coulomb interaction and the other the indirect ion-electron-ion interaction (also referred to as the band-structure contribution), i.e.,

$$V(r) = Z^{*2} e^2/r + V_{\text{ind}}(r)\ , \quad (28)$$

where Z^* is the effective charge, and the indirect contribution is given as an integral

$$V_{\text{ind}}(r) = \frac{\Omega}{\pi^2}\int_0^\infty F(q)\,\frac{\sin qr}{qr}\,q^2 dq\ , \quad (29)$$

with $F(q)$, the energy wave-number characteristic, defined in terms of the local bare pseudopotential $[v_b(q)]$:

$$F(q) = -\frac{q^2}{8\pi e^2 \Omega}\,v_b^2(q)\,\frac{\chi(q)}{1+[1-G(q)]\chi(q)}\ . \quad (30)$$

In Eq. (30) $\chi(q)$ is the Lindhard expression for the

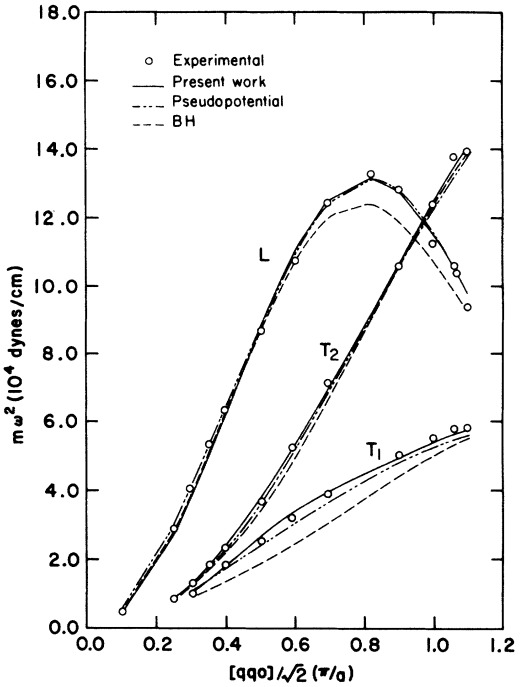

FIG. 2. Comparison of phonon $m\omega^2$ values along [110] direction.

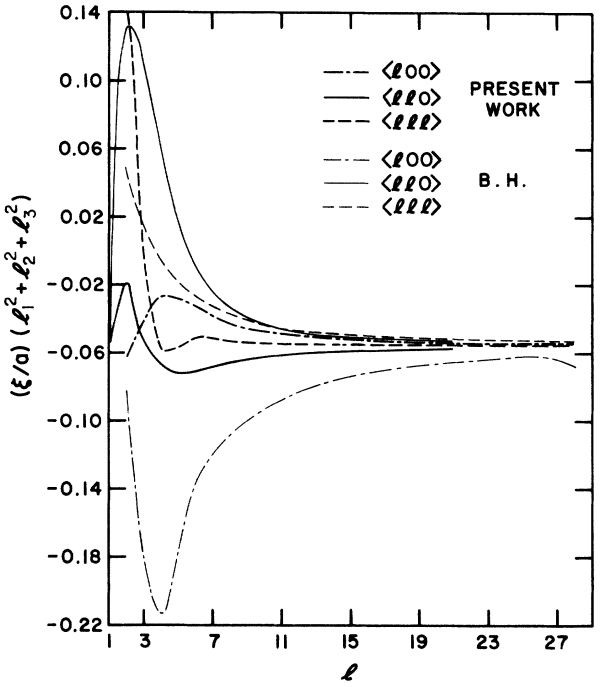

FIG. 4. Lattice relaxation along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions for isotropic aluminum. Present results are compared with those of Boyer and Hardy.

free-electron susceptibility

$$\chi(q) = \frac{4}{\pi k_F a_0}\,\frac{1}{y^2}\left(\frac{1}{2} + \frac{4-y^2}{8y}\ln\left|\frac{2+y}{2-y}\right|\right) , \qquad (31)$$

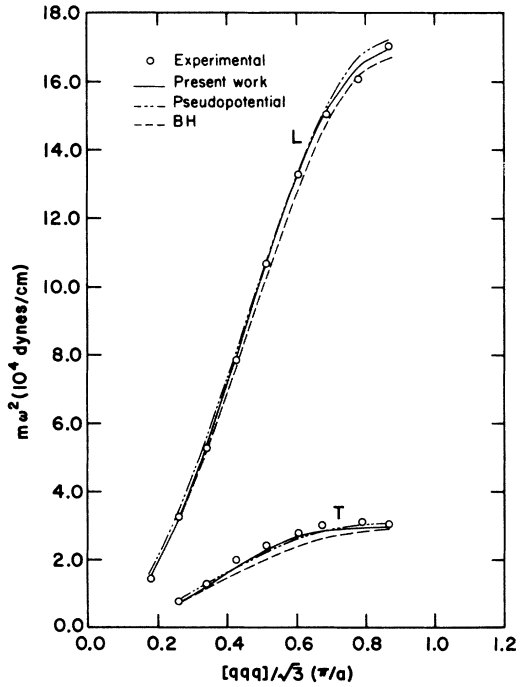

FIG. 3. Comparison of phonon $m\omega^2$ values along [111] direction.

with $y = q/k_F$, and a_0 is the Bohr radius. The quantity $G(q)$ in Eq. (30) is a static term to correct the charge densities for the effects of exchange and correlation. Various forms of $v_b(q)$ and the screening have been used in the literature to obtain $V(r)$, which oscillates after a certain distance from the origin. This is of course the result of the Coulombic term being effectively canceled out by the screened indirect contribution leaving behind the effect of the well-known long-range oscillations in the charge density of an electron gas. The point at which these oscillations in $V(r)$ start to show up depends more on the screening factor than the bare pseudopotential.[15]

For this study, we have chosen the Harrison model potential[10]

$$v_b(q) = -\frac{4\pi Ze^2}{q^2} + \frac{\beta}{(1+q^2r_c^2)^2} , \qquad (32)$$

with β and r_c as adjustable parameters, and the screening given by Toigo and Woodruff[16] [the numerical values of $G(q)$ suitably interpolated for $q > 3.5k_F$], evaluating the q integral in Eq. (29) to $40k_F$. The values of β and r_c were varied over a fairly large region to obtain the best possible fit of the phonon spectrum generated by this interaction [the force constants of the dynamical matrix are derivatives of $V(r)$ with respect to r] with experimental data of Stedmann and Nilsson.[9] These

TABLE II. Lattice relaxation for vacancy for points $a(l_1, l_2, l_3)$ for neighbors with $l_1^2+l_2^2+l_3^2 \leq 66$.

Lattice points (l_1, l_2, l_3)	Displacement components ξ_1/a	ξ_2/a	ξ_3/a
(1, 1, 0)	−0.0174	−0.0174	0.0
(2, 0, 0)	−0.0185	0.0	0.0
(2, 1, 1)	−0.0050	−0.0017	−0.0017
(2, 2, 0)	−0.0013	−0.0013	0.0
(3, 1, 0)	0.0009	−0.0024	0.0
(2, 2, 2)	0.0077	0.0077	0.0077
(3, 2, 1)	−0.0075	−0.0054	−0.0025
(4, 0, 0)	−0.0001	0.0	0.0
(4, 1, 1)	−0.0010	−0.0002	−0.0002
(3, 3, 0)	−0.0023	−0.0023	0.0
(4, 2, 0)	−0.0022	−0.0011	0.0
(3, 3, 2)	0.0004	0.0004	−0.0015
(4, 2, 2)	−0.0033	−0.0019	−0.0019
(4, 3, 1)	−0.0029	−0.0025	−0.0006
(5, 1, 0)	−0.0008	−0.0002	0.0
(5, 2, 1)	−0.0014	−0.0005	−0.0003
(4, 4, 0)	−0.0016	−0.0016	0.0
(4, 3, 3)	−0.0010	−0.0010	−0.0010
(5, 3, 0)	−0.0015	−0.0009	0.0
(4, 4, 2)	−0.0006	−0.0006	−0.0007
(6, 0, 0)	−0.0003	0.0	0.0
(6, 1, 1)	−0.0007	−0.0002	−0.0002
(5, 3, 2)	−0.0016	−0.0011	−0.0006
(6, 2, 0)	−0.0009	−0.0003	0.0
(5, 4, 1)	−0.0016	−0.0014	−0.0003
(6, 2, 2)	−0.0012	−0.0004	−0.0004
(6, 3, 1)	−0.0011	−0.0005	−0.0002
(4, 4, 4)	−0.0009	−0.0009	−0.0009
(5, 4, 3)	−0.0008	−0.0007	−0.0005
(5, 5, 0)	−0.0011	−0.0011	0.0
(7, 1, 0)	−0.0005	−0.00003	0.0
(6, 4, 0)	−0.0011	−0.0007	0.0
(5, 5, 2)	−0.0007	−0.0007	−0.0004
(6, 3, 3)	−0.0010	−0.0005	−0.0005
(7, 2, 1)	−0.0007	−0.0002	−0.0001
(6, 4, 2)	−0.0010	−0.0007	−0.0004
(7, 3, 0)	−0.0008	−0.0003	0.0
(6, 5, 1)	−0.0010	−0.0008	−0.0001
(7, 3, 2)	−0.0009	−0.0004	−0.0003
(8, 0, 0)	−0.0005	0.0	0.0
(5, 5, 4)	−0.0006	−0.0006	−0.0005
(7, 4, 1)	−0.0008	−0.0005	−0.0001
(8, 1, 1)	−0.0005	−0.00006	−0.00006

curves are shown in Figs. 1–3 for the parameters $\beta = 47.5$ Ry a_0^3 and $r_c = 0.2765 a_0$. The force constants obtained are compared in Table I with those from a least-squares fit of phonon curves for 16 parameters (empirical force constants for up to eighth-neighbor interactions) and with those of previous workers.

The interionic potential $V(r)$ is plotted against r in Fig. 5 and shows the first minimum slightly past the second-neighbor distance, in agreement with Duesbery and Taylor.[15]

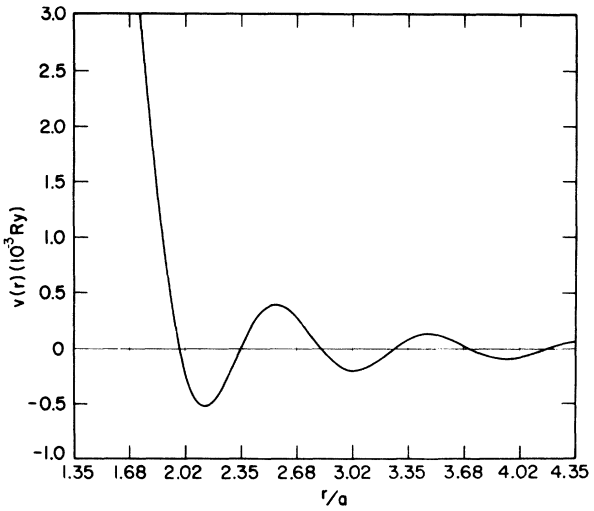

FIG. 5. Interionic potential for aluminum as a function of distance, from the semiempirical fit of pseudopotential to the phonon spectrum.

B. Relaxation

Once $V(r)$ and its derivatives are known, we proceed as in the case of the vacancy (with a sign difference for the force)

$$\mathcal{F}_l = -\left.\frac{\partial V(r)}{\partial r}\right|_{r=|\vec{R}^l+\vec{\xi}^l|} , \tag{33}$$

where $\vec{R}^l$ is the position of the lth neighbor of the interstitial. Defining quantities similar to α_i earlier,

$$\alpha_{2l}^I = \frac{2}{r}\left.\frac{\partial V(r)}{\partial r}\right|_{r=|\vec{R}^l|} \tag{34a}$$

and

$$\alpha_{2l-1}^I = 2\left.\frac{\partial^2 V(r)}{\partial r^2}\right|_{r=|\vec{R}^l|} , \tag{34b}$$

we get

$$\mathcal{F}_l = -\tfrac{1}{2}\alpha_{2l}^I|\vec{R}^l| - \tfrac{1}{2}\alpha_{2l-1}^I|\vec{\xi}_r^l| , \tag{34c}$$

with $\vec{\xi}_r^l$ being the radial displacement of the lth neighbor of the interstitial. Since the force $\mathcal{F}_1$ on

TABLE III. Lattice relaxation and the forces at the relaxed positions for the first few neighbors of the nominal interstitial.

Lattice points (l_1, l_2, l_3)	Force at relaxed position (dyn/cm)	Displacement components ξ_1/a	ξ_2/a	ξ_3/a
(1, 0, 0)	19507	0.1738	0.0	0.0
(1, 1, 1)	830	0.0088	0.0088	0.0088
(2, 1, 0)	−180	0.0279	0.0210	0.0
(2, 2, 1)	7.4	0.0071	0.0071	0.0041
(3, 0, 0)	5.6	0.0140	0.0	0.0
(3, 1, 1)		0.0097	0.0039	0.0039

the first neighbors will be much larger than the force on any other neighbors, we take only up to $l = 5$ and solve (34c) simultaneously with Eqs. (11). However, the displacement of the first neighbor being fairly large (approximately $0.15a$) and $V(r)$ changing rapidly for small r, we replaced (34c) for $l = 1$ by

$$\mathfrak{F}_1 = -\tfrac{1}{2}\beta_2^l|\vec{R}^1 + \vec{\xi}_0| - \tfrac{1}{2}\beta_1^l|\vec{\xi}_r^1 - \vec{\xi}_0|, \qquad (35)$$

where $\vec{\xi}_0$ is a displacement of the first neighbor from the use of (34c). Actually, we evaluated the values of $\partial V/\partial r$ and $\partial^2 V/\partial r^2$ at intervals of 0.1 (units of a) and used successive values (β's are same as α's except evaluated at the point $R^1 + \xi_0$ instead of R^1) until a reasonable convergence was reached.

The results obtained for forces at the five neighbors and the relaxations of the first six neighbors are shown in Table III. A comparison was made using the dynamical matrix obtained from the pseudopotential instead of our eight-neighbor fit with the results differing by 0.5% (of the unit a) or less, indicating the dominating effect of the large forces between the interstitial atom and its first neighbors.

VI. CONCLUSIONS

We have found that the phonon spectrum of aluminum can adequately be reproduced by the Harrison pseudopotential except for deviations in the elastic constants confirming the usefulness of the pseudopotential to give interionic interaction for problems where long-range effects ($q \to 0$) can be ignored.

The lattice relaxation in the vicinity of a vacancy has been evaluated using a more reliable eight-neighbor interaction dynamical matrix, fitting the experimental phonon spectrum as well as the elastic constants. The results show a much better convergence for the elastic continuum result for isotropic aluminum than previously obtained. The lattice relaxation is found to be 2.5% (of the unit a) for the first neighbors and smaller for the other neighbors.

In the case of an interstitial atom at the nominal site, we have found that the large interaction between this atom and its first neighbors dominates, as should be expected. The lattice relaxation obtained is about 17% for the first neighbors while the largest value for the rest of the lattice is only about 2.6%.

We repeated the calculations using the dynamical matrix from the pseudopotential to check for possible differences in relaxations between the more accurate empirical eight-neighbor fit and the semiempirical two-parameter pseudopotential interaction. We found that the relaxations varied by a maximum of 1% (of the unit a) for either of the two defect cases (vacancy or the nominal interstitial) even though the force constants varied by large amounts.

ACKNOWLEDGMENT

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