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Application of Pseudopotentials to the Calculation of Vacancy Formation Energy and Volume for Alkali Metals*

Paul S. Ho
Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14850
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Based on the pseudopotential formalism, a calculation for vacancy formation energy and formation volume in metals has been formulated. The calculation is carried out in three steps: First, the structural energy required to create the vacancy is calculated; then the lattice-statics method is used to calculate the relaxed vacancy configuration and the energy; finally, the dilatation of the whole defect lattice is determined according to the equilibrium condition. When applying this calculation to alkali metals, it was found that (a) the contribution from the volume-dependent lattice energy to the vacancy formation energy is very large compared to that due to the relaxation around the vacancy. Therefore, such energy must be considered in calculating vacancy volume and energy. (b) The relaxed displacements near the vacancy are highly anisotropic and quite large but the related relaxation energy contributes only about 25% of the formation energy. A local potential and an optimized nonlocal potential were chosen as pseudopotentials in the calculation, both of which have corrections for the electron exchange and correlation interactions in the screening function. The results are in quantitative agreement with the available experimental data of alkali metals. Some general problems about defect calculations for metals are also discussed.

I. INTRODUCTION

There are three basic problems in the atomistic calculation of defect properties in metals. The first and probably the most important one is how to construct a realistic interatomic potential which can take into account the nature of the metallic bond. The second is how to calculate properly the defect volume and energy in the presence of the volume-dependent lattice energy, which is usually large in metals, and the origin of which can be attributed to the conduction electrons. The last problem is how to calculate self-consistently the electron redistribution around the defect. All these problems can be attributed to the many-body nature of the interaction between the conduction electrons and the ions, which is complicated even for metals with relatively simple electronic structures.

Since the classical work by Huntington and Seitz[1] on copper, many defect calculations have been performed for metals.[2] Most of the interatomic potentials used are empirical Born-Mayer- and Morse-type potentials. Such potentials when determined according to suitable lattice and defect properties have yielded believable results. Nevertheless, their use is probably due to their simplicity and, more likely, because of the lack of better potentials. The defect volume is usually determined by a matching scheme, in which the displacements of the boundary atoms in a discrete region are matched to the elastic displacements outside this region. The reliability of this procedure has been subjected to question recently, particularly for elastically anisotropic materials such as alkali metals. In a lattice-statics calculation of vacancy relaxation of alkali metals, Flocken and Hardy[3] showed that the displacement does not approach the elastic limit even after 15 shells. Perhaps a more fundamental objection to the matching scheme arises from the effect of the volume-dependent part of the cohesive energy in determining defect properties. For example, the average kinetic energy per electron is $0.6E_F$ (E_F, the Fermi energy) which will contribute about 1 eV to the vacancy formation energy E_f of Na if the formation volume is about half the atomic volume. This 1 eV is more than twice the measured E_f of Na.[4] Clearly, the volume-dependent energies must be taken into account when calculating defect properties. Generally, the defect properties depend on the relaxation of the whole crystal and not just the relaxed configuration around the defect. Consequently, in order to calculate the defect energy, one must extend the calculation to find the dilatation of the defect crystal.

The problem of calculating charge redistribution around the defect is a difficult one since it must be treated self-consistently. Huntington[1] made the first serious attempt for this problem in his work on copper according to a variational method. Fumi[5] used a simplified approach by calculating the phase shift of the free-electron wave function near the defect according to the Friedel sum rule. March and co-workers[6] have also considered this problem by calculating the screening charge around the defect which is considered as a point charge. In general, electron redistribution for defects with high symmetry such as vacancy has been calculated and shown to have a significant effect on the defect ener-

gy. In these calculations the effect of the relaxation around the defect on the charge redistribution has not been taken into account. In later calculations of using empirical two-body force models, this problem is generally ignored.

It is the purpose of this paper to apply the pseudopotential formalism for calculating the formation energy and formation volume for vacancies in alkali metals. The theory of pseudopotentials has been developed recently based on the cancellation theorem of the ionic potential in an orthogonal-plane-wave (OPW) expansion of the wave functions for the conduction electrons.[7,8] According to this theory, the total lattice energy can be separated into two parts: One depends only on the crystal volume and the other, the so-called structural energy, depends on the detailed atomic arrangement. This energy partition is very convenient in calculating crystal atomic properties. Feit and Huntington[9] have calculated the migration energy of interstitials based on the change of the structural energy due to relaxation around the defect. An effective interionic potential can be derived from the structural energy, which was used to calculate the relaxed configuration and energy for vacancies in alkali metals.[10,11] The relaxation energy obtained for Na is significantly smaller than that obtained based on Morse potentials.[12]

Besides the fact that we base our calculation on pseudopotentials, there are two other aspects making our work different from most of the previous defect calculations. First, we use the lattice-statics method to calculate the relaxed configuration and energy around the vacancy. It is found that the relaxation is of a long-range oscillatory nature and difficult to be matched by elastic displacements. The second aspect is that we determine the vacancy energy and volume by minimizing the total energy of the defect lattice. This turns out to be an important criterion since we found that the volume-dependent energy has significant effect on the vacancy properties and must be taken into account in addition to the structural energy.

II. METHOD OF CALCULATION

This calculation is carried out in three steps. First, the vacancy is introduced through the structure factor and the structural energy required to produce the vacancy is calculated (Sec. II A). Then the relaxed configuration about the defect is calculated by the lattice-statics method under the condition of constant atomic volume (Sec. II B). Finally, the whole lattice containing the vacancy is allowed to relax to its equilibrium configuration, i.e., the minimum-energy configuration by a uniform dilatation (Sec. II C).

The formulation in this section is intended to be general so it is applicable for any pseudopotential. In Sec. III, we will show our choice of the potentials used in our calculation. Then in Sec. IV we will report our results and compare them with experimental values and other calculations.

A. Structural Energy of Vacancy

In the pseudopotential theory, the total lattice energy per atom can be written as

$$U_T = U_0 + U_e + U_b \ , \tag{1}$$

where U_0 is the volume-dependent energy. For monovalent metals, it has the form, in atomic units,

$$U_0 = 1.105/r_s^2 - 0.458/r_s - (0.0575 - 0.0155 \ln r_s) + \sum_k \langle k|w|k\rangle \ , \tag{2}$$

where the first term in U_0 is the average kinetic energy ($0.6E_F$) of the electron, the second and third terms are the exchange and correlation energies[13] of the free-electron gas, and the last term is the average value of the electron-ion interaction in the pseudopotential. The value of the last term can be calculated according to the form of the pseudopotential and is inversely proportional to the atomic volume. The charge density parameter r_s is defined in terms of the atomic volume Ω_0 by

$$\tfrac{4}{3}\pi r_s^3 = \Omega_0 \ . \tag{3}$$

The sum of the electrostatic energy U_e and the band-structure energy U_b is the structural energy. The expression of U_e was first derived by Fuchs[14] as

$$U_e = \sum_{q_0}{}' S(q)S^*(q)F_e(q) + \sum_l \varphi(r^l) - \frac{Z^{*2}\xi^{1/2}}{\pi^{1/2}} - \frac{\pi Z^{*2}}{2\xi\Omega_0} \ , \tag{4}$$

where

$$F_e(q) = \frac{2\pi Z^{*2}}{\Omega_0}\frac{e^{-q^2/4\xi}}{q^2}$$

and

$$\varphi(r^l) = \frac{Z^{*2}}{(\pi r^l)^{1/2}}\int_{\xi^{1/2}r^l}^{\infty} e^{-x^2}\,dx \ .$$

Z^* is the effective valence charge, and ξ is a parameter to be chosen to optimize the convergence of two series sums. The last two terms in Eq. (4) can be considered as the self-energies of the ion and the background negative charges, respectively. They correspond to the zero-point terms excluded from the sums as indicated by the prime on the summation. The $S(q)$ is the structure factor which is defined for a lattice containing N atoms as

$$S(q) = \frac{1}{N}\sum_l^N e^{-i\vec{q}\cdot\vec{r}^l} \ . \tag{5}$$

For a perfect lattice $S(q)$ vanishes except when $\vec{q}$ is a reciprocal-lattice vector $\vec{q}_0$, then $S(q_0)=1$.

The band-structure energy can be expressed as

$$U_b=\sum_{q_0}{}'S(q)S^*(q)F_b(q)\ , \tag{6}$$

where $F_b(q)$ is the energy–wave-number characteristic.[7] The detailed expression of $F_b(q)$ depends on the pseudopotential chosen, which will be given in Sec. III. Here it is sufficient to know that $F_b(q)$ is an explicit function of Ω_0, q, and k_F, the Fermi wave vector.

By the structural energy of the vacancy E_s, we imply the change in the structural energy of the crystal when a vacancy is created without any lattice relaxation. The vacancy is created by removing an atom at $\vec{r}^{\,l}=0$ and placing it on the crystal surface. This gives the structure factor for the defect lattice

$$S'(q)=\frac{1}{N}\sum_{l}^{N+1}e^{-i\vec{q}\cdot\vec{r}^{\,l}}-\frac{1}{N}\ . \tag{7}$$

We consider first the changes in both U_b and the first term in U_e. The sum of these two terms after the vacancy is introduced can be written as

$$U_s'=N\sum_{q}{}'S'(q)S'^*(q)F(q)-\sum_{q_0}{}'F(q)\ , \tag{8}$$

where $F(q)=F_b(q)+F_e(q)$. The last term which sums only over the reciprocal-lattice vectors $\vec{q}_0$ accounts for the change in structural energy for that surface atom which was removed from the origin.[15]

Now we expand U_s' in terms of the atomic displacement $\vec{\xi}^{\,l}$ from the equilibrium position $\vec{r}_0^{\,l}$. (The expansion is carried out here for convenience of later relaxation calculation; it is not necessary for calculating E_s.) Let $\vec{r}^{\,l}=\vec{r}_0+\vec{\xi}^{\,l}$ and expand $S'(q)$ to harmonic terms in $\vec{\xi}^{\,l}$; we have

$$S'(q)=S_0(q)+S_1(q)+S_2(q)-1/N\ , \tag{9}$$

where

$$S_0(q)=\frac{1}{N}\sum_{l}^{N+1}e^{-i\vec{q}\cdot\vec{r}_0^{\,l}}\ ,$$

$$S_1(q)=-\frac{1}{N}\sum_{l}^{N+1}e^{-i\vec{q}\cdot\vec{r}_0^{\,l}}(\vec{q}\cdot\vec{\xi}^{\,l})\ ,$$

$$S_2(q)=-\frac{1}{2N}\sum_{l}^{N+1}e^{-i\vec{q}\cdot\vec{r}_0^{\,l}}(\vec{q}\cdot\vec{\xi}^{\,l})^2\ .$$

Substituting Eq. (9) into Eq. (8) and after some manipulation, we obtain

$$U_s'=N\sum_{q_0}{}'F(q)+\frac{1}{N}\sum_{q_0}{}'F(q)-\frac{N+1}{N}\sum_{q_0}{}'F(q)$$
$$+\frac{2}{N}\sum_{q}{}'\left|[S_0^*(q)-1][S_1(q)+S_2(q)]\right|F(q)$$
$$+\frac{1}{N}\sum_{q}{}'\left|S_1(q)+S_2(q)\right|^2F(q)\ . \tag{10}$$

In this expression, the first term is U_s for a perfect lattice, called U_s^0. The last two terms are at least of linear order in $\vec{\xi}^{\,l}$, so they are part of the relaxation energy. The second and third terms come from changes in the structural energy due to the addition of the vacancy and the surface atom, therefore, they are part of E_s. The sum in the second term is not limited only to the reciprocal-lattice vectors but includes all allowed Bloch states. It can be converted into an integral in the q space

$$\frac{1}{N}\sum_{q}{}'F(q)=\frac{\Omega_0}{(2\pi)^3}\int F(q)\,d^3q$$
$$=\frac{\Omega_0}{(2\pi)^3}\int F_b(q)\,d^3q+\frac{Z^*\xi^{1/2}}{\pi^{1/2}}\ , \tag{11}$$

where the last expression is obtained by separating $F(q)$ into $F_b(q)$ and $F_e(q)$ and carrying out the integration on $F_e(q)$.

To complete the calculation for E_s, we have to consider the change of the last three terms in U_e. We shall omit the details of the calculation here since they are quite similar to that for U_s' and given only the results.[16] For the defect lattice, we call the total sum of these terms for N atoms U_r', which has the expression

$$U_r'=U_r^0-\sum_{l}{}'\varphi(r^l)+\frac{Z^{*2}\pi}{2\xi\Omega_0}-\sum_{l,\alpha}\frac{\partial\varphi(r^l)}{\partial x_\alpha^l}\xi_\alpha^l$$
$$-\frac{1}{2}\sum_{ll'}\sum_{\alpha\beta}\frac{\partial^2\varphi(r^l-r^{l'})}{\partial x_\alpha^l\partial x_\beta^{l'}}\xi_\alpha^l\xi_\beta^l\ . \tag{12}$$

Again, the second and third terms are part of E_s and the last two terms are part of the relaxation energy, and U_r^0 is the energy sum for the perfect lattice.

Summing up the contributions from U_s' and U_r', we obtain the total structural energy required for creating the vacancy,

$$E_s=\frac{\Omega_0}{(2\pi)^3}\int F_b(q)\,d^3q-\sum_{q_0}{}'F_b(q)+\frac{\alpha Z^{*2}}{2r_s}\ , \tag{13}$$

where the last term is the negative electrostatic energy for an ion; α is the Madelung's constant, being 1.791 86 for bcc metals. The first two terms are contributions from the band-structure energies associated with the vacancy and the surface atom, respectively. Because of the shape of $F_b(q)$, the integral term is very large compared to the discrete

sum. The magnitudes of these two terms depend on the pseudopotential used.

B. Relaxed Configuration Around a Vacancy

We apply the lattice-statics method to calculate the relaxation around the vacancy. This method was originally formulated by Kanzaki,[16] then modified by Hardy[17] and reformulated by Flinn and Maradudin.[18] The advantage of using this method is that the displacements from the equilibrium position, i.e., $\vec{\xi}^l$'s, are solved simultaneously for all the atoms around the defect by minimizing the relaxation energy. However, the solution is exact only in the harmonic approximation; hence, its validity is open to question for large relaxation displacements.

First, $\vec{\xi}^l$ is expanded in terms of the normal coordinates $\vec{a}_Q$:

$$\vec{\xi}^l = \sum{}'_Q (\vec{a}_Q e^{-i\vec{Q}\cdot\vec{r}^l} + \vec{a}_Q^* e^{i\vec{Q}\cdot\vec{r}^l}) , \tag{14}$$

where $\vec{Q}$ sums over all the Bloch states in the Brillouin zone.

For the relaxation energy E_R, we have to consider only the last two terms in both U_s' and U_r'. Substituting Eq. (14) into these terms, we obtain an expression for E_R as a function of a_Q's. The calculation is involved and will not be shown in detail here. However, it is very similar to that used in lattice dynamics except that in addition to the usual quadratic terms in a_Q, we have also linear terms due to the presence of the vacancy. E_R can be minimized by setting

$$\frac{\partial E_R}{\partial a_Q} = 0 \qquad \text{for all } Q .$$

This condition yields a set of equilibrium equations for each $\vec{a}_Q$, which can be written as

$$\sum_\beta V_{\alpha\beta}(Q) a_Q^\beta = G_\alpha(Q), \quad \alpha, \beta = 1, 2, 3 \tag{15}$$

where[19]

$$G_\alpha(Q) = \sum_{q_0} [(q_0 - Q)_\alpha F(q_0 - Q) - (q_0 + Q)_\alpha F(q_0 + Q)] - 2Q_\alpha F(Q) + \sum_l \frac{\partial \varphi}{\partial x_\alpha}\bigg|_{r=r^l} e^{-i\vec{Q}\cdot\vec{r}^l} ,$$

$$V_{\alpha\beta}(Q) = (N+1)\{\sum_{q_0} [(q_0 - Q)_\alpha (q_0 - Q)_\beta F(q_0 - Q) + (q_0 + Q)_\alpha (q_0 + Q)_\beta F(q_0 + Q) - 2q_{0\alpha} q_{0\beta} F(q_0)] + 2Q_\alpha Q_\beta F(Q)\} + (N+1)\sum_l \varphi_{\alpha\beta}^{0l} e^{-i\vec{Q}\cdot\vec{r}^l} ,$$

and

$$\varphi_{\alpha\beta}^{0l} = \frac{\partial \varphi(r^l)}{\partial x^l{}_\alpha \partial x^l_\beta}\bigg|_{r=r^l} , \quad \varphi_{\alpha\beta}^{00} = -\sum_l \varphi_{\alpha\beta}^{0l} .$$

After solving the a_Q in Eq. (15), one can obtain the relaxation energy

$$E_R = \sum_{Q,\alpha} G_\alpha(Q) a_Q^\alpha . \tag{16}$$

The relaxation displacement ξ^l can also be calculated according to Eq. (14). Due to the symmetry of the vacancy, one can show that $\vec{a}_Q = -\vec{a}_Q^*$; then

$$\xi_\alpha^l = -2i \sum_Q a_Q^\alpha \sin\vec{Q}\cdot\vec{r}^l . \tag{17}$$

C. Formation Energy and Formation Volume

To sum up the results obtained so far, we have for the total energy of the defect lattice

$$NU_T' = NU_0 + U_s^0 + U_r^0 + E_s + E_R . \tag{18}$$

The calculation has been carried out under the condition of constant atomic volume. To calculate the formation volume and energy, we can let the whole defect lattice dilate uniformly by δ and then minimize the change in NU_T' with respect to δ. For metals, there is one complication when applying this procedure to calculate vacancy properties, i.e., in the defect lattice there is one extra atomic cell but no change in the number of electrons. Accordingly, if the lattice dilatation is expressed as

$$\vec{r}^l = \vec{r}^l{}_0(1 - \delta) ,$$

then

$$\vec{q} = \vec{q}_0(1 + \delta) ,$$

but k_F relaxes first by the factor $(1 - 1/3N)$, then by $(1 + \delta)$, so that

$$k_F = k_F^0(1 - 1/3N)(1 + \delta) .$$

Expanding NU_T' in terms of δ to the second order, we see then δ can be determined according to

$$\frac{\partial NU_T'(\delta)}{\partial \delta} = 0 .$$

The formation volume is related to δ simply by

$$\Omega_f = \Omega_0(1 - 3N\delta) . \tag{19}$$

We obtain the expression for δ

$$\delta = A/B , \tag{20}$$

where

$$A = \frac{4}{3}\frac{2.21}{r_s^2} - \frac{0.458}{3r_s} + 3\sum_k \langle k|w|k\rangle - \frac{\alpha Z^{*2}}{2r_s} - \frac{\Omega_0}{(2\pi)^3}\int \frac{\partial F_b}{\partial q} d^3q + \sum_{q_0}{}' \frac{\partial F_b}{\partial q} q + \frac{1}{3}\sum_{q_0}{}' \frac{\partial^2 F_b}{\partial (k_F/q)\partial q} k_F + \sum_{Q,\alpha}\left(G_\alpha(Q) - \frac{\partial G_\alpha(Q)}{\partial Q} Q^\alpha\right) a_Q^\alpha$$

and

$$B = 3\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.0155 + 12\sum_k{}'\langle k|w|k\rangle - \frac{\alpha Z^{*2}}{r_s} + \sum_{q_0}{}'\frac{\partial^2 F_b}{\partial q^2}q^2 .$$

The formation energy E_f is the difference between the energies for the dilated defect lattice and the perfect lattice. We find that

$$E_f = E_v + E_s + E_R , \tag{21a}$$

where

$$E_v = (\tfrac{1}{3} - N\delta)\times\left(-\frac{2.21}{r_s^2} + \frac{0.458}{r_s} + 0.0155 - 3\sum_k\langle k|w|k\rangle\right) + N\delta\left(\sum_{q_0}{}'\frac{\partial F_b}{\partial q}q - \frac{\alpha Z^{*2}}{2r_s}\right) - \frac{1}{3}\sum_{q_0}{}'\frac{\partial F_b}{\partial(k_F/q)}\left(\frac{k_F}{q}\right) . \tag{21b}$$

Based on our results, we note that:

(a) In deriving Ω_f and E_f, we have used the equilibrium condition for the perfect lattice, i.e., $\partial U_T/\partial\Omega = 0$ at Ω_0. Therefore, in our calculation it is important to satisfy this equilibrium condition when choosing the lattice pseudopotential.

(b) The value of E_v depends on δ; therefore, in order to calculate E_f, one has to determine Ω_f also.

(c) Harrison[20] has calculated the contribution from the electrostatic energy to E_f without lattice dilatation, which corresponds to our case when $N\delta = \frac{1}{3}$. He obtained the value of $-\frac{2}{3}U_e$, in agreement with our result of $-(1-N\delta)U_e$ [the sum of the last term in Eq. (13) and the second term in the square bracket of E_v in Eq. (21b)].

III. SELECTION OF PSEUDOPOTENTIAL

To carry out the calculations described in Sec. II, we need to choose a pseudopotential. Several pseudopotentials have been determined according to various experimental quantities for alkali metals. Recently Coulthard[21] and Shaw and Pynn[22] have investigated the effects on phonon dispersion curves due to the locality and screening correction for electron exchange and correlation of the pseudopotentials. They found that in general it is important to take into account the exchange and correlation corrections in order to obtain good agreement with experimental results. It was further concluded that when such corrections were made, Shaw's nonlocal model potential consistently gave the best results. However, the local Heine-Abarenkov (HA) pseudopotentials were found to give also satisfactory results. In the present calculation we choose a nonlocal model potential and a local HA-type pseudopotential, both of which have taken into account, though by slightly different forms, the exchange and correlation corrections. The nonlocal potentials are the optimized model potentials recently published by Shaw and Pynn[22] and the local potentials were determined by us according to the measured elastic constants.[23] The local potential is less desirable in principle, but its relatively simple form of $F_b(q)$ significantly reduces the labor of numerical calculation.

For local pseudopotentials, the energy–wave-number characteristic can be written as

$$F_b(q) = [w(q)]^2 x(q)/\epsilon(q) , \tag{22}$$

where $w(q)$ is the Fourier transform of the bare-ion potential, $x(q)$ is the so-called perturbation characteristic, and $\epsilon(q)$ is the dielectric function.

For the bare-ion potential, we use a simplified Heine-Abarenkov form:

$$v^{\text{ion}}(r) = -v_0 \quad \text{for } r < R_M ; \qquad = -Z/r \quad \text{for } r > R_M , \tag{23}$$

which has the Fourier transform

$$w(q) = -\frac{2\pi}{\Omega_0 q^2}\left[\frac{V_0 \sin qR_M}{q} + (Z - V_0 R_M)\cos qR_M\right] . \tag{24}$$

We have also

$$x(q) = -\frac{3Z}{4E_F}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q}\ln\left|\frac{2k_F^2 + q}{2k_F - q}\right|\right) \tag{25}$$

and

$$\epsilon(q) = 1 - (8\pi/\Omega q^2)[1 - f(q)]\,x(q) . \tag{26}$$

The factor $1-f(q)$ is the approximate correction for the exchange and correlation. For $f(q)$, we adopt a form similar to that used by Hubbard and Sham[24]:

$$f(q) = \frac{q^2}{2(q^2 + \eta k_F^2)} . \tag{27}$$

For this model potential, we can derive an explicit expression for $\sum_k \langle k|w|k\rangle$ as

$$\sum_k \langle k|w|k\rangle = \frac{4\pi Z^2}{\Omega_0 q^2} + \lim_{q\to 0} w(q) = \frac{2\pi R_M^3}{\Omega_0}\left(\frac{Z}{R_M} - \frac{2V_0}{3}\right) . \tag{28}$$

V_0, R_M, and η were considered to be adjustable parameters which can be determined according to the measured elastic constants. In addition, the equilibrium condition was imposed at Ω_0, i.e., $\partial U_T/\partial\Omega|_{\Omega 0} = 0$. Because of this extra condition, our potential parameters have been redetermined. They

TABLE I. Local pseudopotential parameters and some relevant data for alkali metals (atomic units).

	Li	Na	K	Rb	Cs
V_0	0.698	0.570	0.379	0.402	0.373
R_M	1.68	2.40	3.04	3.54	3.95
η	1.84	1.81	1.77	1.76	1.74
B^T [a]	13.30 (13.25)	7.329 (7.528)	3.563 (3.657)	2.784 (2.825)	2.112 (2.127)
a (lattice parameter)	6.58	8.01	9.90	10.60	11.47

[a]Given are the calculated and the measured (in parenthesis) isothermal bulk moduli. Units are 10^{10} dyn/cm^2. The effective charge is taken to be unity for the local potentials.

differ somewhat from those listed in Ref. 23. For alkali metals, it was found that it is possible to find a set of V_0, R_M, and η to satisfy these conditions reasonably well. Table I lists the potential parameters together with the bulk moduli and lattice parameters for alkali metals.

The nonlocal forms of $F_b(q)$ for Li, Na, and K can be found in Ref. 22. The normalized energy-wave-number characteristics $F_N(q)$ of the local and nonlocal potentials are compared for these three metals in Fig. 1. In Shaw's potential the value of $\sum_k \langle k|w|k\rangle$ is not given, even though it could have been determined when calculating $F_b(q)$. In this paper, calculation of this term was not attempted, instead it was determined simply according to the lattice equilibrium condition. Also, the complex functional dependence of Shaw's potential on k_F and Ω_0 was not unraveled, which is needed to calculate the various derivatives for determining δ and E_v. Such values were obtained by extrapolation according to the results from the local potentials. Fortunately, it was possible to calculate exactly most of the large terms in E_v and δ; nevertheless, the extrapolated terms contribute a certain uncertainty in our results for Shaw's potential. It would be very desirable to repeat the calculation for Shaw's potential in a more exact manner.

IV. RESULTS

In the calculation, 422 Q's were included in the first Brillouin zone and the summation was extended over q_0 to 3.5b ($b = 2\pi/a$). In real space, this corresponds to a discrete region consisting of 422 atoms and extending to the 22nd shell. These summations were found to give the convergence of $\vec{\xi}^{\,l}$ to approximately 1%, which is sufficiently accurate for calculating E_f since E_R is only about 25% of E_f. The calculated $\vec{\xi}^{\,l}$ for Na is tabulated in Table II. The displacements, in general, are not radial except along the symmetry directions of ⟨100⟩, ⟨110⟩, and ⟨111⟩. The relaxed vacancy configuration shown displays a cubic symmetry characteristic of the anisotropic interaction of the alkali atoms. The atom displacements on the (100) and (110) planes are

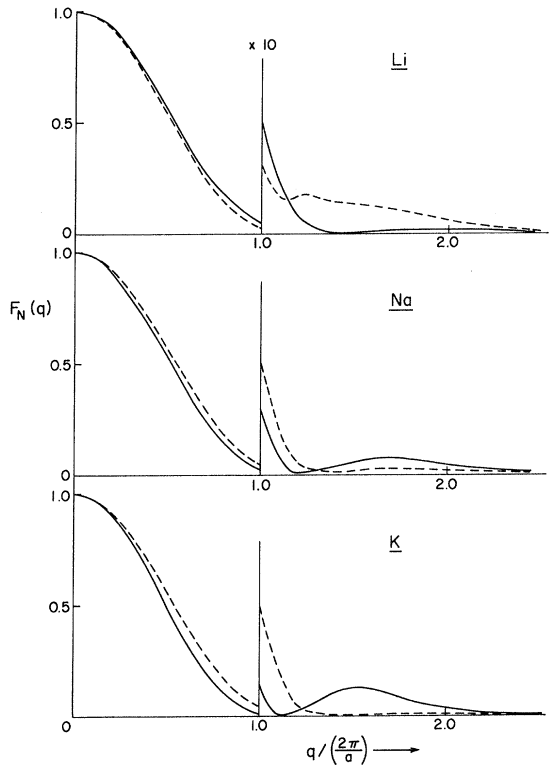

FIG. 1. Normalized energy–wave-number characteristics $F_N(q)$ obtained from the local (solid line) and the nonlocal (dash line) pseudopotentials for Li, Na, and K [$F_N(q) \equiv -(q^2\Omega_0/2\pi Z^{*2})F(q)$].

TABLE II. Results of the relaxed vacancy configuration and energy for Na calculated according to the local and nonlocal pseudopotentials. (Displacements are expressed in percent of the lattice parameter.)

Atom position (units = $\frac{1}{2}a$)	$\vec{\xi}^{\,l}$ (Local potential)			$\vec{\xi}^{\,l}$ (Nonlocal potential)		
(111)	−4.19	−4.19	−4.19	−3.06	−3.06	−3.06
(200)	4.96	0	0	5.08	0	0
(220)	−0.67	−0.67	0	−0.58	−0.58	0
(311)	0.13	0.70	0.70	0.20	0.71	0.71
(222)	−1.73	−1.73	−1.73	−1.15	−1.15	−1.15
(400)	0.13	0	0	0.03	0	0
(331)	−0.42	−0.42	0.18	−0.30	−0.30	0.10
(420)	0.19	−0.44	0	0.18	−0.34	0
(422)	0.76	−0.02	−0.02	0.69	−0.01	−0.01
(333)	−0.72	−0.72	−0.72	−0.54	−0.54	−0.54
(511)	0.24	0.11	0.11	0.19	0.06	0.06
(440)	−0.51	−0.51	0	−0.39	−0.39	0
E_R (eV)		0.108			0.064	

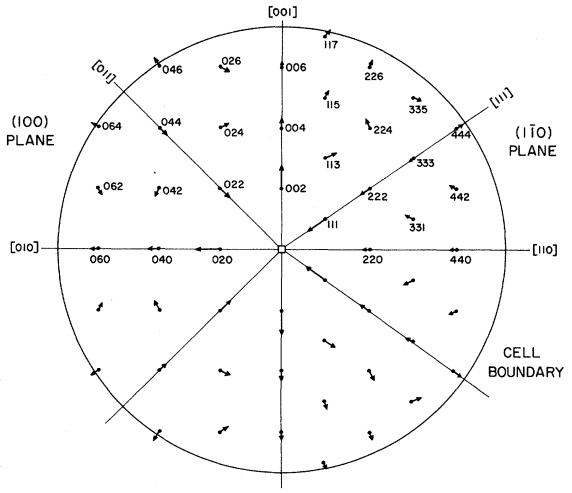

FIG. 2. Relaxed configuration around the vacancy for Na calculated according to the local pseudopotential. The vectors show the direction and magnitude of the displacements projected on the (100) and (1$\bar{1}$0) planes. The numbers associated with the lattice points are the atom positions in units of $\frac{1}{2}a$.

shown in Fig. 2: Generally $\vec{\xi}^{\,l}$ displaces inward toward the vacancy near the ⟨110⟩ and ⟨111⟩ directions and away from the vacancy near the ⟨100⟩ directions. Since the lattice-statics method guarantees minimum energy for the final relaxed configuration, the outward displacements of some atoms must result from the inward displacements of the other atoms in order to minimize the relaxation energy. The relaxed configurations were found to be very similar for all the alkali metals with $\vec{\xi}^{\,l}$ slightly increased for heavier atoms, e.g., the displacements for the nearest-neighbor atom are, in terms of a, -0.068 for Li, -0.072 for Na, -0.076 for K, -0.077 for Rb, and -0.078 for Cs.

In Table III, the results of our calculation are summarized based on the local and nonlocal potentials. It is seen that the results based on these two potentials are very close for Na and K but not for Li, which is very probably because of the difference in $F_b(q)$ of Li.[25] Our results show that for all alkali metals except Li, E_f decreases for heavier elements whereas Ω_f is about constant. However, the change is generally quite small. The relaxation energy is found to be about 0.1 eV for all alkali metals, which is only about 25% of the formation energy.

TABLE III. Results of vacancy calculation for alkali metals.

	Li		Na		K		Rb	Cs
	L[a]	NL	L	NL	L	NL	L	L
E_s[b]	3.02		2.67		2.32		2.14	1.99
		3.96		2.90		2.59		
E_v	−2.56		−2.17		−1.84		−1.68	1.56
		−2.88		−2.42		−2.10		
E_R	−0.093		−0.11		−0.12		−0.11	−0.10
		−0.20		−0.06		−0.07		
E_f	0.37		0.39		0.36		0.35	0.33
		0.88		0.42		0.42		
Ω_f	0.53		0.54		0.53		0.52	0.52
		0.59		0.62		0.57		

[a]The results in L column are for the local potentials and NL for nonlocal potentials.

[b]All energies are expressed in eV.

TABLE IV. Comparison of the present work with other calculations on vacancy relaxed configuration and energy. (For simplicity we compare only the magnitude of the displacements. Units in percent of radial distance.)

Atom position	WG (Ref. 12b)	GR (Ref. 12c)	SBF (Ref. 10)	FH (Ref. 3)	TG (Ref. 11)	Present work
(111)	−10.0	−11.53	−4.77	−5.86	−8.18	−8.38
(200)	3.2	3.45	2.66	3.18	3.41	4.96
(220)	−1.2	−1.59	−0.62	−0.95	−1.20	−0.67
(311)	0.7	0.34	0.44	0.32	0.47	0.61
(222)		−2.27	−0.86	−1.43	−2.00	−1.73
(400)		0.38		0.10	0.30	0.07
(331)		−0.36		−0.34	−0.37	−0.29
(420)		0.05		0.03	0.08	0.20
(422)				0.05	0.08	0.31
(333)				−0.51	−0.69	−0.48
E_R(eV)	−0.446	−0.520	−0.071	−0.045	−0.113	−0.108

For comparison with experiments there are the recent Simmons-Balluffi-type measurements of E_f for[26] Li and[4] Na, and earlier resistivity measurements on E_f for[27] Li, Na, and K; for Ω_f there is no direct measurement except that of the activation volume of diffusion for Li and Na.[28] In Table IV, the results in this paper are compared with the experimental values. The agreement is satisfactory except for Ω_f of Li. In case of Li, even if the migration volume is negligible, the measured value is considerably smaller than our calculated Ω_f, which indicates that the actual lattice dilatation, and possibly the relaxation around the vacancy, may be bigger than what we calculated. However, the measured entropy of formation for Li is only $0.9k$[26] as compared to $5.8k$ for Na.[4] If the entropy is a correct measure of the vacancy relaxation, then the experimental values do not indicate a more relaxed configuration for Li than for Na. At present, there appears to be no satisfactory explanation for these discrepancies. Further investigation on Li, particularly in measuring Ω_f and determining better pseudopotentials, is needed. Except for the Ω_f of Li, our results appear to support the fact that the defects observed in Li, Na, and K are single vacancies.

Concerning the previous theoretical investigations of alkali metals, the effort seems to be concentrated on the calculation of the relaxed vacancy configuration and energy. There are several such calculations based on pseudopotentials[3,10,11] and several others based on Morse potentials.[12] For E_f, there

is only the work by Fumi[5] and a short note by Kojima,[29] and there is no calculation on Ω_f.[30] The various relaxation calculations of Na are compared in Table IV and the calculated and measured values of E_f and Ω_f in Table V. In Table V, the work of particular interest to us is that of Torrens and Gerl[11] who used a different relaxation method but based their calculation on a local pseudopotential which is almost identical to ours. Their results are generally in good agreement with ours. This is very pleasing and useful in checking the numerical computations in both papers. The value of E_R obtained by Shyu *et al.*[10] is close to our value but their relaxation is about 50% of our value. Both the relaxed displacement and energy obtained by Flocken and Hardy[3] are only about half of our value. The results based on the Morse potentials yield too large E_R and $\tilde{\xi}^I$ as compared to ours, which is apparently due to the difference in potentials. [See Fig. 1(c) in Ref. 11 for the large difference between Morse potential and the interionic potential derived from Na pseudopotential.] If the contribution of E_R to E_f is indeed as small as calculated, then the Morse potential used in previous calculations must be considerably larger than the actual potential. Fumi's calculation[5] neglected both the relaxation about the vacancy and the lattice dilatation. In comparing his E_f values our E_R value was subtracted but no attempt was made to calculate the energy change due to lattice dilatation in his formulation. If such energy is included, then his E_f would probably be further reduced.

V. DISCUSSIONS

It has been stressed in this paper that to calculate the vacancy formation energy in metals, one must consider the change in the volume-dependent lattice energy U_0 due to the lattice dilatation. Such energy arises because of the many-body nature of the electron-ion interactions, part of which cannot be properly expressed in terms of pairwise potentials. E_f usually depends on the dilatation δ, so to calculate E_f, one has to determine δ first, which can be done by minimizing the total energy of the defect lattice with respect to δ. This point is particularly important for metals with small Ω_f, such as the alkali metals. For such metals, the dilatation is large, consequently the contribution of U_0 to E_f will be significant. Our results show that in Na, the structural energy required to create a vacancy is 2.67 eV and the energy gained by relaxing the atom around the vacancy is only 0.11 eV, but an energy of 2.17 eV is gained because of lattice dilatation.

In calculating the relaxed vacancy configuration, the boundary was extended to include the 22nd shell. The resultant displacements are highly anisotropic; in fact the displacements for atoms along and near the ⟨100⟩ directions are outward, even up to the boundary. Recently Lie and Koehler[31] have solved the elasticity equation for general point forces in an anisotropic cubic crystal. However, because of difficulties with convergence caused by the large elastic anisotropy of alkali metals (for Li the anisotropy factor is about 8), they were unable to obtain the elastic relaxation about a vacancy. Even if the elastic solution can be obtained, it would still be difficult to obtain a reliable Ω_f by matching the discrete atom displacement to the elastic relaxation since both the direction and the magnitude of the displacements for the boundary atoms are not expected from the elastic continuum theory.

Even though our results are in good agreement with experimental measurements, there are several basic problems concerning the application of model potential to defect calculations. One basic objection is that the pseudopotential theory, which is based on perturbation theory, cannot be adequately used for point-defect calculations, particularly for the vacancies since there is an extreme change in charge density at the vacant site.[32] The second problem is the effect of electron redistribution near the vacancy. In our formulation, the change in the electron density near the defect was not calculated. Finally, there is the problem of anharmonic corrections to the relaxation around the vacancy. Displacements were obtained for the first two neighbors as high as 8 and 5% of the radial distance, respectively; since the lattice-statics method calculates the displacements only to the harmonic order, such large displacements may require anharmonic corrections.

It is quite difficult to give really satisfactory answers to the first two questions without carrying out detailed calculations. Nevertheless, Ziman[33] in advocating the "pseudoatom" concept for defect calcu-

TABLE V. Comparison of theoretical and experimental E_f and Ω_f for alkali metals.

	Li	Na	K
E_f[a] (calc)	0.37	0.39	0.36
	0.46	0.42	0.24
E_f (expt)	0.34 ± 0.04[b]	0.42 ± 0.03[c]	
	0.40[d]	0.39	0.39
Ω_f (calc)	0.53	0.54	0.53
Ω_a[e] (expt)	0.28	0.41	

[a]The values of E_f in row 1 and Ω_f (calc) are our results based on the local potentials. The values of E_f in row 2 are those of Fumi's with E_R subtracted.
[b]Reference 26.
[c]Reference 4.
[d]Reference 27.
[e]Reference 28. Given is the activation volume of diffusion.

lations pointed out that when a vacancy is introduced through the structure factor in the pseudopotential formulation, what one removes is the (weak) quasipotential associated with the ion together with its self-consistent screening charge as seen by the conduction electrons. The electrons are still in Bloch states which are readjusted in a "zeroth-order" manner by a uniform dilatation. As a result, the change in the charge density does not have to be drastic and it might not be such a poor approximation to apply perturbation method for calculating defect problems. For the second problem, the change in the electron wave functions was indeed not included, but when the relaxed-vacancy configuration was calculated, not only the position of the bare ions was obtained, but also the displacements of their associated screening charges. Therefore, the charge redistribution can be considered to be accounted for in such an approximate manner. The approximation is not a particularly good one since the change in the screening charge near the vacancy was not considered self-consistently.

In principle, it is possible to include anharmonic corrections in the lattice-statics calculation. Such a calculation was not attempted, mainly because of the small effect of such a correction to the resultant formation energy and the labor required in actual numerical calculation. The contribution of E_R to E_f is about 25%, the anharmonic correction would be, at most, a few percent of E_f, which is quite insignificant if one considers all the other approximations used in determining the pseudopotentials.

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