Interatomic potential for vanadium suitable for radiation damage simulations

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The ability to predict the behavior of point defects in metals, particularly interstitial defects, is central to accurate modeling of the microstructural evolution in environments with high radiation fluxes. Existing interatomic potentials of embedded atom method type predict disparate stable interstitial defect configurations in vanadium. This is not surprising since accurate first-principles interstitial data were not available when these potentials were fitted. In order to provide the input information required to fit a vanadium potential appropriate for radiation damage studies, we perform a series of first-principles calculations on six different interstitial geometries and vacancies. These calculations identify the \( ^{111} \) dumbbell as the most stable interstitial with a formation energy of approximately 3.1 eV, at variance with predictions based upon existing potentials. Our potential is of Finnis–Sinclair type and is fitted exactly to the experimental equilibrium lattice parameter, cohesive energy, elastic constants and a calculated unrelaxed vacancy formation energy. Two additional potential parameters were used to obtain the best fit to the set of interstitial formation energies determined from the first-principles calculations. The resulting potential was found to accurately predict both the magnitude and ordering of the formation energies of six interstitial configurations and the unrelaxed vacancy ground state, in addition to accurately describing the migration characteristics of the stable interstitial and vacancy. This vanadium potential is capable of describing the point defect properties appropriate for radiation damage simulations as well as for simulations of more common crystal and simple defect properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1555275]

I. INTRODUCTION

Vanadium-based alloys are among the candidate structural materials for use in future fusion reactors. These alloys combine several appealing properties: they do not readily become radioactive under a 14 MeV neutron flux, they exhibit good strength at elevated temperatures, are compatible with liquid lithium and exhibit a high thermal stress factor (low thermal expansion and elastic modulus). As a result, these materials have received considerable experimental and theoretical attention. Modeling of radiation damage must account for radiation-induced microstructural evolution that leads to severe degradation of a wide range of important mechanical properties and significant dimensional changes. A comprehensive modeling program must be inherently multiscale (both in space and time) since the evolution is mediated by a combination of atomic level dynamics, defect physics, nonequilibrium thermodynamics and transport kinetics. The simulations at larger scales must be parameterized either using data obtained from experiment or from simulations on the smaller scales. Hence, the multiscale simulation framework rests on the reliability of the atomistic simulation results. At a minimum, atomistic simulations must be able to reproduce the structure and energetics of the point defects that are present in the irradiated material, in addition to the perfect crystal properties. The point defect properties are of particular interest in these materials since their production, migration and annihilation control the radiation-induced swelling, yield strength and ductility of metallic alloys in such applications.

The reliability of the atomistic simulations depends largely on the accuracy of the modeled atomic interactions.

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While first-principles methods constitute the most reliable approach to determining atomic interactions, application of these methods to systems with more than a few hundred atoms is not feasible. Most atomistic simulations of defects in metals are performed using semiempirical or empirical descriptions of atomic interactions, such as tight binding methods,\textsuperscript{3} bond order potentials,\textsuperscript{6} embedded-atom-method (EAM) potentials,\textsuperscript{7,8} Finnis–Sinclair\textsuperscript{9} (FS) potentials, or simple pair potentials. Each approach represents a different trade-off between errors due to small simulation size and inaccurate forces. While simple pair potentials are often capable of predicting some crystal properties, they also have some dramatic shortcomings that arise from their oversimplistic form in predicting the sign of the surface relaxation, in reproducing the experimental Cauchy pressure \( (C_{12} - C_{44})/2 \), and in predicting some defect properties.\textsuperscript{10,11}

EAM/FS many-body potentials have been proven to be widely applicable to surfaces,\textsuperscript{7,12} vacancies,\textsuperscript{13,14} phonon spectra,\textsuperscript{15} dislocations,\textsuperscript{16} and alloy properties.\textsuperscript{17} Most of the recent atomistic radiation damage (cascade) simulation have used potentials of EAM/FS type, which are both computationally efficient and provide a reasonable description of many types of crystal defects. Typically, potentials of this type are fit to bulk properties (lattice parameter, cohesive energy, elastic constants) and to the vacancy formation energy.

Because interstitial properties have not previously been included in the fitting procedure for most EAM/FS potentials, it is not surprising that different EAM/FS potentials yield widely disparate predictions for the energetics of self-interstitials in vanadium as well as the structure of the stable interstitial,\textsuperscript{18,19,20} as shown in Table I. This failure may be traced to the fact that the minimum interatomic separation near interstitials is much smaller than the equilibrium nearest neighbor spacing in a perfect crystal and that the atomic rearrangements are very anisotropic close to the interstitials. This deficiency arises because of the dearth of experimental data for self-interstitials: they are present in large quantities only in irradiated specimens.\textsuperscript{21} One approach by which to address these deficiencies is to obtain accurate predictions of point defect properties from first-principles methods and use these in the fitting procedure for the interatomic potential. First-principles calculations can also be used to provide reliable predictions of self-interstitial properties that can be used in molecular dynamics and kinetic Monte Carlo studies of point defect evolution in irradiated materials.\textsuperscript{22} First-principles calculation of self-interstitial properties for iron have been reported previously.\textsuperscript{23} The large lattice distortions associated with self-interstitials imply that accurate first-principles calculations of interstitial properties will require some of the largest calculation cells ever used.

In this study, we describe the procedure employed to fit an interatomic potential for vanadium that is suitable for radiation damage simulations, report this potential, and compare predictions made using this potential to first-principles results and experiments. We first report the results of systematic first-principles calculations of point defects (self-interstitials and vacancies) in vanadium. Several different possible self-interstitial structures were investigated to determine which is stable and to provide additional data to be used in the potential fitting procedure. In addition to fitting to both point defect formation and migration energies, we fit to perfect crystal data (lattice parameter, cohesive energy, elastic constants). Simulations performed with this potential confirm that it reproduces both perfect crystal properties and point defect formation energies. In addition, we use the potential to determine phonon spectra and to determine the activation energy for diffusion and the threshold displacement energy for neutron irradiation of vanadium (i.e., the minimum kinetic energy of a neutron required to produce stable point defects) using molecular dynamics.

### II. FIRST-PRINCIPLES METHOD

Within the density functional pseudopotential framework,\textsuperscript{24} the total energy of a system with a given ionic configuration is expressed in atomic units \( (m_e = 1, \ h = 1, \ e = 1) \) as

\[
E_{\text{tot}} = E_{\text{kinetic}} + E_{\text{el-ion}} + E_{\text{el-el}} + E_{XC} + E_{\text{ion-ion}}
\]

\[
= \sum \sum \langle \psi_{i,k} | -\frac{1}{2} \nabla^2 + V_{\text{ion}} | \psi_{i,k} \rangle + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} \, d\mathbf{r} d\mathbf{r}' + \int \epsilon_{XC} [\rho(r), \nabla \rho(r)] \rho(r) \, d\mathbf{r} + \sum \frac{Z_iZ_J}{|R_i-R_J|} + \sum \langle \psi_{i,k} | \psi_{i,k} \rangle,
\]

where \( R_i \) and \( Z_i \) are coordinates and ionic charges of the \( i \)th atom, respectively. \( \psi_{i,k} \) is a valence pseudowave function corresponding to the \( k \)th band at the \( \mathbf{k} \) point in the Brillouin zone (BZ). For the exchange-correlation energy density \( \epsilon_{XC} \), which reflects the quantum many-body interaction of the

<table>
<thead>
<tr>
<th>Reference</th>
<th>(100) dumbbell</th>
<th>(110) dumbbell</th>
<th>(111) dumbbell</th>
<th>(111) crowion</th>
<th>Octahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>4.58</td>
<td>4.90</td>
<td>4.78</td>
<td>...</td>
<td>4.64</td>
</tr>
<tr>
<td>19</td>
<td>4.96</td>
<td>4.16</td>
<td>4.61</td>
<td>4.60</td>
<td>...</td>
</tr>
<tr>
<td>21</td>
<td>4.24</td>
<td>4.80</td>
<td>5.21</td>
<td>4.06</td>
<td>...</td>
</tr>
</tbody>
</table>
A plane wave basis is used to expand the wave function:

$$\psi_{i,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{i,k}(\mathbf{G}) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}},$$

where summation over the $\mathbf{G}$ vectors is bounded by the energy cutoff ($E_{\text{cut}}$) in such a way that $|\mathbf{k}+\mathbf{G}|^2 < 2E_{\text{cut}}$. For the electron–ion interaction represented by $V_{\text{ion}}$, we use an ultrasoft pseudopotential\(^{26}\) which has good transfer properties while requiring only a relatively small energy cutoff for plane wave expansion of the valence orbitals. In pseudopotential formalism, the core electrons which do not contribute to interatomic bonding are implicitly included in repulsive interaction near the core. This dramatically accelerates the computation by reducing the number of electrons that has to be treated explicitly in the calculation. Including plane waves with kinetic energy less than 408 eV ensures convergence of the total energy to within 0.02 eV/atom in crystalline vanadium. In generating the pseudopotential, we employ the $3d^44s^24p^0$ valence electron configuration while underlying core electrons are frozen. We use one projector for each $s$ and $p$ orbital and two projectors for each $d$ orbital in order to accurately describe the $d$ bands. The cutoff radii employed for the ionic potential are 1.13, 1.34, and 0.95 Å for the $s$, $p$, and $d$ channels, respectively. We include nonlinear core corrections\(^{27}\) in the exchange-correlation energy to account for the interaction between valence and core charges.

The computer package PWSCF\(^{28}\) was used for the first-principles calculations. This program not only calculates the electronic structure at a given ionic configuration but also relaxes the atomic coordinates as well as the size and shape of the simulation cell. In our calculations, we optimize the atomic positions until the Hellmann–Feynman forces are less than $5 \times 10^{-2}$ eV/Å. Damped cell dynamics\(^{29}\) are used to relax lattice vectors and we ensure that all components of the average stress tensor are less than $5 \times 10^{-4}$ eV/Å\(^3\). As a simple test of the method, we calculate several bulk properties of vanadium (see Table II). The lattice parameter, bulk modulus, and its derivative are obtained by fitting the energy–volume curve to Birch’s equation of state.\(^{33}\) The elastic constants are obtained from the stress–strain relation,\(^{34}\) i.e., we apply ±1% strain and calculate the resulting stress tensor. The values in parentheses in Table II are evaluated at the experimental equilibrium lattice parameter. To estimate the errors inherent in the pseudopotential, we generate another pseudopotential for which the $3s$ and $3p$ electrons are removed from the core and treated as valence electrons. Table II also shows a comparison of our pseudopotential results with all-electron (FLAPW) calculations\(^{31,32}\) and experiment.\(^{33}\) Overall, the agreement between the elastic constants $C_{ij}$ and the bulk modulus $B$ from the calculations and experiment (and other reference calculations) is quite good except for $C_{44}$ which shows relatively large deviation from experiment. The agreement in the elastic constants is improved when the calculations are performed at the experimental lattice parameter, indicating that the errors in the elastic constants are associated to a large extent with underestimation of the lattice parameter.

### III. POINT DEFECT ENERGIES IN VANADIUM

#### A. Self-interstitials

Figure 1 shows a schematic illustration of the six high-symmetry self-interstitials that we examined via first-principles calculations. Before considering the relative energies of these different configurations, we first examine the convergence of the formation energy with respect to supercell size in a system containing a single $\langle 111 \rangle$-dumbbell interstitial. The supercell consists of a simple cubic arrange-
whereas the fixed cell calculations lead to an overestimate of within 0.05 eV for supercells larger than 3

where the supercell size on

0.05 eV for supercells larger than 3×3×3 (i.e., at least 129 atoms). Although relaxation of the cell shape significantly lowers E^f, this type of relaxation gives an underestimate of the formation energy at large supercell sizes, whereas the fixed cell calculations lead to an overestimate of E^f. If the relaxation of the supercell were purely dilational, the elastic energy of this relaxation would be E_{el} = V_0 P^2/2B, where V_0 is the equilibrium volume and P is the pressure found in the fixed supercell calculation. Examination of Table III shows that E_{el} provides a measure of the effect of the supercell size on E^f. The overall convergence of the first-principles calculation in Table III is faster than in studies with empirical potentials^5^,6^ (see also below), where typically thousands of atoms are included in the supercell. A similar convergence check for the (100)-dumbbell self-interstitial also suggests that a 4×4×4 supercell is sufficient to ensure convergence to within 0.05 eV (see Table III).

Table IV shows the interstitial formation energies E^f for all of the interstitials in Fig. 1 evaluated with the fixed-volume 4×4×4 supercell. The stable self-interstitial in V is either a (111) dumbbell or a crowdion. The very small difference in energy (≤0.01 eV) between the (111) dumbbell and the crowdion is beyond the accuracy of density functional calculations. The prediction that the (111) dumbbell is the most stable interstitial contradicts earlier results obtained using EAM/FS potentials.^18^,19^,20^ The (110) dumbbell, which is the most stable interstitial in some of the EAM studies, has the third smallest formation energy. Furthermore, the predicted magnitude of E^f (3.14 eV) is well below that found in previous EAM/FS calculations (4.61–4.78 eV).

The physics underlying the relative values of E^f for the (111), (110), (100) dumbbells can be understood by examining the type of strain produced by these differently oriented dumbbells. In each case, the predominant deformation is uniaxial strain along the direction of symmetry of the dumbbell. This suggests that the modulus associated with uniaxial strain in the direction of the dumbbell, M_{(ijk)}, should be correlated with the formation energy. This is confirmed in Table V which shows that theoretical and experimental values of M_{(ijk)} are exactly of the same order as the E^f of the corresponding dumbbell (see Table IV).

No direct experimental data exist from which we can determine the symmetry of the self-interstitial in V. However, it is well known from radiation-damage experiments that the migration barrier of the self-interstitial is very small (<0.01 eV) and that diffusion occurs even at 4 K.^3^ The first-principles data, presented above, suggest that the lowest activation energy migration path for the (111) dumbbell corresponds to a transformation from a (111) dumbbell to a crowdion (i.e., the transition state) before and then back again to a (111) dumbbell. The diffusion barrier for this path is simply the difference in E^f between the (111) dumbbell and the crowdion configuration. As shown in Table IV, this energy is very small (~0.01 eV), consistent with experiment. Interestingly, these results suggest that at low temperatures, self-interstitial diffusion should be one dimensional (along the (111) direction). The transition state for rotation from a given (111) direction to another corresponds to the (110)-dumbbell configuration. Therefore, the activation en-

TABLE III. Convergence of E^f for the (111)-dumbbell self-interstitial in V with respect to the supercell size. E^f(1) and E^f(2) indicate the formation energy for the fixed and relaxed cells, respectively. E_{el} is the elastic energy assuming dilational relaxation of the supercell. N_k is the number of k points sampled in the first BZ. The energies and pressure (P) are in eV and GPa, respectively. We define the pressure as minus one third of the trace of the stress tensor for the fixed cell. ΔE^f = E^f(1) − E^f(2) indicates the change in the formation energy when the cell is relaxed. For comparison, the convergence of the (100) dumbbell is shown in the last column.

<table>
<thead>
<tr>
<th>Supercell size</th>
<th>N_{atom}</th>
<th>N_k</th>
<th>E^f(1)</th>
<th>P</th>
<th>E_{el}</th>
<th>E^f(2)</th>
<th>ΔE^f</th>
<th>E^f(1)[100]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a_0×2a_0×2a_0</td>
<td>16(+1)</td>
<td>64</td>
<td>4.49</td>
<td>17.3</td>
<td>0.80</td>
<td>3.46</td>
<td>1.03</td>
<td>5.86</td>
</tr>
<tr>
<td>3a_0×3a_0×3a_0</td>
<td>54(+1)</td>
<td>27</td>
<td>3.28</td>
<td>4.6</td>
<td>0.23</td>
<td>2.99</td>
<td>0.29</td>
<td>3.91</td>
</tr>
<tr>
<td>4a_0×4a_0×4a_0</td>
<td>128(+1)</td>
<td>8</td>
<td>3.14</td>
<td>1.4</td>
<td>0.06</td>
<td>3.10</td>
<td>0.04</td>
<td>3.57</td>
</tr>
<tr>
<td>5a_0×5a_0×5a_0</td>
<td>250(+1)</td>
<td>8</td>
<td>3.12</td>
<td>0.5</td>
<td>0.01</td>
<td>3.06</td>
<td>0.06</td>
<td>3.57</td>
</tr>
</tbody>
</table>

FIG. 2. Variation of the (111)-dumbbell self-interstitial formation energy E^f with the linear dimension of the cubic supercell. In fixed cell data, the internal coordinates of the atoms are fully relaxed but the cell size and shape are fixed, whereas in variable cell data, both the internal coordinates and the size/shape of the cell are relaxed.
energy for dumbbell rotation should be 0.44 eV (see Table IV). This suggests that at a sufficiently high temperature, the dumbbell should exhibit three-dimensional diffusion.

B. Monovacancy

Unlike the self-interstitial, a monovacancy creates relatively small simple (i.e., centro symmetric) distortion. A $3 \times 3 \times 3$ supercell is sufficient to study the isolated monovacancy when relaxing both internal coordinates and supercell size/shape. We used 4 $k$ points in the irreducible BZ wedge. Earlier studies on vacancies in tantalum$^{38}$ and tungsten$^{39}$ suggest that this is sufficient to obtain adequate convergence for the formation energy. The vacancy formation energy $E_V$ can be computed as

$$E_V = E_{tot}(N-1) - \frac{N-1}{N}E_{tot}(N),$$

(5)

where $E_{tot}(N-1)$ and $E_{tot}(N)$ are the total energies of the system with and without a vacancy, respectively. Our calculated formation energy is 2.6 eV of which 0.07 eV comes from the volume relaxation. This is within the error bar of the experimentally determined vacancy formation energy, 2.2±0.4 eV.$^{40}$ By assuming that the transition state is midway between two nearest neighbor atom positions along the $\langle 111 \rangle$ direction, we estimate the monovacancy migration energy as 0.33 eV, which is close to the estimated experimental value of 0.5 eV.$^{40}$

IV. INTERATOMIC POTENTIALS

A. Fitting method

A surprising result of the first-principles calculations is that the self-interstitial formation energy is much smaller than previously predicted on the basis of atomistic simulations using EAM/FS potentials (cf. Tables I and IV). These potentials modeled the nearest neighbor approach using the high pressure data from electronic structure calculations$^{19}$ or from the “universal equation of state.”$^{41}$ Such input data correspond to purely hydrostatic deformation (i.e., one that equally compresses all eight bonds around each atom), while deformation along a $\langle 111 \rangle$ dumbbell is more closely uniaxial (i.e., corresponding to compressing only two opposing bonds). The implication is that it is more than eight times harder to compress eight neighboring atom bonds together than it is to compress two. This can, in turn, be traced to a fundamental misconception in fitting empirical potentials, namely, that the short range repulsion is due to pairwise overlap of core electrons. This can be clearly seen in the predictions of pseudopotential calculations which specifically exclude this effect, and show that the energy cost of compression arises primarily from the increased kinetic energy of the electrons. This observation does not, of course, invalidate previous potentials. Rather, it is essentially a transfer problem, and merely indicates that we should not expect a potential fitted to high pressure data to perform well in applications involving the close approach of atoms without hydrostatic compression of the lattice. In EAM/FS formalism, this suggests that some of the resistance to compression is intrinsically many body, and so for the study of defect fitting should be done to interstitial energy rather than to high pressure data.

For this work, we parameterized a potential for vanadium following FS formalism of the second-moment approximation to tight-binding theory, which is valid for $d$-band transition metals where charge transfer is unimportant.$^{42}$ The basic equation for the energy of an atom $(i)$ is given by$^{43}$

$$E_i = \sum_j V(r_{ij}) - \rho_i^{1/2},$$

(6)

where

$$\rho_i = \sum_j \phi(r_{ij}).$$

(7)

We use a cubic spline representation of the functions $V(r_{ij})$ and $\phi(r_{ij})$ given by

$$V(r) = \sum_{k=1}^6 a_k(r_k - r)^3 H(r_k - r),$$

(8)

$$\phi(r) = \sum_{k=1}^2 A_k(R_k - r)^3 H(R_k - r),$$

(9)

where $r_k$ and $R_k$ are knot points such that $r_1 > r_2 > r_3 > r_4 > r_5 > r_6$ and $R_1 > R_2$. $H(x)$ is the Heaviside step function; $H(x) = 0$ for $x<0$ and $H(x) = 1$ for $x>0$. We fit six parameters (the $r_k$ and $R_k$ are fixed) exactly$^{44}$ to reproduce the three cubic elastic constants, the cohesive energy, the lattice parameter and the unrelaxed vacancy formation energy of vanadium. These quantities are summarized in Table VI.

The fit to the vacancy formation energy was made for the energy of an unrelaxed vacancy using a Taylor expansion for the many-body part (E$_V^{\text{fs}}$), and subtracted from the cohesive energy. Assuming the range extends to second neighbors [$x_1 = (\sqrt{3}/2)a_0$; $x_2 = a_0$] this has an analytic form of

$$E_{\text{coh}} - E_{V} = 14 \sqrt{8} \phi(x_1) + 6 \phi(x_2) - 8 \sqrt{7} \phi(x_1) + 6 \phi(x_2) - 6 \sqrt{8} \phi(x_1) + 5 \phi(x_2),$$

(10)

$$\approx \frac{1}{2} \sqrt{8} \phi(x_1) + 6 \phi(x_2).$$

(11)
Only after the potential has been constructed is it possible to fully relax the vacancy. With previous vanadium potentials\textsuperscript{19} the relaxation energy has been about 0.25 eV. We assumed a similar value would apply here, so we set $E_V^f = E_V^r + 0.25$ eV for fitting, taking $E_V^r = 2.6$ eV from the first-principles data. We take the value of $E_{\text{coh}}$ from the caloricometric data.\textsuperscript{46} The Cauchy pressure $C_{12} - C_{44}$ also depends on the many-body term only, and with $E_{\text{coh}} - E_V^r$ it provides a set of two linear equations for $A_1$ and $A_2$. The equilibrium value of $\rho$ is fully determined by the difference between $E_V^{r,a}$ and $E_{\text{coh}}$: $\rho_0 = 2(E_{\text{coh}} - E_V^{r,a})^2$. This is true for any EAM model when the “squared” operator is replaced by the inverse of the embedding operator. Once $A_1$ and $A_2$ are fit, the other quantities have a linear dependence on $a_1$.

With six constraints satisfied exactly, the problem is reduced to determining the two remaining free parameters, which we took to be the value of the “effective” potential $\left(V(r_{ij}) - \phi(R_{ij})/\sqrt{\rho_0}\right)$ at the nearest neighbor separation and the value of $a_6$. These were adjusted to give the best fit to the difference in energy between bcc and face-centered-cubic (fcc) structures,\textsuperscript{47} correct ordering of the interstitial formation energy, the relaxation energy of the vacancy and the high pressure equation of state. The relaxation energy of the interstitials is much larger than that for the vacancy and, in the case of dumbbells, the “unrelaxed” state cannot be uniquely defined because the dumbbell separation is arbitrary. Similarly, the lattice parameter of the fcc phase was not fitted because it is not possible to express the fcc formation energy analytically.

The fact that a reasonable fit to all these data can be obtained with two parameters indicates that fitting the first six quantities captures much of the physics of vanadium. A similar result was obtained for iron.\textsuperscript{48} The fitted coefficients are compiled in Table VII.

### B. Point defect properties

The properties of the relaxed point defects were determined by minimizing the total energy with respect to all atomic coordinates using a conjugate-gradient method. Periodic boundary conditions were employed and the simulation cell size was varied to ensure that the formation energies were independent of the cell size to the desired accuracy (0.01 eV). The convergence of $E_f^f$ with the simulation cell size using this potential is shown in Fig. 3. The variable cell $E_f^f$ converges to the asymptotic value from below, while that for the fixed cell converges from above, as observed in the first-principles results in Fig. 2. The saturation of the formation energy occurs at a slightly larger supercell than that for the corresponding first-principles calculation.

Table VIII shows the resultant point defect formation energies in vanadium. Excellent agreement between the formation energies using the present potentials and first-principles results was obtained in all cases (i.e., within 5% or 0.18 eV). As in the first-principles results, the (111) dumbbell and (111) crowdion are degenerate in energy and represent the most stable self-interstitial configurations. This result is in contrast with that obtained using other EAM/FS interatomic potentials (shown in Table I), which show a variety of stable self-interstitial configurations. As for the first-principles results, the self-interstitial formation energies determined here are approximately 1 eV lower in energy compared with predictions made using other potentials. For additional comparison, the distance between two atoms that compose a dumbbell is reported in Table IX for high-symmetry self-interstitials. The agreement is within 5% and it is even better when data are scaled by the lattice parameter in each theoretical approach.

Perhaps a more sensitive test of the quality of the interatomic potential is its ability to predict kinetic parameters, such as the activation energies for point defect migration. The activation energies for vacancy migration determined from the present potential, from first-principles calculations, and estimated from experimental data\textsuperscript{42} are 0.42, 0.33, and 0.5 eV, respectively. The activation energies for (111)-dumbbell self-diffusion determined using this potential and first-principles are 0.04 and 0.01 eV, respectively, while the experimental value is less than 0.01 eV (Ref. 39) (recall in Sec. III A that the first-principles results are not accurate for energies smaller than approximately 0.05 eV). Three-dimensional diffusion requires rotation of the (111) dumbbell from one (111) direction to another. The activation energy for such a rotation is 0.41 and 0.34 eV based upon the potential and first-principles calculations. In all of these cases, the agreement is very good, especially given the limits of accuracy of the first-principles calculations and the uncer-

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**Table VI.** Data used to fit the vanadium potential. The elastic moduli are from compilation by Simmons and Wang (Ref. 45), and the relaxed vacancy formation energy and the cohesive energy are from the present first-principles calculations.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>$a$ (Å)</th>
<th>$E_{\text{coh}}$ (eV)</th>
<th>$C_{11}$ (eV/Å$^2$)</th>
<th>$C_{12}$ (eV/Å$^3$)</th>
<th>$C_{44}$ (eV/Å$^3$)</th>
<th>$E_V^f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>3.03</td>
<td>5.3</td>
<td>1.42</td>
<td>0.743</td>
<td>0.269</td>
<td>2.85</td>
</tr>
</tbody>
</table>

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**Table VII.** Fitted coefficients for the present vanadium potential [Eqs. (8) and (9)]. $r_1$ and $R_4$ are in units of the bcc lattice parameter ($a_0$) while coefficients $a_1$ and $A_1$ are in eV/$a_0^6$ and eV$^2/a_0^{12}$, respectively. In order to simulate primary knock-on events, modification of the short range potential to, e.g., the Biersack form (Refs. 48 and 50) is used.

<table>
<thead>
<tr>
<th>$r_1$</th>
<th>$1.300 000$</th>
<th>$a_1$</th>
<th>$-71.861 297$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_2$</td>
<td>$1.220 000$</td>
<td>$a_2$</td>
<td>$221.019 869$</td>
</tr>
<tr>
<td>$r_3$</td>
<td>$1.150 000$</td>
<td>$a_3$</td>
<td>$-203.133 261$</td>
</tr>
<tr>
<td>$r_4$</td>
<td>$1.060 000$</td>
<td>$a_4$</td>
<td>$118.249 184$</td>
</tr>
<tr>
<td>$r_5$</td>
<td>$0.950 000$</td>
<td>$a_5$</td>
<td>$-93.678 070$</td>
</tr>
<tr>
<td>$r_6$</td>
<td>$0.866 025$</td>
<td>$a_6$</td>
<td>$141.643 266$</td>
</tr>
<tr>
<td>$R_1$</td>
<td>$1.300 000$</td>
<td>$A_1$</td>
<td>$26.834 293$</td>
</tr>
<tr>
<td>$R_2$</td>
<td>$1.200 000$</td>
<td>$A_2$</td>
<td>$6.118 468$</td>
</tr>
</tbody>
</table>
tainty in the experimental data. Preliminary displacement cascade simulations performed using the present interatomic potential in a molecular dynamics (MD) simulation have shown that the vast majority of the point defects generated were vacancies and (111)-dumbbell self-interstitials. This is consistent with the predictions made above based upon static relaxation using the potential (and first principles). Additional MD simulations show the transition from one-dimensional (111)-dumbbell diffusion at low temperature to three-dimensional (111)-dumbbell diffusion at high temperature. These MD simulations further demonstrate that the present potential yields reasonable high temperature properties.

C. Phonon spectrum

We have calculated the phonon spectrum that corresponds to the present potential. We use the second derivative of the potential to evaluate force constants and dynamical matrices. The many-body form of the potential introduces several extra terms into the force constants which extend their effective range to double that of the potential. In principle, this could be used to fit the phonon spectrum, but here no information about the phonons was included in the fitting process so the dispersion relation provides a severe test, although for use in radiation-damage simulations pre-considered high formation energies. Some of this can be attributed to thermal effects, and the underestimate seems to be typical of other similar potentials.

V. CONCLUSIONS

Modern multiscale modeling of radiation-damage phenomena relates atomic scale molecular dynamics simulation of cascades to point defect production and migration which, in turn, feeds into kinetic Monte Carlo and rate equation modeling of the temporal evolution of point defect distribu-

<table>
<thead>
<tr>
<th>Defect Type</th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First principles</td>
<td>2.60</td>
<td>3.57</td>
<td>3.48</td>
</tr>
<tr>
<td>FS (present)</td>
<td>2.63</td>
<td>3.60</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Unstable configuration; decays to a (100) dumbbell.
from one orientation to another occur, giving rise to three-dimensional diffusion.

The present FS type of potential was fit exactly to the experimental values of the equilibrium lattice parameter, cohesive energy, and three elastic constants and an estimated unrelaxed vacancy formation energy and two parameters were used to obtain the best fit to the set of interstitial formation energies determined from the first-principles calculations. The potential was modified at very short ranges to attain adhesion energy, and three elastic constants and an estimated experimental values of the equilibrium lattice parameter, co-dimensionnal diffusion.

FIG. 4. Phonon spectrum along the high-symmetry axis calculated with the structures. Further, the of the first-principles calculations at Princeton. One of the authors

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30 If the WENGT code was used with the GGA functional.
36 S. Dudarev (unpublished results).
46 The present GGA computation gives 5.72 eV as the cohesive energy of the bcc vanadium crystal.
47 The first-principles value of 0.243 eV/atom is used.