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Structure-Factor Approach to Migration Energy of Interstitials*

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Many lattice defects migrate by processes which involve cooperative motion of a number of interacting atoms on a nearly equal basis, e.g., interstitialcies, crowdions, and dislocations. In particular, migration of the interstitialcy involves only small atomic displacements and electronic redistribution, so it seems likely that its motion energy will be sensitive to the structural configuration around the defect. For this reason, we have applied the pseudopotential formulation of Harrison, which directly includes the effects of structure, to an investigation of interstitial energy differences. Our application has been to the energy difference between body-centered and [100] split interstitials in fcc metals. The numerical results compare reasonably well with earlier calculations employing different force laws, the energy difference in Al being 0.3–0.4 eV.

I. INTRODUCTION

Because of strong interest in the motion energies for lattice defects, particularly interstitialcies and dislocations, there have been several calculations of the energies of various configurations using two-body potentials.[1–5] While the motion of vacancy defects usually involves considerable shifting of the defect's near neighbors and appreciable electron density redistribution, the motion of interstitialcies is accomplished with only small displacements of several atoms and slight alteration of the electron distribution. It seems probable that the motion energy for the latter defects might depend rather sensitively on the exact structural disposition of the atoms. The technique developed by Harrison[6] for calculating energies and elastic constants of arbitrary crystal structure explicitly involves a term which depends on this distribution through the square of the structure factor of the configuration. We were consequently motivated to apply the Harrison procedure to the interstitial configurations. In addition to the direct dependence on structure, the method has the added advantage that it corresponds to a more sophisticated two-body potential than had been used earlier in that it incorporates the Friedel oscillations which have been shown to be effective in several contexts.

II. STRUCTURE-FACTOR APPROACH TO ENERGY OF A METAL

We give here a simplified outline of the structure-factor method based on a perturbation of free electrons. The full pseudopotential treatment of Harrison[6] starts from an expansion of electronic wave functions in orthogonalized plane waves (OPW); other complications arise from the fact that the potential is nonlocal. We will not treat these here.

The basic assumption in this presentation is that the effective potential energy of an electron under the influence of all the ions and all the other electrons may be written as a superposition of local, rigid-ion potentials

$$V(\mathbf{r})=\sum_{i=1}^{N} w(\mathbf{r}-\mathbf{R}_i)\,, \tag{1}$$

where the potential $w(\mathbf{r}-\mathbf{R}_i)$ is due to the ion at $\mathbf{R}_i$; there are N ions in the metal. This effective potential $V(r)$ is generally small[7,8] and so a perturbation treatment is appropriate. The advantage of the present formulation is that matrix elements of $V(r)$ between plane waves normalized in the crystal volume Ω can be factored as shown in Eq. (2):

$$\begin{aligned}\langle k|V|k+q\rangle&=\frac{1}{\Omega}\int e^{-i\mathbf{k}\cdot\mathbf{r}}V(r)e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}d^3r\\&=S(q)\langle k|w|k+q\rangle\,.\end{aligned} \tag{2}$$

Here $S(q)$ is the structure factor familiar from diffraction theory and

$$\langle k|w|k+q\rangle=\frac{1}{\Omega_0}\int e^{-i\mathbf{k}\cdot\mathbf{r}}w(r)e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}}d^3r$$

is the Fourier transform of $w(r)$; Ω_0 is the volume per atom in the crystal. The importance of separating the structure from the matrix element will become obvious below.

The sum of the one-electron energy parameters can now be expressed by second-order perturbation theory as

$$\mathcal{E}_{\mathrm{el}}=\sum_{\mathbf{k},\sigma}\left(\mathcal{E}_k^0+\langle k|V|k\rangle+\sum_q{}'\frac{|\langle k|V|k+q\rangle|^2}{\mathcal{E}_k^0-\mathcal{E}_{k+q}^0}\right). \tag{3}$$

The first summation is over wave and spin quantum

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numbers, and the second is over all plane-wave numbers of the crystal, other than zero. In this expression $\mathcal{E}_k{}^0$ is the kinetic energy $\hbar^2k^2/2m$. The total electronic kinetic energy is $\frac{3}{5}ZN\mathcal{E}_F$, with $\mathcal{E}_F$ the Fermi energy. This term and the next may be lumped together to give an energy contribution dependent only on volume (later we subtract from this half the electron-electron interaction energy which has been counted twice in $\mathcal{E}_{\mathrm{el}}$). The resulting energy term is called the "free-electron energy." In the second-order term, we factor the matrix elements and interchange the order of the two summations:

$$\mathcal{E}_{\mathrm{el}}=\mathcal{E}_{\mathrm{fe}}+ZN\sum_q{}' S^*(q)S(q)E(q). \tag{4}$$

In Eq. (4), $E(q)$ is called the energy–wave-number characteristic function and has dimensions of energy per electron. It is defined as shown in Eq. (5):

$$E(q)=\frac{1}{ZN}\sum_{k,\sigma}\frac{|\langle k|w|k+q\rangle|^2}{\mathcal{E}_k{}^0-\mathcal{E}_{k+q}{}^0}. \tag{5}$$

For a local potential $w(r)$, $E(q)$ can be evaluated analytically as

$$E(q)=-(\Omega_0q^2/8\pi Ze^2)|\langle k|w|k+q\rangle|^2[\epsilon(q)-1]/\epsilon(q), \tag{6}$$

where $\epsilon(q)$ is the Hartree dielectric screening function. Harrison has carried out the evaluation of $E(q)$ with nonlocal pseudopotentials for aluminum, magnesium, and sodium. The second-order term is called the "band-structure energy" $\mathcal{E}_{\mathrm{bs}}$.

In addition to $\mathcal{E}_{\mathrm{el}}$, the energy of interaction of the ions among themselves must be included. Because of the electron-electron term previously passed over, it is appropriate[9] to evaluate the ion-ion energy as that of a lattice immersed in a compensating background of negative charge. In the full pseudopotential treatment this energy is combined with terms arising in $\mathcal{E}_{\mathrm{el}}$ due to using a nonlocal potential and an OPW basis (terms which do not appear in our simplified treatment), and the resulting term is called the "electrostatic energy." $\mathcal{E}_{\mathrm{elec}}$ is the Coulomb energy of a lattice of ions, having a charge slightly larger[10] than the valence ($3.237e$ in Al), immersed in a uniform negative compensating background. The effective charge is determined by the constant part of the charge density associated with an OPW.

We now have the total energy in the form

$$\mathcal{E}_{\mathrm{total}}=\mathcal{E}_{\mathrm{fe}}+\mathcal{E}_{\mathrm{bs}}+\mathcal{E}_{\mathrm{elec}}. \tag{7}$$

III. EVALUATION OF INTERSTITIAL ENERGIES

In our application we want to compare the energies of two related defect configurations involving several atoms on a nearly equal basis. Although the more recent defect calculations have used an elastic-displacement function at large distances, the explicit evaluation of the structure factor in our method made it necessary to treat only a finite number of displaced atoms. With $\mathbf{r}_i'$ for the displaced positions of these atoms and $\mathbf{r}_i$ for their original locations, the structure factor can be written as a small number of terms:

$$NS(q)=\sum_i^N e^{-i\mathbf{q}\cdot\mathbf{r}_i'}=\sum_i^n(e^{-i\mathbf{q}\cdot\mathbf{r}_i'}-e^{-i\mathbf{q}\cdot\mathbf{r}_i})+e^{-i\mathbf{q}\cdot\mathbf{r}_d}+N\delta_{qK}. \tag{8}$$

Here n designates the number of atoms in the specimen that are displaced. The second term represents the lattice defect situated at $r=r_d$. The band-structure energy is now expressed as an integral plus a sum:

$$\begin{aligned}\mathcal{E}_{\mathrm{bs}}=\frac{z\Omega_0}{(2\pi)^3}\int E(q)\Big[\sum_{i,j}^n(e^{-i\mathbf{q}\cdot\mathbf{r}_i'}-e^{-i\mathbf{q}\cdot\mathbf{r}_i})(e^{i\mathbf{q}\cdot\mathbf{r}_j'}-e^{i\mathbf{q}\cdot\mathbf{r}_j})\\+2\sum\cos\mathbf{q}\cdot(\mathbf{r}_i'-\mathbf{r}_d)-\cos\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_d)+1\Big]d^3q\\+2z\sum_{\mathbf{K}}E(K)\Big[\sum_i(\cos\mathbf{K}\cdot\mathbf{r}_i'-\cos\mathbf{K}\cdot\mathbf{r}_i)+\cos\mathbf{K}\cdot\mathbf{r}_d\Big].\end{aligned} \tag{9}$$

In the final term the summation is over the reciprocal lattice vectors $\mathbf{K}$.

We have applied this procedure to a comparison of the "split interstitial" (SI) and cube-center interstitial (CC) in the face-centered cubic lattice. In each case the same number of displaced atoms was used ($n\sim 87$) and, since the outer atoms were held fixed, the volume was considered to be approximately the same for both defects. For our configuration we have chosen the displacements found by Johnson and Brown[2] using a Born-Mayer-type potential on the basis that the equilibrium positions for ions in a given configuration for a particular force law would be satisfactory for calculating the energy under another force law. The energy difference between these two configurations has been calculated for aluminum and the hypothetical fcc metals of magnesium and sodium at their normal densities. The results for $E_{\mathrm{CC}}-E_{\mathrm{SI}}$ are given in eV in Table I and in each case the split-interstitial configuration is energetically favored. This energy difference between the interstitial configurations is an upper limit for the activation energy of interstitialcy motion. Most calculations show the [100] split interstitial to be at a real minimum, but the cube center is a local maximum rather than a saddle

TABLE I. Results for $E_{\mathrm{CC}}-E_{\mathrm{SI}}$ (eV).

	Aluminum	Magnesium	Sodium
Electrostatic energy	0.2711	0.1403	0.0288
Integral term	0.0326	0.0099	0.0038
Discrete sum term	−0.1285	−0.0441	−0.0129
Total	0.175	0.106	0.020

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[9] For complete details on how the various terms in the total energy are combined see Sec. 8-6 of Ref. 6.

[10] See p. 40 of Ref. 6.

point. Usually the motion energy is about half the energy difference $\mathcal{E}_{\rm CC}-\mathcal{E}_{\rm SI}$ on the basis of these models.

IV. SENSITIVITY TO CHOICE OF IONIC DISPLACEMENTS

As mentioned above, these results were obtained by using the set of displacements found by Brown and Johnson with a Born-Mayer potential in an fcc lattice. We wanted to explore how sensitive the results were to the choice of ion displacements and repeated the calculations with two other sets (1) from fcc-defect calculations by Cotterill and Doyama[4] using a Morse potential and (2) from calculations by Johnson[3] using a special potential. Comparison of the results with these displacements indicated the error of neglecting the volume-dependent terms in Eq. (3). The different sets of displacements corresponded to different defect volumes, i.e., different magnitudes of radial displacements in the elastic region, and our device of setting the displacements equal to zero in this region had a very negligible effect in stabilizing the volume. It turned out that the volume dependence of the first term in Eq. (7) had to be -1.58, -0.616, and -0.1259 Ry/Ω_0 for aluminum, magnesium, and sodium, respectively, to equilibrate our model at the chosen lattice constant, and a positive pressure P of this magnitude was invoked accordingly. The resulting $P\Delta V$ term made the energies associated with the various displacements more reasonably comparable. The various ΔV's were determined by examining the displacements in a region far from the defect. The uncertainty in the ΔV so determined, coupled with the large value for P, unfortunately increased the over-all uncertainty of the calculations quite considerably.

In Table II we give a comparison of $E_{\rm CC}-E_{\rm SI}$ in eV for the three sets of displacements. Considering the uncertainty in the final term our internal consistency is better than could be expected.

For intercomparison between the results with the different displacements (to determine which gave the minimum energy values for our energy model) and to cross check with prior calculations, we made an approximate absolute energy determination for the complete defect configuration in aluminum. First we added to the electrostatic and band-structure terms the energy to take three valence electrons and an ion from the surface (sublimation plus ionization energies) which was approximated by $\frac{1}{2}\alpha(Z^*e)^2/r_0=70.75$ eV, where r_0 is the shortest interatomic distance and α is the appropriate Madelung constant. As the ion and its electrons were inserted at the interstitial site, it was necessary to bring in the free-electron energy as calculated by Harrison for the electrons, 46.96 eV. Finally, we must add the energy done against the stabilizing pressure which was, for the CC case, 9.89 eV for the Johnson-Brown displacements, 1.59 eV for the Johnson displacements, and 0.159 eV for the Doyama and Cotterill displacements. After these additions all results fell between 3.2 and 5.2 eV. These results have been displayed for both configurations and all three displacement choices on the left half of Fig. 1. On the right half are shown the corresponding numbers from earlier calculations. One notes that the new values lie in the same range as found by other investigators mostly for copper, even though they result from the close cancellation of much larger numbers. Perhaps, for purposes of comparison, the values for aluminum should be scaled down in proportion to the melting-temperature ratio of aluminum to copper. Also it appears that the Johnson displacements come closest to minimizing the energy according to this model.

TABLE II. $E_{\rm CC}-E_{\rm SI}$ (eV) for three sets of displacements.

	Johnson and Brown[a]	Cotterill and Doyama[b]	Johnson[c]
Electrostatic energy	0.271	0.069	0.413
Integral term	0.032	0.122	0.244
Discrete sum term	−0.14	−0.18	−0.09
$P\Delta V$ term	0.21	0.43	−0.21
Total	0.39	0.44	0.35

[a] Reference 2. [b] Reference 4. [c] Reference 3.

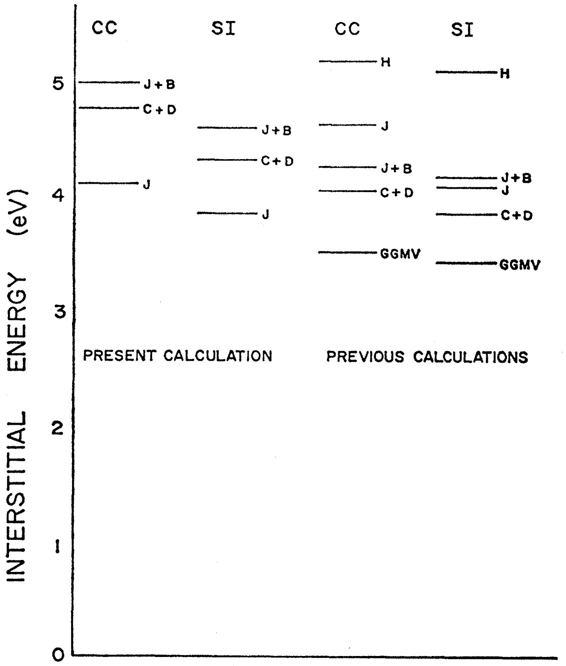

FIG. 1. Comparison of results with previous calculations. Initials on the left side of the figure refer to the source of displacements used in calculating the configurational energy. Those on the right side identify the previous calculations; H: Huntington (Ref. 1); J+B: Johnson and Brown (Ref. 2); J: Johnson (Ref. 3); C+D: Cotterill and Doyama (Ref. 4); and GGMV: Gibson *et al.* (Ref. 5).

Finally, we present in Table III the values for $E_{\rm CC}-E_{\rm SI}$ for the three pseudopotentials using in each case the Johnson and Brown displacements and taking into account the $P\Delta V$ term.

V. DISCUSSION

The application of the pseudopotential technique to the calculation of the energy difference between two configurations of the interstitialcy has given consistent results in essential agreement with corresponding earlier calculations. The configurational energies were obtained via the characteristic energy functions $E(q)$ rather than through the equivalent two-body potentials. (Actually little work has been done with such potentials, which show the characteristic Friedel oscillations.)

On the other hand, the method has proved less promising for these defect problems than was anticipated. The accuracy has been impaired by the close cancellation between large numbers and by the uncertainties in ΔV for the $P\Delta V$ terms. It had also been hoped that the display of the various structure factors against q might yield some insight as to the essential differences, energywise, between the different configurations, but the pattern proved too complex to be directly useful. For these reasons, we do not anticipate extensive application of this technique to problems of this kind.

TABLE III. $E_{\mathrm{CC}}-E_{\mathrm{SI}}$ for three pseudopotentials.

	Aluminum	Magnesium	Sodium
$E_{\mathrm{CC}}-E_{\mathrm{SI}}$ (Table I)	0.175	0.106	0.020
$P\Delta V$ term	0.2	0.08	0.02
$E_{\mathrm{CC}}-E_{\mathrm{SI}}$ (final)	0.38	0.19	0.04

On the other hand, with the availability of more accurate pseudopotentials, useful results should be obtainable for problems where the change in volume is not too critical. For example, the structure-factor method should prove particularly valuable in treating the scattering from complex defect configurations that have up to now been passed over.

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Limitation of the Phonon Heat Conductivity by Edge-Dislocation Dipoles, Single Dislocations, and Normal Processes

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The scattering of phonons by edge-dislocation dipoles leads to deviations from the quadratic temperature dependence of the lattice thermal conductivity found when the latter is limited by the interaction of phonons with isolated dislocations. At temperatures where the dominant wavelength λ_d of the phonons is large compared with the distance R between the two dislocations of a dipole, it is found that the conductivity is almost independent of the absolute temperature T and larger than the corresponding value for isolated dislocations. With increasing temperature ($R\gg\lambda_d$), the thermal conductivity due to dipoles approaches asymptotically the conductivity limited by isolated dislocations. The interaction of the phonons with the dipoles is treated by nonlinear continuum theory which includes also the normal three-phonon interaction. Numerical results, obtained with the material constants of copper, show that dipoles with distances R smaller than $|\mathbf{b}|(370°\mathrm{K}/T)$ ($\mathbf{b}$=Burgers vector) can be distinguished from isolated dislocations by measuring the thermal conductivity.

1. INTRODUCTION

ANY deviation from the periodic arrangement of the atoms in a crystal and from the harmonicity of the forces binding them to their equilibrium positions causes scattering of phonons. The probability that a phonon will be scattered by a defect depends on its wavelength. It also depends on the kind of the defect, i.e., phonons with large wavelengths are more effectively scattered by extended defects than by defects that distort the lattice only in a small spatial region of the lattice. Klemens[1] was the first one who investigated the

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