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POINT DEFECT CALCULATIONS IN TUNGSTEN

by Ronald L. Danilowicz

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ABSTRACT

Calculations were made with a computer code developed for making point-defect calculations in body-centered-cubic metals. A semi-empirical cubic potential based on experimental data was also developed for tungsten for these calculations. The vacancy migration energy for tungsten was calculated. The calculated value of 1.73 electron volts, together with experimental data, suggests that vacancies migrate in stage III recovery in tungsten. The formation energies for six possible equilibrium interstitial configurations were also calculated. The ⟨110⟩ split interstitial was the most stable configuration for tungsten with a formation energy of 9.73 electron volts.

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SUMMARY

Calculations were made with a computer code developed for making point-defect calculations in body-centered-cubic metals. A semi-empirical cubic potential based on experimental data was also developed for tungsten for these calculations. The vacancy migration energy for tungsten was calculated. The calculated value of 1.73 electron volts, together with experimental data, suggests that vacancies migrate in stage III recovery in tungsten, the formation energies for six possible equilibrium interstitial configuration were also calculated. The ⟨110⟩ split interstitial was the most stable configuration for tungsten with a formation energy of 9.73 electron volts.

INTRODUCTION

All real crystal lattices contain a variety of imperfections. Some of these, such as impurity atoms, dislocations, etc., are produced during the preparation and handling of the crystals. Structural point defects and clusters of these point defects, on the other hand, are necessary at any finite temperature to keep the crystal in thermal equilibrium. There are two basic types of structural point defects, hereinafter simply referred to as point defects: one is a vacancy or vacant lattice site, and the other is an interstitial or an atom in a nonlattice site.

The mechanical and physical properties of a material are very sensitive to point defects. The reliability of nuclear reactors depends partially on the strength of the materials with which they are composed. Radiation damage primarily produces point defects that have a pronounced effect on the strength of the reactor materials. A thorough understanding of the properties of these point defects for any particular material is essential for studying the more complex problem of how radiation damage affects certain properties, like strength, of the material.

In an effort to develop analytical tools for the study of point defects, an analytical program was undertaken to study the properties of point defects in tungsten. Tungsten

was chosen because of its potential application as a high-temperature reactor material.

A computer program was written to calculate the formation and migration energies of point defects and clusters of point defects in body-centered-cubic metals. Only results of point-defect calculations are discussed herein. The computer has often been applied to the study of point defects in metals (refs. 1 to 11). In the present study, an approach similar to those of Anderman (ref. 6) and Domingos (ref. 7) is used where the strain field associated with a defect is allowed to propagate freely through the lattice. For the interaction between tungsten atoms, a cubic potential was developed for this investigation similar to that first used by Johnson (ref. 2) for α-iron. After Johnson's original work, Anderman has used cubic potentials for copper, and Johnson (ref. 3) for tungsten as an extension of his α iron work. For tungsten, Johnson calculated a vacancy formation energy of 4.96 electron volts. He also calculated that the $\langle 110 \rangle$ split interstitial is the most stable tungsten interstitial configuration with a formation energy 9.77 electron volts. Johnson's value for the vacancy formation energy does not agree with the experimental value of 3.14 electron volts obtained by Kraftmakher and Strelkov (ref. 12). Therefore, he has suggested (refs. 3 and 13) that, when possible, the cubic potentials generated for a particular metal should be chosen so that the computer calculations yield the experimental value for the vacancy formation energy. This approach has been adopted in the present study to generate a new tungsten potential which, in turn, was used to calculate the vacancy migration energy and the most stable interstitial and its formation energy.

CALCULATIONAL TECHNIQUES

In general, a computer program to study properties of point-defect configurations usually operates in the following manner. The point defect of interest is introduced into a perfect lattice. Because of the point defect, the surrounding atoms will experience nonzero forces so that the lattice must be relaxed into its new equilibrium state. Formation energies and migration energies of point defects are determined by comparing the potential energy of a perfect lattice with that of the appropriate relaxed lattice. For the interaction between atoms, it is usually assumed that the many-body interaction of a large number of mutually interacting atoms can be closely approximated by a set of independent two-body central-force interactions.

There are several different techniques available for solving the individual problems associated with writing a computer program as described previously. Some of the major problems are generating a short-range interatomic potential, cataloging the particles for easy access, finding a systematic approach for relaxing the lattice, and developing

the convergence criteria. The following describes some of the techniques used for this study.

To keep computing time within reasonable limits, a short-range potential that goes to zero between the second and thirs nearest neighbor distances is used with this program. At least second nearest neighbor separations must be included because a body-centered-cubic lattice is unstable when only first nearest neighbor interactions are considered. The interatomic potential for tungsten used in this study will be described in detail in the next section.

To determine the potential of a single atom and the force acting on it, it is essential to know the position coordinates of every atom that interacts with it. This could be done by searching through all the atoms in the lattice to find the ones close enough to interact with a particular atom. This is a very time-consuming technique, particularly for large lattices. Therefore, the following technique was adopted.

All atoms were located in boxes with the dimensions 2 by 2 by 2, where a unit of length is equal to one-half the lattice constant. Each box has a unique identification number associated with it, which depends on the coordinates within the box. These identification numbers are also subscripts of an array, IBOX, in the computer program. Any atoms with position coordinates that give a particular box identification number, for example, I, have their identification numbers, for example, J and K, stored in the IBOX location with subscript I. The boxes were set up so that, for the interior of a perfect body-centered-cubic lattice, there would be two atoms per box at the locations $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$ and $\left(1\frac{1}{2}, 1\frac{1}{2}, 1\frac{1}{2}\right)$ with respect to the corner of a box. Thus, there would be identification numbers of two atoms stored in each IBOX location for the perfect lattice.

All the atoms that interact with atom J in box I can now be found by searching only the 3 by 3 by 3 cube of boxes centered around box I. There is a unique set of increments, INCR(1) to INCR(27) in the program, which is independent of position in the lattice, that can be added to I to get the identification numbers of the surrounding boxes.

For the relaxations expected for the vacancy, it could be seen that, throughout the relaxation process, the atoms would remain in their original boxes. Thus, there is no need for more than two atoms in a box except when interstitials are being studied. When this is the case, the interstitial identification numbers are stored in the JBOX array. A negative value in the IBOX array is used as a signal to search the JBOX array for additional atoms.

To actually achieve the relaxation of the lattice into its new equilibrium state, a method for propagating the strain field associated with a group of point defects throughout the lattice is necessary. Initially due to the short-range interaction potential, only a small number of atoms near the point-defect configuration experience nonzero forces. These will all be within a 3 by 3 by 3 array of boxes centered about the point-defect configuration. The forces on all the atoms in these boxes are calculated along with the total potential energy of the crystal. The atoms are relaxed in the direction of and

proportional to the net force acting on them. This process is repeated until forces on atoms bordering the 3 by 3 by 3 array of boxes exceed a predetermined value. Then the group of atoms being relaxed is expanded to all atoms in a 5 by 5 by 5 array of boxes centered on the point-defect configuration. (The identification numbers of the boxes being considered are always determined from the identification number of the center box and values from the INCR array: the first 27 values for the 3 by 3 by 3 array, the first 125 values for the 5 by 5 by 5 array, etc.). This iterative process is repeated, occasionally expanding the volume of boxes being considered, until predetermined convergence criteria have been met. This was usually that the value of the total energy of the crystal on two successive iterations agreed within 0.001 electron volt. For this study, a 13 by 13 by 13 array of boxes was always sufficiently large for the convergence criteria to be met.

The output from the program included the total potential energy of the lattice for each iteration, the volume of boxes considered for that iteration, the total potential energy of the perfect lattice and the relaxed lattice, and the final position of all of the atoms in the relaxed lattice.

INTERATOMIC POTENTIAL

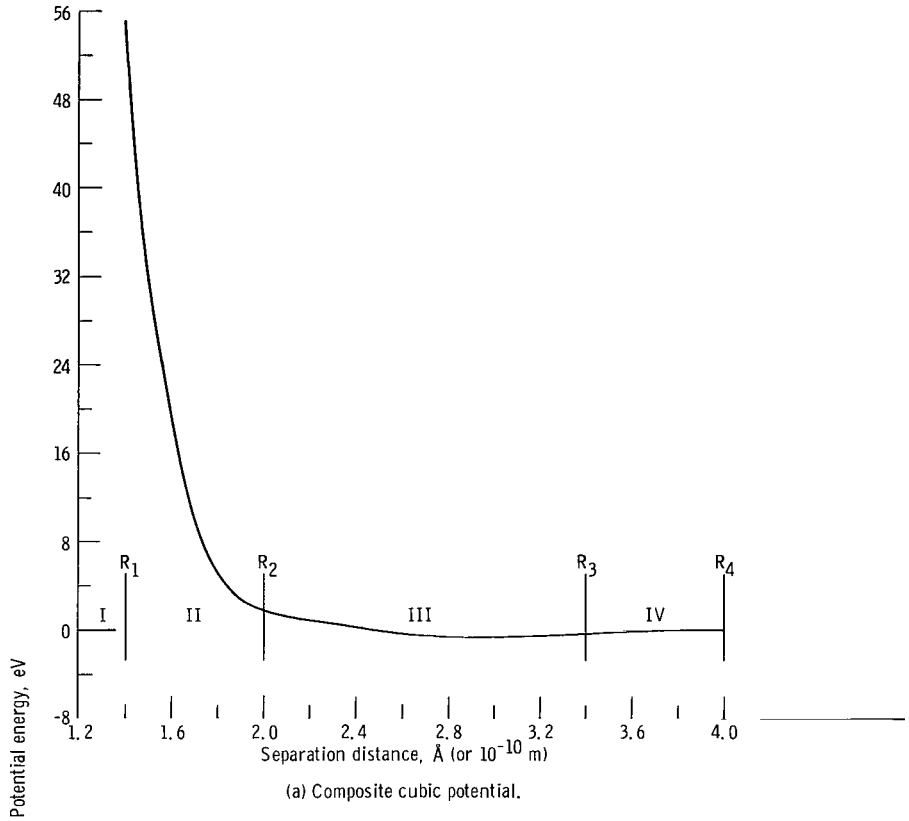
A composite cubic potential was used for these calculations based on experimental elastic constant data. Assuming that the elastic constants arise mainly from the short-range ionic interactions, the following equations from reference 2 can be used for determining the potential. These equations for a body-centered-cubic lattice, when second nearest neighbor interactions are assumed, are

$$\left(C_{11} - C_{12}\right)_{sr} = \frac{4}{r_2}\left(\frac{1}{r_1}\varphi_1' + \frac{1}{2}\varphi_2'' + \frac{1}{2r_2}\varphi_2'\right) \tag{1}$$

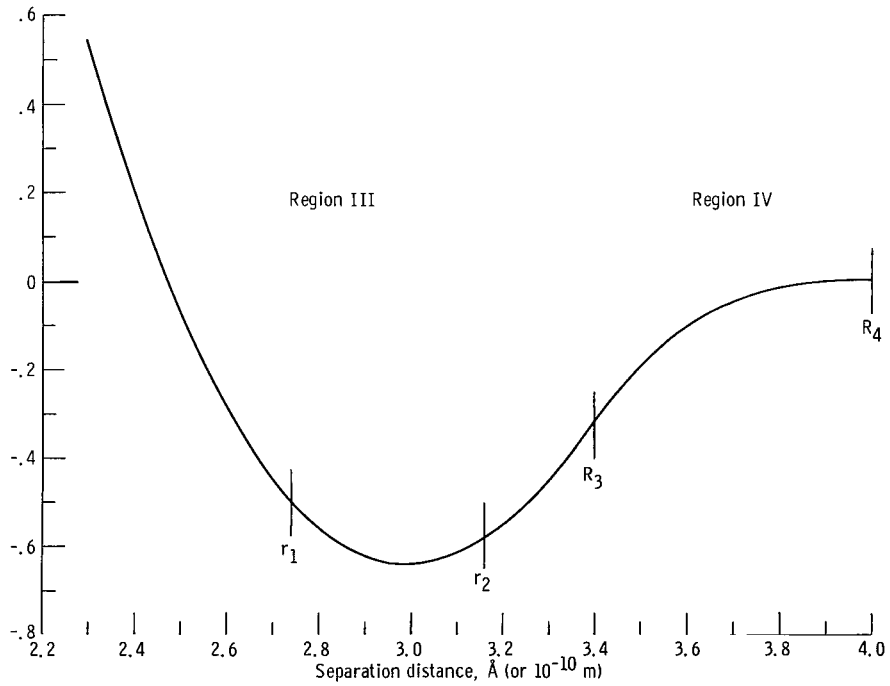
$$\left(C_{44}\right)_{sr} = \frac{2}{3r_2}\left(\varphi_1'' + \frac{2}{r_1}\varphi_1' + \frac{3}{r_2}\varphi_2'\right) \tag{2}$$

and

$$(B)_{sr} = \frac{2}{3r_2}\left(\varphi_1'' - \frac{2}{r_1}\varphi_1' + \varphi_2'' - \frac{2}{r_2}\varphi_2'\right) \tag{3}$$



(a) Composite cubic potential.



(b) Detail of regions III and IV.

Figure 1. - Interatomic potential for tungsten.

where r_1 and r_2 are the first and second nearest neighbor separations; φ_1', φ_1'', φ_2', and φ_2'' are first and second derivations of the potential at r_1 and r_2; C_{11}, C_{12}, and C_{44} are elastic constants; B is the bulk modulus; and the subscript sr means short range.

The long-range electronic contributions to the elastic constants, as pointed out in reference 13, are small and difficult to calculate and are, therefore, neglected herein. Thus, the short-range elastic constants are assumed to be equivalent to the total elastic constants. The values used for the elastic constants for tungsten were taken from reference 14. At 300 K the values are $C_{11} = 2.6091 \times 10^7$ newtons per square centimeter, $C_{12} = 1.5743 \times 10^7$ newtons per square centimeter, $C_{44} = 0.8182 \times 10^7$ newtons per square centimeter, and $B = 1.9192 \times 10^7$ newtons per square centimeter. The values used for r_1 and r_2 are $r_1 = \sqrt{3}\, r_2/2$ and $r_2 = 3.16$ Å (3.16×10^{-10} m).

The composite cubic potential (fig. 1) is made up of four separate regions. The potential for region III, which contains r_1 and r_2, was derived using equations (1) to (3). Because there are three equations in four unknowns, the potential in this region was determined to within an arbitrary constant. It was suggested by Johnson in reference 3 that, when possible, this arbitrary constant should be chosen to give agreement between the calculated and the experimental values of the vacancy formation energy. The constant, therefore, was chosen to match the experimental value of the vacancy formation energy (3.14 eV) obtained by Kraftmakher and Strelkov as reported in reference 12. This was accomplished by changing the constant until the computer program calculated 3.14 electron volts for the vacancy formation energy.

After determining the potential in region III, a cubic potential for region IV is determined by matching the value and slope of the potential in region III at R_3 and by having zero value and zero slope at R_4. The potential is cut off between the second and third nearest neighbors to reduce the number of calculations that are necessary. At close separations (region I) a Born-Mayer potential was used. This has the form, Ae^{-r/r_o}, where A and r_o are experimentally determined constants for different materials. Constants for tungsten, obtained from reference 15, were A = 33 000 electron volts and $r_o = 0.219$ Å. The cubic potential for region II, used to smoothly join regions I and III, is determined by matching the value and slope of the potential is region I and III at R_1 and R_2, respectively. The potential used for these calculations is given in table I.

The values for R_1, R_2, R_3, and R_4 were chosen to keep regions II and IV as small as possible while maintaining a smooth overall curve. Because regions I and III are based on experimental data, it was felt that they should make up as much of the interatomic potential curve as possible.

TABLE I. - COMPOSITE INTERATOMIC POTENTIAL

Region	Range, Å (or 10^{-10} m) (a)		Potential, eV (a)
I	$0 < r$	1.4	$33000.0\ e^{-r/0.219}$
II	$1.4 < r$	2.0	$-222.33434\ r^3 + 1339.4185\ r^2 - 2695.2541\ r + 1813.4138$
III	$2.0 < r$	3.4	$-0.46394017\ r^3 + 6.2929771\ r^2 - 25.196918\ r + 30.839$
IV	$3.4 < r$	4.0	$1.2347657\ r^3 - 14.960808\ r^2 + 60.417687\ r - 81.322972$

[a]Interatomic separation distance.

RESULTS AND DISCUSSION

Calculations were made for both vacancies and interstitials in tungsten. For the vacancy, the migration energy was calculated. For the interstitial, the stable configuration was determined by comparing the formation energies of six possible equilibrium interstitial configurations.

Vacancy

To verify the mechanics of the computer code, the vacancy formation energy in tungsten was calculated using the tungsten potential used by Johnson (ref. 3). Using this potential, a vacancy formation energy of 4.95 electron volts was calculated. This compared well with Johnson's value of 4.96 electron volts, even though different approaches were used.

The potential used for the rest of the calculations was then developed as outlined in the previous section. The vacancy migration energy was then calculated by placing an atom halfway between two nearest neighbor half-vacancies, which is the saddle point for vacancy migration. A value of 4.87 electron volts was calculated for the saddle-point energy. This gives a value of 1.73 electron volts for the vacancy migration energy, which is the difference between the saddle-point energy and the formation energy.

Assuming that self-diffusion is by vacancy migration, then 4.73 electron volts is also the calculated self-diffusion energy. This calculated value is lower than Danneberg's experimental value of 5.23±0.2 electron volts (ref. 12) and the value, 6.66 electron volts, measured by Krieder and also Andelin, Knight, and Kahn (ref. 16). The calculated value, however, does support the lower experimental value for the self-diffusion energy.

TABLE II. - EXPERIMENTAL STAGE III

ACTIVATION ENERGIES IN TUNGSTEN

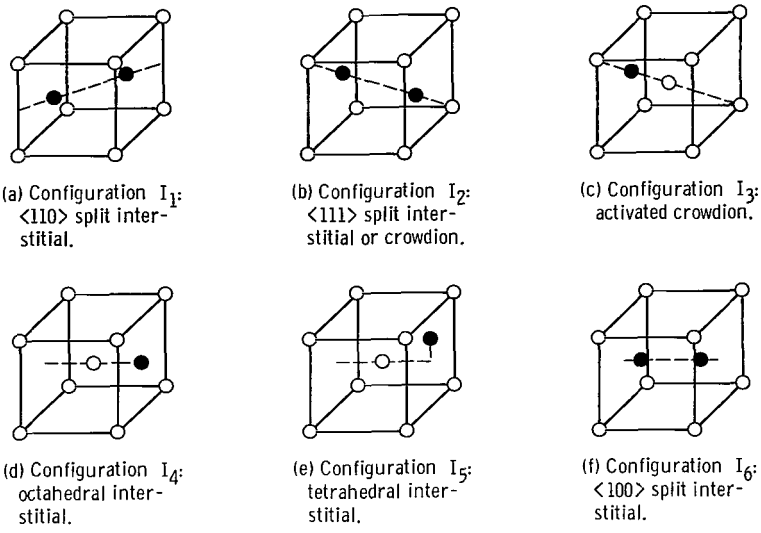
Investigator (a)	Stage III activation energy in tungsten, eV
Kinchin and Thompson	1.7
Johnson	1.7
Niemark and Swalin	1.7±0.1
Koo	1.7±0.1

[a]Data reported in ref. 17.

The calculated vacancy migration energy of 1.73 electron volts agrees well with experimental activation energies measured for stage III (0.15 T_m, the melting temperature) recovery in tungsten. These are presented in table II (ref. 17). These investigators all believe that stage III recovery is due to vacancy migration. There are investigators who disagree. Among these are Jeannotte (ref. 16) who feels that vacancies migrate in stage V recovery for tungsten with a migration energy of 3.3 electron volts. He uses the higher experimental value of 6.66 electron volts for the self-diffusion energy as support for his argument. Adding the vacancy formation energy of 3.14 electron volts to his vacancy migration energy, gives 6.44 electron volts which gives reasonable agreement with the 6.66-electron volt value. However, the calculated results from this study support those who believe that vacancy migration is responsible for stage III recovery in tungsten.

Interstitial

There are six equilibrium interstitial configurations that were considered. These configurations will be referred to as I_1, I_2, I_3, I_4, I_5, and I_6 and are shown in figure 2. Configuration I_1 is the ⟨110⟩ split interstitial and was found to be the most stable configuration in tungsten with a formation energy of 9.73 electron volts. Configuration I_2 is the ⟨111⟩ split interstitial, or crowdion. Configuration I_3 is the activated crowdion, and I_4 is the octahedral interstitial. Configuration I_5 is the tetrahedral interstitial and is halfway between two octahedral interstitial sites. Configuration I_6 is the ⟨100⟩ split interstitial. The formation energy and the energy above the ⟨110⟩ split interstitial formation energy for each configuration are shown in table III. Johnson (ref. 3) has also calculated that the ⟨110⟩ split interstitial is the stable interstitial con-



(a) Configuration I_1: <110> split interstitial.

(b) Configuration I_2: <111> split interstitial or crowdion.

(c) Configuration I_3: activated crowdion.

(d) Configuration I_4: octahedral interstitial.

(e) Configuration I_5: tetrahedral interstitial.

(f) Configuration I_6: <100> split interstitial.

Figure 2. - Interstitial configurations investigated.

TABLE III. - RELATIVE STABILITY OF INTERSTITIAL CONFIGURATIONS

Configuration		Formation energy, eV	Energy above ⟨110⟩ formation energy, eV
Symbol	Description		
I_1	⟨110⟩ split interstitial	9.73	0
I_2	⟨111⟩ split interstitial	9.90	.17
I_3	Activated crowdion	10.01	.28
I_4	Octahedral interstitial	11.11	1.38
I_5	Tetrahedral interstitial	10.47	.74
I_6	⟨100⟩ split interstitial	11.20	1.47

figuration in tungsten with a formation energy of 9.77 electron volts in good agreement with the 9.73-electron volt value reported herein. The reason for this agreement is unclear because the tungsten potential used by Johnson is completely different, especially in regions I and II, than the one used in this study. Other calculations by Johnson (ref. 4) and Erginsoy, et al., (ref. 9) show the ⟨110⟩ split interstitial to be the most stable interstitial configuration for α-iron, another body-centered-cubic metal. The relative stability of these six configurations for tungsten from this study is the same as that calculated by Johnson (ref. 4) for α-iron.

SUMMARY OF RESULTS

A vacancy migration energy of 1.73 electron volts for tungsten was calculated. This calculated value coupled with experimental results suggest that stage III recovery in tungsten may be due to vacancy migration. The relative stability for six possible equilibrium interstitial configurations in tungsten was also calculated. The ⟨110⟩ split interstitial was found to be the most stable interstitial configuration with a formation energy of 9.73 electron volts.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 27, 1968,
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