Atomistics of helium bubble formation in a face-centered-cubic metal*

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Atomistic calculations of helium interstitial clustering in the absence of a vacancy and helium clustering about vacancies have been performed for up to ten helium atoms in up to four associated vacancies in copper. It is found that clusters of six helium atoms in a vacancy (He_6V) are bound by 0.86 eV relative to dissociation by loss of helium. Using this and other information, a system of 42 coupled, stiff, rate equations are solved to determine the kinetics of defect formation and migration under irradiation conditions. Complexes of from five to eight helium atoms in a vacancy are shown to form rapidly at room temperature. Monte Carlo calculations are presented to quantify the concept of interconnection of these defects as a function of the range of their interaction. The calculations suggest that helium-bubble formation may occur because of the fourth-neighbor site-percolation of He_nV complexes.

I. INTRODUCTION

The energetic-particle environment to which the first wall of a controlled thermonuclear reactor will be subjected has been simulated by ion-implantation experiments.[1-5] Several materials including W, Mo, Pd, Nb, stainless steel, Ti, and Cu have been explored experimentally and the effects of implant energy, flux, and temperature investigated. The theoretical understanding of microscopic radiation-damage phenomena is most sophisticated in Cu, making this material the best suited for theoretical helium-ion-implantation studies as well. Our attention will, therefore, be devoted mainly to Cu although many of the results should be easily applied to other materials as well.

The specific experimental results motivating these calculations are those of Bauer[5] and Blewer.[6] Blewer[6] has implanted He^+ in Cu at 54 keV at room temperature and at low flux density ($\sim 5\mu A/cm^2$ sec) to avoid heating the thin Cu foil. He then measured the helium concentration profile as a function of depth from the surface using non-Rutherford proton back scattering techniques. This profile was measured after subsequent anneals to temperatures up to 450 °C. Bauer, in an unpublished work,[5] implanted Cu with 300-keV He ions at liquid-nitrogen temperature to high fluences, of the order of 1×10^{18} He atoms/cm^2. A subsequent linear ramp (1 °C/min) anneal was performed and the He released was measured by mass spectrometry. It is to these experiments that the theory developed here is most directly applicable.

Our principal interests are in developing an atomistic understanding of the many defects and defect clusters produced by the helium implantation and thermal treatment, and the kinetic processes by which the defects are formed and dissociated. We have, therefore, calculated the binding energies of interstitial helium clusters in the absence of a vacancy, clustering of helium atoms in a single vacancy and helium aggregation in multiple vacancies. These calculations include up to ten helium atoms in up to four vacancies and are presented in Sec. II. These energies are required in any rate-theoretical treatment of the implantation phenomena. We have developed a solution to a set of 42 coupled rate equations describing the motion and trapping of defects such as helium interstitials, vacancies, etc. These equations are "stiff" in the sense that certain defects are highly mobile at a given temperature while others are essentially immobile. As such, they require special numerical-integration techniques. This rate theory is presented in Sec. III.

The rate-theoretical results lead us to a discussion of helium defect aggregation which involves percolation theory. Several Monte Carlo calculations were, therefore, performed in order to put these concepts on a quantitative basis and are given in Sec. IV.

II. FUNDAMETAL BINDING ENERGIES

The activation energy for interstitial helium migration in Cu has been determined previously to be about 0.5 eV independent of the chosen interatomic potentials.[7] The activation energy for detrapping of a He atom from a vacancy in Cu has been determined to be 2.15 eV using one of the same potentials.[8] Here we shall present more complicated calculations involving multiple He atoms and vacancies in Cu. Continuity with earlier work has been maintained by choosing potential III of Ref. 7; He-He interactions were taken from Beck.[9] We allow 666 Cu atoms surrounding the defect to relax to their minimum energy configurations except as otherwise noted; this number was found to be sufficient for eliminating boundary effects. We will return to this point later.

In order to determine if the strain field produced by one He interstitial atom would be sufficient to

TABLE I. Binding energies, in eV, of the jth helium atom in a cluster, (i,j), where i is the number of vacancies in Cu. The energies were calculated for "end points" only, the path of migration was not determined in each case.

Number of vacancies	Number of helium atoms in cluster									
	1	2	3	4	5	6	7	8	9	10
0	•••	0.08	0.18	0.08	0.18	−0.02	•••	•••	•••	•••
1	1.84	0.79	0.57	0.66	0.60	0.86	0.25	0.24	0.20	0.20
2	1.84	1.84	1.09	0.66	0.85	0.90	0.75	0.85	0.67	0.85
3	1.84	1.84	1.84	1.25	0.89	0.99	0.69	0.78	0.98	0.70
4	1.97	1.84	1.73	1.93	1.25	1.13	1.12	1.10	0.65	0.82

trap and bind a second helium, and whether two helium atoms would produce a distortion such as to trap a third, etc., we calculated the binding energies of up to six helium atoms in adjacent interstitial positions in Cu. The He atoms were free to relax throughout the calculation but not every possible geometric configuration was calculated, in part because of the results which are shown in the first row of Table I. Binding energies were found to be very small: a second He atom energetically prefers an adjacent interstitial position to an isolated site by less than 0.1 eV; a third He will prefer clustering by ~0.18 eV; the sixth is not bound at all. Within the approximations involved in the calculations we can say with some certainty that if interstitial clustering occurs at all, it is not a predominant effect and is unimportant at room temperature and above. This contrasts sharply with the situation in the presence of even a single vacancy.

In row two of Table I we have compiled the results of our calculations for up to ten helium atoms in the vicinity of vacancy in Cu.[10] Clearly, the number of possible ways to initialize the coordinates of the defect atoms grows rapidly with the number included; some judgment was, therefore, exercised in order to reduce the computational effort.

The calculations show that each of two helium atoms in a single vacancy, He_2V, share the vacancy and lie along a ⟨100⟩ direction, equidistant at $0.46r_0$ (r_0 is the half-lattice constant, 1.8102 Å) from the vacant site (see Fig. 1). Several initial positions, along a ⟨111⟩ and a ⟨110⟩ were chosen as starting configurations for the two helium atoms, but a ⟨100⟩ direction, the same distance from the vacancy and the same energy were always obtained by energy minimization. Three helium atoms in a vacancy, He_3V, are found to lie in a {100} plane forming an equilateral triangle of side ~r_0 as reported earlier.[11] Two possible configurations were found differing by less than 0.01 eV from each other, indicating a very flat planar potential for the three He atoms. The channeling experiments of Picraux and Vook in[12] W confirm this planar configuration, but perhaps not the uniqueness of the defect assigned.

Two configurations were also found for four helium atoms in a vacancy, He_4V, differing by 0.19 eV. The higher-energy configuration has planar symmetry with the He atoms located near (0.78, 0, 0), (0, 0.56, 0), (0, − 0.56, 0), and (−0.78, 0, 0) in units of the half-lattice constant with the vacant site at the origin. That is, a diamond-shaped, rather than square arrangement, was obtained. In the energetically preferred configuration, the helium atoms were found to lie near (−0.24, −0.24, −0.24), (0.71, 0, 0), (0, 0.71, 0), and (0, 0, 0.71). That is, a {111} plane of atoms is formed along [100] directions and the fourth atom lies along the normal to and below this plane. It is reasonable to conclude from these calculations and those that follow that much more accurate and detailed calculations are required to unambiguously distinguish between these geometrical arrangements. Fortunately, binding energies are less sensitive to the configuration and are determined with sufficient accuracy for our purposes.

Only ~0.04 eV separate two configurations we found for five helium atoms in a vacancy, He_5V. The energetically preferred location of the five helium atoms was found to be near (−0.70, 0, 0), (0.70, 0, 0), (0, 0.70, 0), (0, −0.70, 0), and (0, 0, 0.76). That is, four helium atoms lie in a {100} plane, each equidistant from the vacancy along a ⟨100⟩ direction, with the fifth helium atom lying above the plane, along the [001] axis somewhat further from the vacancy forming a "chandelier."

Six helium atoms in a vacancy, He_6V, were found to occupy ⟨100⟩ positions, each at $0.73r_0$ from the vacancy. As is seen in Table I, the sixth helium is bound to the existing cluster of five by 0.86 eV. No attempt was made to distort this highly symmetrical configuration to search for a higher binding energy. Note that He_6V forms naturally from an He_5V defect cluster with only a slight rearrangement of the existing five helium atoms.

The He_7V calculations were performed by initializing the seventh atom at the cluster center and

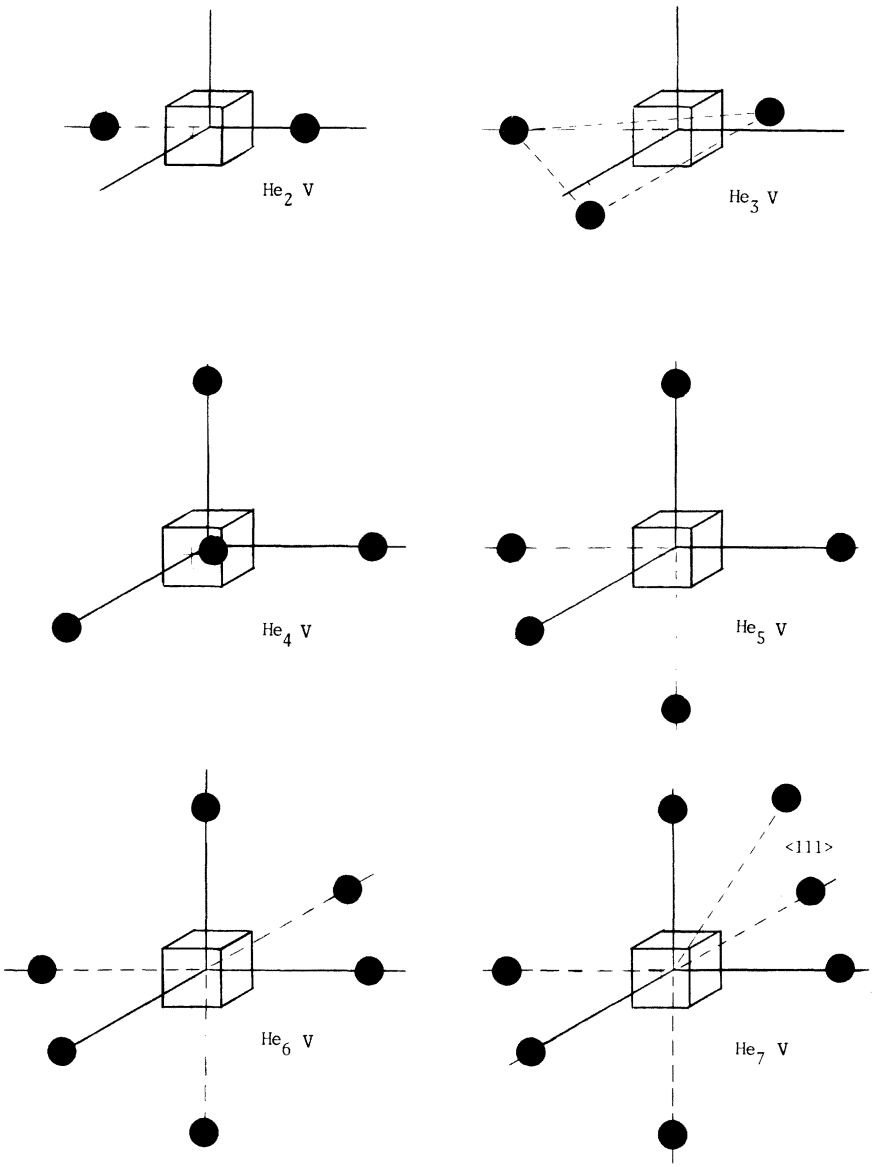

FIG. 1. Minimum-energy configurations of from two to seven helium atoms in a single vacancy in Cu. Helium atoms are described by solid spheres and the vacancy by the empty cube. In several cases, a different configuration was found which was higher in energy than those shown by an insignificant amount (see text). The actual coordinates are given in the text.

also outside the region of six helium atoms in He_6V. This latter calculation forms the first case we are reporting in which an additional helium was placed "outside," but in the "vicinity" of the vacancy; six helium atoms essentially "fill" a vacancy. The calculations show that with one of the seven in the vacancy the repulsion of the helium atoms is large enough to make this symmetric configuration 0.94 eV less favorable than with the seventh atom "outside" the vacancy. With the seventh He atom initially placed at (1, 1, 1) and the others initially in a symmetric He_6V geometry, He_7V is formed with only slight distortions of the He_6V (the three helium atoms nearest (1, 1, 1) move outward $\sim 0.02r_0$ while the three most distant from (1, 1, 1) relax toward the vacancy $\sim 0.01r_0$) and the seventh He lies at (0.94, 0.94, 0.94). We also initialized the He_7V configuration by placing the seven helium atoms along ⟨111⟩ directions with the vacancy at the origin but obtained a much higher energy.

Similarly, the He_8V cluster had its lowest energy in the arrangement obtained by adding another helium to the He_7V case along a ⟨111⟩ direction. Furthermore, it was found that the eighth helium atom preferred to lie adjacent to its geometrically equivalent ⟨111⟩ partner, rather than in a random ⟨111⟩ direction. Again, the eightfold-coordinated ⟨111⟩ positions gave rise to a high-energy configuration. For nine and ten helium atoms in a vacancy, He_9V and $He_{10}V$, one builds upon the same He_6V basis together with a filling of ⟨111⟩ positions (adjacent to each other) in order to obtain the lowest

TABLE II. Binding energies, in eV, of the ith vacancy in a cluster (i,j) containing j helium atoms. The energies were calculated for "end points" only, the path of migration was not determined in each case.

Number of vacancies	0	1	2	3	4	5	6	7	8	9	10
2	0.22	0.22	1.27	1.79	1.79	2.04	2.08	2.58	3.19	3.66	4.31
3	0.45	0.45	0.45	1.20	1.79	1.83	1.92	1.86	1.79	2.10	1.95
4	0.58	0.71	0.71	0.60	1.28	1.64	1.78	2.21	2.53	2.20	2.32

energies.

It is clear from Table I that the He_6V configuration, a highly symmetric defect, has a relatively large binding energy. Because of the possible importance of this effect, we calculated this binding for 1200 atoms in the relaxed region in order to determine the effect of the boundary. The binding energy turned out to be lowered by only 0.02 eV by the inclusion of these ~600 additional atoms.

In the remainder of Table I and in Table II we have summarized the binding energies which we calculated for up to ten helium atoms in up to four vacancies. These energies are employed in our rate-theoretical development presented in Sec. III. In general, the results of Table II indicate that the addition of vacancies to the helium-vacancy clusters results in an increased binding energy of the helium consistent with what one would expect from size considerations. Note also that the binding energy of the kth helium atom to a cluster containing k vacancies is relatively constant.

Note also that the binding energy of the helium atom does not decrease monotonically. From Table II one concludes that the addition of helium to the cluster significantly strengthens the binding of the vacancy. For example, a fourth vacancy is only bound to a trivacancy by ~0.6 eV in the absence of helium, but is bound to a trivacancy containing ten helium atoms by ~2.3 eV! The vacancy clearly reduces the strain surrounding the cluster by attaching itself to the cluster. *In this way, the helium acts as a catalyst for the formation of a void.*

III. KINETICS

Helium-ion implantation of metals is known to produce vacancies by nuclear encounters predominantly at end of range. In metals, most of the energy of the impinging ion is lost to electronic processes which result in little or no damage. Furthermore, for each vacancy created, a highly mobile, self-interstitial (activation energy ~0.1 eV in Cu) is also produced which is correlated with the vacancy and rapidly recombines with the vacancy. The helium ion may initially be stripped of its electron at the surface and if so, it picks up two electrons as it slows down, ending up as a neutral interstitial somewhat further in the target than the last vacancy it produces. Since the helium interstitial in Cu has been calculated to be mobile with an activation energy of ~0.5 eV,[7] the helium atoms and self-interstitials compete for the vacancies. In addition, the self-interstitials predominate in number. Thus, the self-interstitials are much more successful than the helium interstitials in combining with vacancies. Divacancies can also occur because of the finite probability of two vacancies being produced at near-neighbor positions, particularly at high fluences. When a helium atom falls into a vacancy, it is deeply trapped by ~1.84 eV as seen in Table I. This binding energy generally decreases with additional helium-atom occupancy, but there is a rather marked increase in binding due to symmetry for He_6V. Even the tenth He atom is bound although the binding energy, ~0.2 eV, is unimportant at room temperature.

In order to quantitatively describe the implantation process and related phenomena, a system of coupled first-order rate equations was developed. Clusters of i vacancies and j helium atoms are denoted (i,j) and the following processes are explicitly included:

Vacancy capture / Vacancy emission
$$(i,j)+(1,0)\underset{K_{ij}^{VE}}{\overset{K_{ij}^{VC}}{\rightleftharpoons}}(i+1,j);$$

Helium capture / Helium emission
$$(i,j)+(0,1)\underset{K_{ij}^{HE}}{\overset{K_{ij}^{HC}}{\rightleftharpoons}}(i,j+1);$$

Interstitial capture $(i,j)+(-1,0)\xrightarrow{K_{ij}^{IC}}(i-1,j);$

Divacancy capture $(i,j)+(2,0)\xrightarrow{K_{ij}^{V_2C}}(i+2,j);$

where a self-interstitial is denoted by $(-1,0)$. The rate constants generally involve a pre-exponential combinatorial factor and an exponent involving binding energies and activation energies for motion. These latter quantities have been determined by our atomistic calculations, making this kinetic development possible without an unwieldy number of disposable parameters. The details of the rate equations are given in the Appendix.

The results shown here are based upon two widely varying assumptions about the ability of self-interstitials to annihilate clusters containing helium

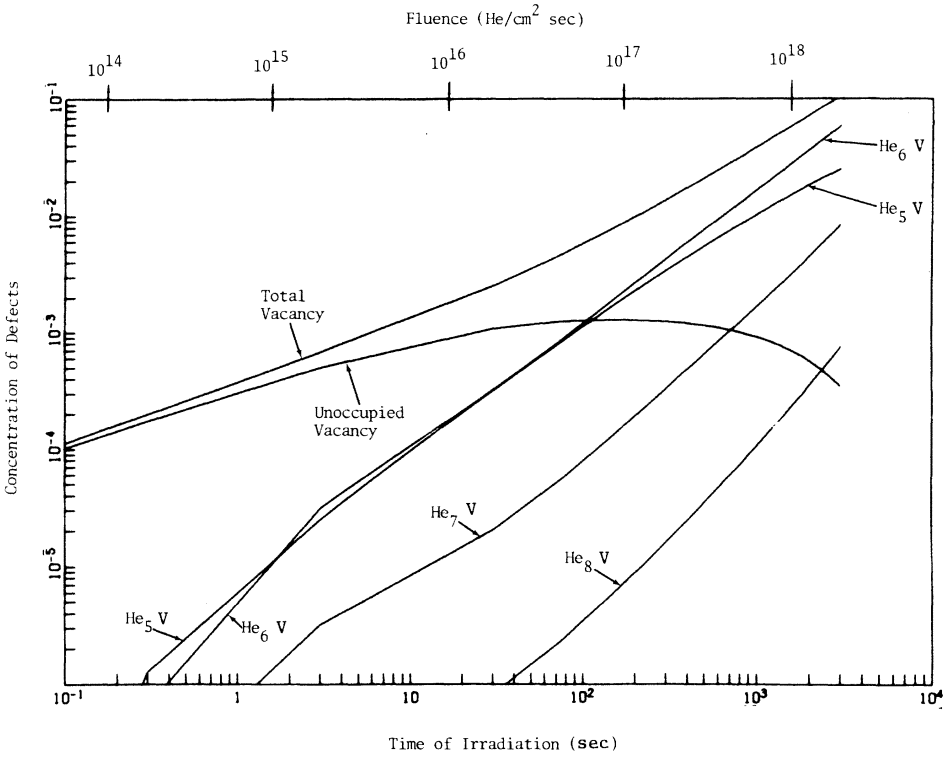

FIG. 2. Defect concentration at a depth of implant equal to the range of helium atom versus fluence (time of implant) for 300-keV He^+ particles incident upon Cu at a flux density of 100 $\mu A/cm^2$. In the calcluations, two or more helium atoms in a single vacancy were sufficient to prevent Frenkel-pair combination.

atoms. In our model, the formation energy of an isolated He interstitial is[7] 1.97 eV; the formation energy of an isolated self-interstitial is[13] 2.74 eV. The energy of a single He atom in a vacancy (i.e., a substitutional helium) *relative to the perfect lattice* is[10] 2.37 eV + 0.13 eV (from Table I: 1.97–1.84 eV), or 2.50 eV. Clearly, $2.50 + 2.74 \gg 1.97$, and a single helium atom cannot prevent the Frenkel-pair recombination by "end-point" considerations alone. Kinetic considerations will not prevent this process either.[14] A similar situation, disregarding kinetics, holds for up to six helium atoms in a vacancy as can be seen from Table I. The energy relative to the perfect lattice for He_6V is[10] 2.37 eV + 6.50 eV (from 1.97×6—sum of the six helium binding energies from Table I), or 8.87 eV. Six isolated helium atoms require $6 \times 1.97 = 11.82$ eV, so that $8.87 + 2.74 \lesssim 11.82$ and the process is disallowed. Certainly kinetic effects will prevent this process also. The actual calculation of the paths required, binding energies, etc. for all of these processes would carry us too far afield here, so we instead choose two limiting approximations. In the first approximation we allow self-interstitials to recombine with only HeV, assuming that two helium atoms will prevent the process. In the second case, we allow self-interstitials to combine with up to He_5V, assuming that six heliums prevent the process.

In Fig. 2, we have plotted the concentration of defects versus time in a layer of the solid near the end of range during irradiation by 300-keV He^+ particles at room temperature at a flux density of 100 $\mu A/cm^2 sec$. We have assumed 100 vacancies and an equal number of self-interstitials to be formed and survive instant recombination per incident He ion during irradiation. The first approximation (interstitial annihilation of only the HeV defect) for Frenkel-pair recombination is used and a sink density of 10^{11} atoms/cm^2 for self-interstitials was also assumed. Variation of this quantity from 10^{10}–10^{12} atoms/cm^2 did not affect the central result. Note from the figure the rapid and near linear growth with time of complexes containing from five to eight helium atoms. Note also that the single (empty) vacancy concentration initially grows and then decreases as the concentration of helium becomes too large to allow an empty vacancy to survive. At very high fluences, the He_6V complexes dominate because of their higher binding energy (0.86 from Table I). Clusters containing more than one vacancy are found to combine rapidly with self-interstitials at this temperature (300 °K).

In Fig. 3, we have made a similar plot of defect concentration versus fluence for the second assumption: that up to He_5V complexes do not prevent Frenkel-pair recombination. Note that for fluences as high as 3×10^{16} He/cm^2 (~ 50 sec) the only difference between Figs. 2 and 3 is that the concentration of He_6V clusters is somewhat larger when

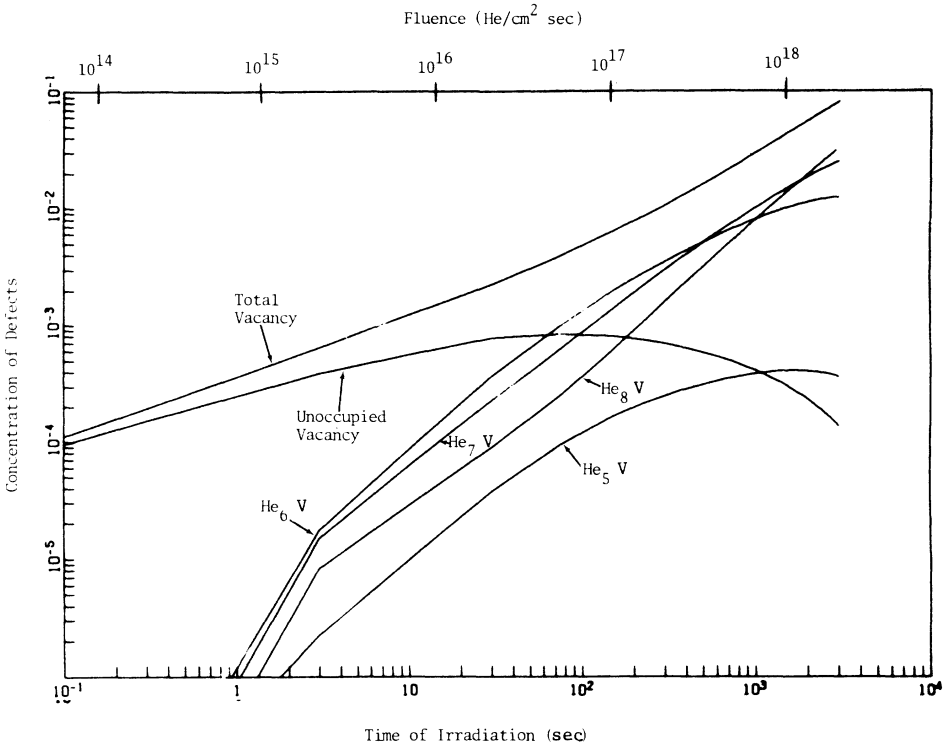

FIG. 3. Defect concentration at a depth of implant equal to the range of helium atom vs fluence upon Cu at a flux density of 100 μA/cm^{-2}. In the calculations, six or more helium atoms in a single vacancy were sufficient to prevent Frenkel-pair recombination.

He_5V clusters may recombine with self-interstitials (Fig. 3). At high fluences (long times), the dominant defect is again He_6V until these complexes begin to saturate and He_7V and He_8V clusters are formed. We do not consider even higher fluences because of the effects of percolation treated in Sec. IV.

IV. DISCUSSION

We ultimately want to relate the results of our calculations to the formation of bubbles, blisters, and flakes in helium-irradiated materials. We recognize the quantitative limitations of two-body defect calculations, their possible interatomic potential dependence, many-body effects, etc. Nevertheless, we feel confident of the higher-order nature of these effects because of our experience that changes in potentials do not affect *relative* energies, such as the binding energies presented here, and activation energies previously determined.[7] The consequences of our calculation of He_nV with $n \sim 6$ to be the dominant defects at low temperatures (Figs. 2 and 3) are of particular importance to us.

A glance at the face-centered-cubic structure of Cu will convince the reader that two He_6V complexes can be considered "interconnected" in the sense of forming an $He_{12}V_2$ complex at interatomic separations of as near as third and fourth neighbors. The complex will spontaneously rearrange to reduce the enormous strain surrounding each individual He_6V cluster, perhaps by the ejection of an intervening Cu atom. This is in addition to, and is to be distinguished from, the long-range strain effects which may actually also tend to enhance clustering. The fundamental question remains as to what concentration of such He_nV clusters is required for the onset of a large interconnected region of helium atoms.

This question leads us to the concept of site-percolation, a theory which relates the probability of site connection to site occupation concentration. To calculate the percolation probability, we performed Monte Carlo calculations in accordance with the development of Holcomb and Rehr.[15] In Fig. 4 we have plotted the probability of interconnection $P(p)$ as a function of (He_nV) concentration, p. The calculations were performed for 100 clusters of 200 atoms each in order to obtain reasonable statistics. There are small deviations from these results in the infinite-atom limit. A slight "shoulder" near the onset concentration would exist in all but the infinite-atom case had we not eliminated it by extrapolation of the $P(p)$ curves onto the p axis. Curve A' in Fig. 4 was calculated for 500 clusters of 500 atoms each for first-neighbor percolation for comparison purposes. The percolative onset for the first-nearest-neighbor interactions has been calculated in the infinite-atom limit to be 0.199 by Shante and Kirkpatrick[16]

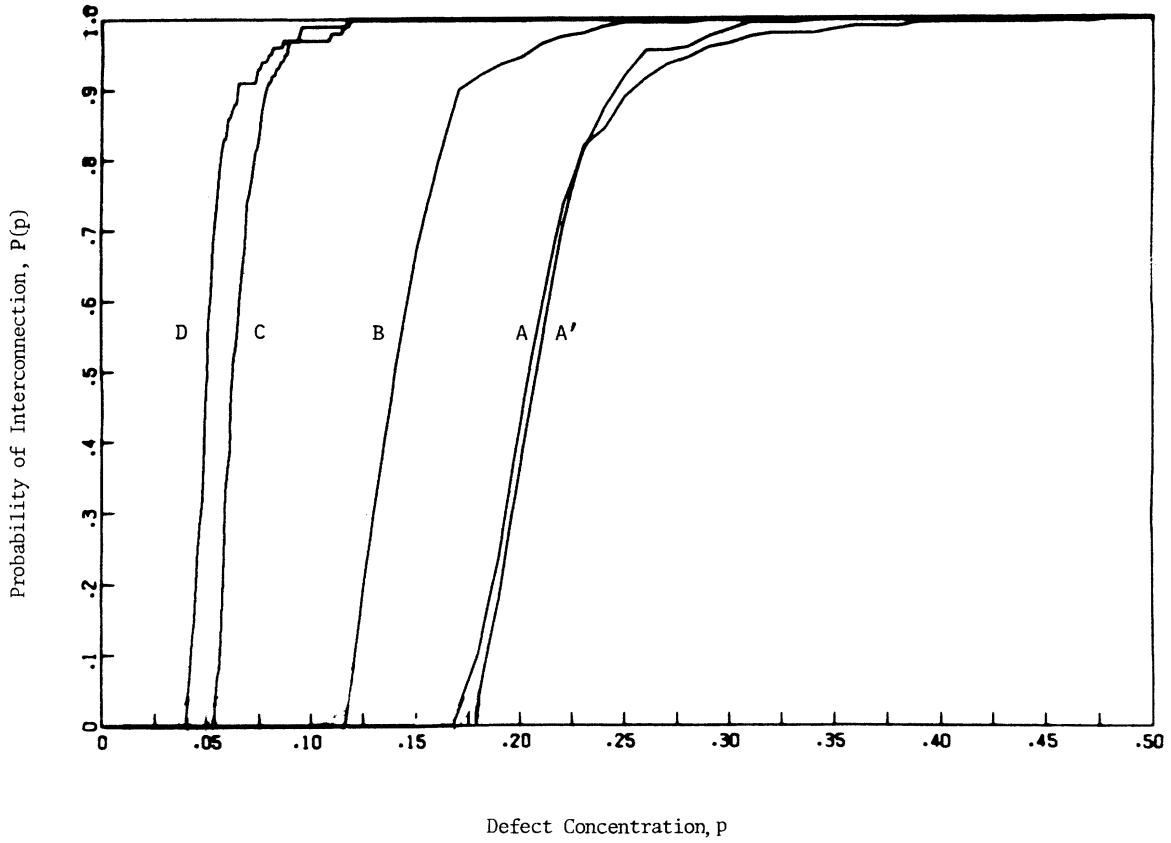

FIG. 4. Probability of interconnection vs concentration for A: first-nearest-neighbor; B: first-and-second-nearest-neighbor; C: first through third nearest-neighbor; and D: first through fourth-nearest-neighbor, percolation in a face-centered-cubic lattice. In curves A–D, 100 clusters of 200 atoms each were used, whereas curve A' was calculated for first-neighbor percolation using 500 clusters of 500 atoms each.

using a series solution. Our accuracy is sufficient to illustrate our point about bubble formation, however.

Figure 4 clearly shows that as more and more neighbors are allowed to participate in the percolation process, the concentration of He_nV clusters required for infinite interconnection dramatically decreases. We find that whereas first-neighbor percolation alone required He_nV fractions of 0.18 (in the 500-atom approximation), fourth-neighbor percolation occurs at He_nV concentrations of ~ 0.05. From Figs. 2 and 3 we find immediately that He_nV concentrations of this order at fluences $\sim 2\times10^{18}$ He atom/cm^2, the known critical fluence for blister formation.

Our basic conclusion from these calculations is that clusters of approximately six helium atoms in a vacancy form early in the helium irradiation of copper at room temperature. These He_6V complexes may be the precursors to the formation of helium bubbles, perhaps via site percolation of fourth-neighbor defects.

In summary, we have shown that calculations of microscopic defects involving several helium atoms and vacancies can yield useful activation and binding energies. Furthermore, these calculated quantities can be used in a rate-theoretical development in order to include kinetic effects such as annealing, flux effects, etc. A plausibility argument is then made involving percolation theory which enables us to demonstrate how bubbles might form. Effects of diffusion (from layer to layer), that is, the effect of solving Fick's Law rather than a system of first-order rate equations is the subject of a forthcoming paper.[17] The predominance of the He_6V defect is not changed by diffusion effects.

ACKNOWLEDGMENTS

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APPENDIX

We consider the nucleation of clusters of i vacancies and j helium atoms of concentration (i,j), to obey a first-order rate process:

$$\frac{d(i,j)}{dt} = (1,0)[(i-1,j)K^{VC}_{i-1,j} - (i,j)K^{VC}_{i,j}] + (i+1,j)K^{VE}_{i,j} - (i,j)K^{VE}_{i-1,j} + (0,1)[(i,j-1)K^{HC}_{i,j-1} - (i,j)K^{HC}_{i,j}]$$
$$+ (i,j+1)K^{HE}_{i,j} - (i,j)K^{HE}_{i,j-1} + (-1,0)[(i+1,j)K^{IC}_{i+1,j} - (i,j)K^{IC}_{i,j}] + (2,0)[(i-2,j)K^{V_2C}_{i-2,j} - (i,j)K^{V_2C}_{ij}]$$
$$+ S_{i,j} + D_{i,j}. \tag{A1}$$

The $K^X_{i,j}$ are defined in the text. In the above, combinations of i and j such that $1 \le i \le N_i$; $0 \le j \le N_j$ are allowed as are $(-1, 0)$ and $(0, 1)$ which represent self-interstitials and helium interstitials, respectively. N_i and N_j are the maximum number of vacancies and helium atoms in a cluster, respectively. All rate constants $K^X_{i,j}$ and concentrations outside this range are zero, and in addition, the rate constants involving interactions between the metal and helium interstitials, $K^{HC}_{-1,0}$, $K^{IC}_{-1,0}$, $K^{HC}_{0,1}$, and $K^{IC}_{0,1}$ are zero. The terms $S_{i,j}$ are source terms (e.g., radiation produced) and the $D_{i,j}$ are additional terms to be included when the (i,j) cluster is mobile. Specifically, the additional mobile species terms are given by

$$D_{1,0} = \sum^{N_i-1} (i+1,j)K^{VE}_{i,j} - (1,0)\left(\sum^{N_i-1}(i,j)K^{VC}_{i,j} + (0,1)K^{VC}_{0,1} + (-1,0)K^{VC}_{-1,0}\right), \tag{A2}$$

$$D_{0,1} = \sum^{N_j-1}(i,j+1)K^{HE}_{i,j} - (0,1)\sum^{N_j-1}(i,j)K^{HC}_{i,j}, \tag{A3}$$

$$D_{-1,0} = -(-1,0)\left(\sum(i,j)K^{IC}_{i,j} + K^I_{SINK}\right), \tag{A4}$$

$$D_{2,0} = -(2,0)\left(\sum^{N_i-2}(i,j)K^{V_2C}_{i,j} + (0,1)K^{V_2C}_{0,1} + (-1,0)K^{V_2C}_{-1,0}\right). \tag{A5}$$

The summation limits are $1 \le i \le N_i$ and $0 \le j \le N_j$ except where explicitly indicated. The first term in Eq. (A2) describes the reaction product of the emission of a vacancy from a cluster; the second term describes the capture of a (mobile) vacancy by a cluster, or a single helium interstitial or self-interstitial. The last terms are written separately because of their exclusion from the sum by our definition of the rate constants.

The number of self-interstitials formed per lattice site per second is taken to be

$$S_{-1,0} = \dot{n}(1 - C_V)R_I, \tag{A6}$$

where R_I is the number of surviving Frenkel pairs produced per incident helium ion; that is, excluding those which instantaneously recombine due to correlation; $\dot{n}$ is the incident number of helium atoms per lattice site per second. The total vacancy concentration C_V is given by

$$C_V = \sum i(i,j), \tag{A7}$$

and the trapped helium concentration C_H is given by

$$C_H = \sum j(i,j). \tag{A8}$$

We consider the source term for helium interstitials $S_{0,1}$ to be given by

$$S_{0,1} = \dot{n} + \dot{n}(C_H)R_H, \tag{A9}$$

where R_H is the number of surviving helium interstitials dissolved from all existing clusters per incident helium ion. The source term for the remaining types of clusters is given by

$$S_{i,j} = \dot{n}(1 - C_V)R_I(P_{i-1,j} - P_{i,j}) + \dot{n}R_H$$
$$\times[(j+1)(i,j+1) - j(i,j)]. \tag{A10}$$

The probability of a site being next to a cluster (i,j) is denoted $P_{i,j}$ and is given by

$$P_{0,0} = (1 - C_V)^{Z_1} \tag{A11}$$

($P'_{0,0}$ is the probability of the site being a near neighbor to no defect),

$$P'_{i,j} = Z_i(i,j), \tag{A12}$$

where Z_i is the number of nearest neighbors to a cluster (i,j) and the prime denotes the probability needs to be normalized. Also, $P'_{N_i,j} = 0$ because we limit the number of vacancies to N_i.

$$Z = \sum^{N_i-1} Z_i(i,j)/(1 - P_{0,0}) \tag{A13}$$

is chosen for normalization purposes ($\sum P_{i,j} = 1$); thus the $P_{i,j}$'s in Eq. (A10) are obtained from the $P'_{i,j}$'s by dividing by Z.

Clearly this development of the $S_{i,j}$ is a zeroth-order approximation only, however, it was found that these considerations did not significantly affect our results. Further details involving the S_{ij} and also the rate constants can be found in an internal report.[17]

Note Added in Proof: The binding energies for helium atoms in one vacancy were recalculated using the Huntington potential to represent the Cu-Cu interaction. The fact that the sixth He is bound more tightly than the fourth, fifth, or seventh is not changed by this variation in the model potential. It was interesting to note that the same geometry as stated above produced the minimum energy with the new potential.

The zero-point energies of an He atom in an isolated interstitial position, a vacancy, and an existing He_6V complex were approximated by fitting a harmonic oscillator potential to the actual potential seen by the helium atom. The results indicate that the zero-point energy in *each* of these configurations was ~ 0.06 eV and hence the inclusion of the zero-point energy does not seem to influence our calculated binding energies.

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