

Calculation of Migration and Binding Energies of Mono-, Di-, and Trivacancies in Copper with the Use of a Morse Function*

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A machine calculation has been made of the migration and binding energy of a trivacancy in copper with the use of a Morse function. It was found that a very large relaxation occurs for one atom into the trivacancy. This relaxation causes the trivacancy to be shared equally by four atomic sites and results in a large contribution (about 2.3 ev) to the binding energy. The migration of a trivacancy requires a partial dissociation of this configuration. The energy of migration is calculated to be 1.9 ev. Thus, a trivacancy is highly stable, quite immobile, and is, therefore, probably the nucleus for void formation. For purposes of comparison the migration energies of mono- and divacancies were also computed by the same method without relaxation. These energies are 1.3 and 0.2 ev, respectively.

I. INTRODUCTION

THE changes which occur in the annealing kinetics of quenched and damaged metallic lattices as a function of annealing temperature and defect concentration are generally interpreted in terms of the migration and/or recombination of defects. At the present time there exists some disagreement on the assignment of activation energies in annealing curves to specific defect migration. A comprehensive review of this problem in radiation damage studies is given by Dienes and Vineyard,¹ and Broom² summarizes the difficulties in cold-work experiments. Koehler *et al.*³ interpret the annealing kinetics of quenched gold in terms of mono- and divacancies, but admit that the role of trivacancies is not known. These few examples describe the speculations which are being made on the role of clusters of point defects in damaged lattices. The simplest cluster is the divacancy and a theoretical estimate of its migration energy has been made by Bartlett and Dienes.⁴ No calculation has been made of the energy of motion of the trivacancy or larger clusters. The present calculation was made in order to estimate the importance of the role of trivacancies in annealing and, as a natural result, to estimate the difficulty of calculating the properties of quadri- and higher vacancy clusters. These latter calculations are important to the field of void formation in metals. More precisely, one would like to know the minimum number of vacancies in a cluster which renders the cluster immobile and forms, therefore, the nucleus of a void.

The calculation of the energy of motion of a trivacancy is rather complex because of large relaxation

effects. An IBM 653 digital computer was therefore used for the calculations with the most important relaxations considered. At the same time the energies of motion of the mono- and divacancy were recomputed with more neighboring atoms considered than had been done by Bartlett and Dienes.

In a face-centered cubic lattice the trivacancy is expected to have, from purely geometric considerations, its lowest energy configuration in the form of an equilateral triangle whose side is the nearest neighbor distance. (It will be shown later that because of large relaxation effects this configuration is not the most stable one.) An example of this configuration is shown in Fig. 1 where the vacancies, labeled V , are at (000), (110), and (01-1), the coordinates being given in units of one half of the lattice parameter. There is one atom only, (10-1), that is equidistant from the three vacancies. This atom and the three vacancies form a

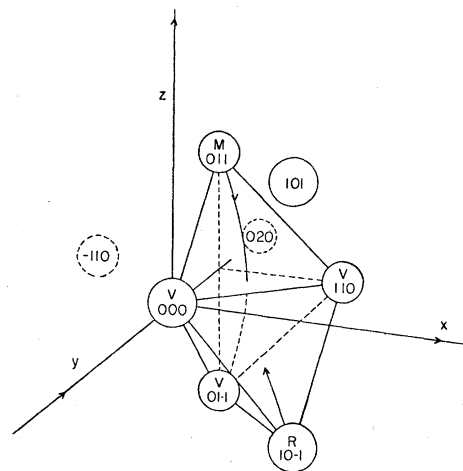


FIG. 1. Schematic diagram of atoms involved in trivacancy motion in face-centered cubic lattice. The V 's are vacancies, M is the moving atom, and R is the relaxing atom. The line from R to the center of the tetrahedron shows the path of relaxation. The line from M including the lower dashed portion shows the path of the moving atom.

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¹ G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).

² T. Broom, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 26.

³ Koehler, Seitz, and Bauerle, *Phys. Rev.* **107**, 1499 (1957).

⁴ J. H. Bartlett and G. J. Dienes, *Phys. Rev.* **89**, 848 (1953).

tetrahedron. The word tetrahedron will be used throughout this paper and will refer to this group. The simplest type of motion which the trivacancy can have is for one of the vacancies to interchange with this fourth atom in tetrahedron. This motion, however, will not allow the trivacancy to migrate through the lattice for it cannot escape from this tetrahedral box. And, as will be shown later, this motion has no physical meaning because of the large relaxation around the trivacancy. If a trivacancy is to migrate it must partially dissociate. If the atom at (011) is considered to be the moving atom there are two possible paths. The (011) atom can exchange with the vacancy at (000), which causes the trivacancy to partially dissociate. A second jump is required, (020) to (011), to complete one unit jump of the trivacancy. It would then be re-formed in an equilateral triangle at (01-1), (110), and (020). Instead of this double jump the atom at (011) may exchange directly with the vacancy at (01-1) and in this case the trivacancy will be re-formed at (000), (011), and (110). Both of these paths had to be considered and it will be shown that the atom at (011) moves directly to the (01-1) vacancy in one jump.

II. METHOD OF COMPUTATION

The interaction energy of the atoms in a copper crystal was represented by a Morse function, according to which the potential energy $E(r_{ij})$ of two atoms i and j separated by a distance r_{ij} is given as

$$E(r_{ij}) = D[e^{-2\alpha(r_{ij}-r_0)} - 2e^{-\alpha(r_{ij}-r_0)}], \quad (1)$$

where α and D are constants and r_0 is the equilibrium distance of approach of the two atoms.

The atom at (011) was selected as the moving atom and the volume bounded by it and the three vacancies was made into a three-dimensional grid in units of one tenth of a half-lattice parameter, e.g., the X distance 0 to 1 was divided into tenths. Such a grid of about 500 points contains both of the paths previously discussed by which a trivacancy may move.

The moving atom (011), referred to as M , has two nearest neighbors in equivalent positions (020) and (-110). The relaxation of these atoms was computed as the fourth atom in the tetrahedron, (10-1), was relaxed. It was found that, although (020) and (-110) relaxed inward about 7% of a half-lattice distance, (10-1) relaxed into the geometric center of the tetrahedron. The calculation of the energy of the moving atom at different grid points was therefore done for several positions of (10-1), the relaxing atom, referred to as R . The energy of the system for each position of the moving atom and the relaxing atom can then be represented by

$$E_s = E_M + E_R - (E_{R,M}) + E_L, \quad (2)$$

where E_s is the energy of the system, E_M is the sum of the interaction energies of the moving atom, E_R is the

sum of the interaction energies of the relaxing atom, E_L is the sum of all of the other interaction energies in the crystal which are not changed in this calculation, and $E_{R,M}$ is the individual interaction energy between R and M which has been counted twice, once in E_M and once in E_R , and is therefore subtracted. The path of the moving atom will then be that in which E_s is a minimum, and the energy barrier for the migration of a trivacancy will be the difference between the smallest and largest energies encountered by the moving atom in following this path.

The writers relied on the results of an unpublished calculation for the choice of α , r_0 , and D in Eq. (1). Girifalco and Weizer⁵ have recently determined the constants of Eq. (1) for copper by summation over the lattice and by matching the cohesive energy, compressibility, and lattice parameter to experimental values. For copper they obtained $r_0 = 2.866$ Å, $D = 0.3429$ eV, and $\alpha = 1.3588$ Å⁻¹. Since relaxation effects in the present calculation had to be considered, a small number of symmetrical interactions were used; the interactions of the atoms in question with the first and second nearest neighbors of the three vacancies and of the moving atom (i.e., first and second nearest neighbors of 4 sites). A more extended calculation using just the Morse function was not considered since Seeger and Bross⁶ have shown that additional factors such as electronic effects may be important in defect calculations.

Relaxation effects were computed first. The atoms at (011), (-110), and (020) were relaxed inward and the minimum energy position was found to be about 12% of a half-lattice distance. The atom at (10-1) was relaxed next and a minimum position found. This atom was then held in the new position and the first three atoms were again relaxed. They moved back to a position of about 7% of a half-lattice distance. When the position of (10-1) was recomputed, it was found to be in the geometrical center of the tetrahedron with coordinates of ($\frac{1}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$). When (011), the moving atom, is moved, it is opposed by two atoms, (-110) and (020), on one side and one atom, (10-1), on the other side. It was felt that since the relaxation of (10-1) was very large compared to the other two, all of the important relaxation during the passage of the moving atom could be confined to this one. Hence (-110) and (020) were held fixed in their relaxed positions for the remainder of the calculation. Five positions of (10-1) were chosen along the line of relaxation ranging from its original lattice site to its fully relaxed position. The grid of the moving atom was computed five times, one for each position of the relaxing atom. The energy of the relaxing atom was also computed for each of its five positions.

All atoms were held in their original position (un-

⁵ L. A. Girifalco and V. G. Weizer (to be published). For a description of their general procedure, see L. A. Girifalco and J. R. Streetman, *J. Phys. Chem. Solids* **4**, 182 (1958).

⁶ A. Seeger and H. Bross, *Z. Physik* **145**, 161 (1956).

relaxed) and the computation for the moving atom was made first with the addition of an atom at (01-1) and then with the addition of an atom at (110). These two computations gave the energies of motion of the divacancy and the single vacancy in a similar manner to that of Bartlett and Dienes except for the addition of more neighbors and different constants in the Morse function.

III. RESULTS

The first result of importance was that the relaxed position of the atom at (10-1), the fourth atom in the tetrahedron, is in the middle of the tetrahedron. This means that the stable configuration of a trivacancy is not a simple sum of three vacancies but rather the three vacancies are shared equally by four atomic positions. Expressed another way, a trivacancy can be considered as a quadrivacancy in a tetrahedral configuration with an interstitial in the center. This will affect the equilibrium formula for trivacancies which will be considered in more detail in the next section. The relaxation energy of this atom, i.e., the change in energy in going from its lattice site position to its relaxed position, is -2.3 ev. This affects strongly the binding energy of a trivacancy, which will also be discussed later.

The minimum energy path of the moving atom (011) is not to (000) in a two-step jump but directly to (01-1) in a slightly curved path lying in a plane with (011), (101), (10-1), and (01-1) at its corners. This is indicated in Fig. 1. At the midpoint of its motion it is at the coordinates (0.35, 0.65, 0). The path in the lower planes is symmetrical to the first half unit it reaches an equivalent relaxed position near the site (01-1). The trivacancy has geometrically moved to (000), (110), and (011). Now a new tetrahedron is formed with the atom at (101). This atom relaxes into the center of the new tetrahedron and the trivacancy, or the tetrahedral grouping of three vacancies, has moved one unit. When the moving atom, (011), begins its motion, the relaxing atom, (10-1), is obviously at its fully relaxed position. As the moving atom approaches the midpoint of its path the relaxing atom is driven further back towards its lattice site. When the moving is one tenth of a unit in ($Z=0.1$ plane) from the midpoint the relaxing atom has been pushed all the way back to its lattice site, (10-1). The relaxing atom stays in this position for the rest of the path of (011) and remains there even when the moving atom is in its new position near (01-1). The relaxing atom of the new tetrahedron which is being formed, (101), begins to move inward when the moving atom reaches the $Z=-0.1$ plane and is fully relaxed when the moving atom has reached its new position.

A plot of the energy barrier, as a function of Z , encountered by the moving atom is shown in Fig. 2. Each position of Z corresponds to a minimum energy

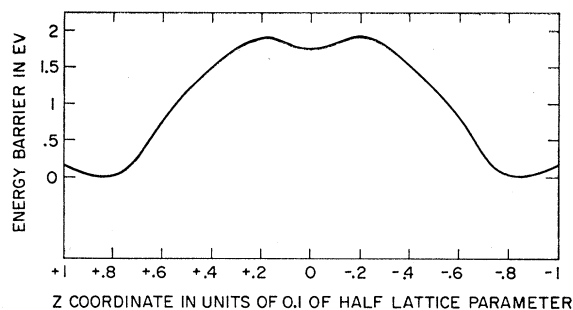


Fig. 2. Energy barrier diagram for motion of trivacancy in fcc lattice. (The dip at $Z=0$ may not be real.)

in the XY plane. The calculation is not sufficiently precise to determine if the dip at the top is real. It is, however, a small percentage of the total energy for the jump, which is 1.9 ev.

The energy of motion of the divacancy was found to be 0.2 ev and that of the single vacancy 1.3 ev.⁷ However, relaxation and electronic effects were not considered and they may alter the energy of motion.

IV. DISCUSSION

The formation of a single vacancy in face-centered cubic materials requires the breakage of 12 bonds and the formation of 6 on the surface. The energy of formation of a vacancy can then be expressed as

$$E_f^{(1)} = (12-6)(E_c/6) - W, \quad (3)$$

where $E_f^{(1)}$ is the energy of formation of a single vacancy, E_c is the cohesive energy, and W is the energy gained by electronic redistribution and atomic relaxation. By simple bond counting, the binding energy of a divacancy is approximately $\frac{1}{6}E_c$ if it is assumed that the change in W is unimportant. In this case the binding energy is near 0.6 ev. If W is taken into consideration the binding energy is estimated to be about 0.3 ev.⁴ Seeger and Bross⁶ also arrive at a value of 0.3 ev, which will be used for the purposes of this discussion. By continuation of this counting process one estimates the binding energy of a trivacancy relative to a divacancy to be 0.3 ev, and the binding energy of a trivacancy relative to isolated vacancies is therefore about 0.6 ev. This energy corresponds to a trivacancy configuration with the three vacancies on adjacent lattice sites. Additional stabilization is gained by the relaxation of the fourth atom into the trivacancy. The present calculation indicates that this is of the order of 2.3 ev so that the total binding energy of a trivacancy is about 2.9 ev. The absolute magnitude of this number

⁷ It should be noted that according to the present calculation the ratio of the activation energies of a divacancy relative to a single vacancy is about 0.15. The earlier and somewhat cruder calculation by Bartlett and Dienes (see reference 4) gave a ratio of 0.35 for a comparable α .

should not be taken too seriously. The energy of formation of three isolated vacancies in copper is about 3 eV and the 2.9-eV value would imply that most of the vacancies are present in the form of trivacancy clusters. This is almost certainly not the case and the true value of the binding energy is less than the 2.9 eV calculated here. The error with respect to a proper quantum mechanical calculation is impossible to estimate. It is well possible that the equilibrium concentration of trivacancies is of the same order of magnitude as that of the monovacancies. The calculations show very clearly that the trivacancy is very stable. This high binding energy plus the high mobility energy indicates that the trivacancy is the original nucleus for a void.

The final configuration for a quadrivacancy is not known. One possibility is that the fourth vacancy will remove the atom from the center of the tetrahedron, making a tetrahedron of four vacancies. The other possibility is that a trivacancy will capture another vacancy in a position that is nearest neighbor distance to only two of the $\frac{3}{4}$ vacancies which made up the tetrahedron, and the atom in the center would shift to a new relaxed position with much less symmetry. A calculation of these configurations would require the successive relaxation of about twelve atoms which is far beyond the scope of the present work.

In order to calculate the concentration of various vacancy clusters, the combinatory pre-exponential factors as well as the energies of formation are required. The equilibrium formulas for the various vacancy clusters are given in the appendix.

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APPENDIX

The equilibrium formulas for vacancy clusters are given by the relations

$$\frac{n_2}{N} = C_2 \left(\frac{n_1}{N} \right)^2 \exp \left(\frac{E_2}{kT} \right), \quad (4)$$

$$\frac{n_3}{N} = C_3 \left(\frac{n_1}{N} \right)^3 \exp \left(\frac{E_2 + E_3}{kT} \right), \quad (5)$$

$$\frac{n_4}{N} = C_4 \left(\frac{n_1}{N} \right)^4 \exp \left(\frac{E_2 + E_3 + E_4}{kT} \right), \quad (6)$$

where N is the number of atoms, n_2 , n_3 , and n_4 are respectively the number of di-, tri-, and quadrivacancies and E_2 , E_3 , and E_4 are their respective incremental binding energies (e.g., E_3 is the binding energy for a trivacancy relative to a divacancy). The numerical coefficients C_2 , C_3 , and C_4 are obtained by computing the number of independent orientations of each cluster. This is done most simply by first considering the vacancies to be distinguishable, computing the number of orientations possible, and then making the vacancies indistinguishable by dividing by the number of possible permutations. For a divacancy the coefficient is

$$C_2 = 12/2! = 6. \quad (7)$$

For a trivacancy in the relaxed configuration determined in this paper,⁸ the coefficient is

$$C_3 = 12 \times 4 \times 1/4! = 2. \quad (8)$$

Until the shape of the quadrivacancy is known, its coefficient cannot be written.

⁸ For a trivacancy in the form of an equilateral triangle (no relaxation), C_3 would be $12 \times 4/3! = 8$.