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Stable and Metastable Tetravacancies in an fcc Metal*

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The lattice distortions and relaxation energies around the various compact forms of tetravacancy have been calculated with the aid of a digital computer. A Morse function was used for the interaction energies and the constants corresponding to copper were used. The most stable configuration is that in which the four vacancies lie on a {111} plane forming a rhombus made up of two equilateral triangles with a common side. The binding energy of this configuration is 2.98 eV. The binding energy of the configuration in which the four vacancies form a square on a {100} plane is 2.60 eV, and the tetrahedral arrangement of four vacancies has a binding energy of 0.97 eV. The results are thought to have a bearing on the formation and nature of larger vacancy clusters.

I. INTRODUCTION

It is now well established that point defects and clusters of point defects play an important role in many of the mechanisms operating in radiation damage, quenching, plastic deformation, and diffusion experiments. Such experiments frequently involve annealing at temperatures at which the point defects migrate and either cluster with other point defects or disappear at sinks. The mechanism of clustering and the intermediate configurations of clusters involved in these processes are still not clear. At the present time, quenching experiments which involve only vacancies and vacancy clusters, are the best understood. Even in these experiments, however, a complete analysis is not yet possible because the properties of only the single and divacancies are known with any degree of certainty. The configurations, binding energies, and migration energies of larger clusters can still only be guessed at. A more exact knowledge of the properties of these larger clusters might permit not only a complete interpretation of the quenching process (including the annealing by which it is invariably followed), but also a better understanding of some of the other processes mentioned above. This paper presents results on the tetravacancy which, as discussed in Sec. IV, may play a vital role in the annealing of vacancies.

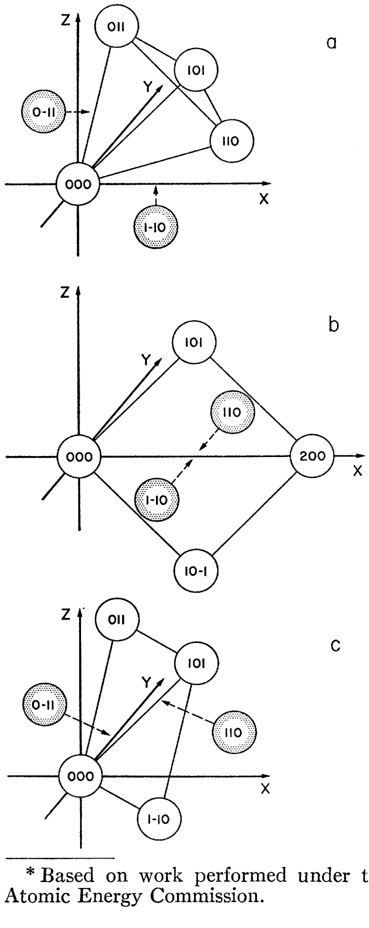

Fig. 1. Configurations of the vacancies and some of the relaxing atoms in the tetravacancies considered in the present study.

Calculations of some tetravacancy configurations have been reported by Vineyard and Gibson[1,2] although details of these calculations have not been published. These configurations are shown in Figs. 1(a) and 1(b). Other configurations of tetravacancy are, of course possible, and Doyama and Koehler[3] and Doyama[4] have recently classified some of these. The configuration shown in Fig. 1(c) is of particular interest because it is as compact as those of Figs. 1(a) and 1(b). The configuration of Fig. 1(a) involves six nearest-neighbor "bonds" (between vacancies). That of Fig. 1(b) involves four such bonds. That of Fig. 1(c) involves five bonds and should, therefore, have an energy before relaxation which is intermediate to the other two. Moreover, it lies completely in a {111} plane, and such planes are known to be favorable to vacancy clustering.[5,6] Finally, it may be noted that the configuration of Fig. 1(c) is related to the trivacancy configuration

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[*] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] G. H. Vineyard and J. B. Gibson, Bull. Am. Phys. Soc. **6**, 158 (1961).

[2] G. H. Vineyard, Discussions Faraday Soc. **31**, 7 (1961).

[3] M. Doyama, and J. S. Koehler, Phys. Rev. **134**, A522 (1964).

[4] M. Doyama, International Conference on Lattice Defects in Quenched Metals, Argonne, Illinois, June, 1964 (Academic Press, Inc., New York, to be published).

[5] J. L. Strudel, F. Vincotte, and J. Washburn, Appl. Phys. Letters **3**, 148 (1963).

[6] R. M. J. Cotterill and R. L. Segall, Phil. Mag. **8**, 1105 (1963).

discussed by Damask, Dienes, and Weizer.[7] The latter configuration is shown in Fig. 2. The atom 000, which is the common nearest neighbor of all the vacancies (which are at the corners of an equilateral triangle), relaxes towards the center and reaches a stable position which is exactly at the center of the tetrahedron formed by position 000 and the three vacancy positions. This configuration is thus equivalent to an atom at the center of a symmetrical arrangement of four three-quarter vacancies. The tetravacancy configuration shown in Fig. 1(c) permits two such relaxations. Atom 110 in this figure can relax towards the center of triangle 000, 101, 011, and atom $0\bar{1}1$ can relax towards the center of 000, 101, $1\bar{1}0$. The configuration of Fig. 1(a) will hereafter be referred to as the tetrahedral form, and those of Figs. 1(b) and 1(c) will be called the square form and the diamond form, respectively (i.e., referring to the initial vacancy arrangement).

The calculations reported here were carried out with the aid of a CDC 3600 digital computer. The configurations discussed by Vineyard and Gibson [Figs. 1(a) and 1(b)] were first repeated. The configuration of Fig. 1(c) was then calculated and compared with the other two and, as is discussed later, found to be the most stable form. The calculations are specifically for copper but could easily be extended to other fcc metals by a simple change of constants.

II. METHOD OF COMPUTATION

The interaction energy of the atoms in the copper crystal was represented by a Morse function. The interaction energy, $E(r_{ij})$ of a pair of isolated atoms is then given by

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

where r_{ij} is the distance between the two atoms, D is the dissociation energy of the pair, r_0 is the equilibrium separation distance of the two atoms, and α is a constant. The energy of any atom in the crystal is then E_i where

$$E_i=\sum_{j=1}^{J} E(r_{ij})\,, \quad (2)$$

and where J is the number of atoms considered in the summation. In the present calculations some of the values of the constants given by Girifalco and Wiezer[8,9] were used. Others required modifications as is discussed below. For copper, these authors give $\alpha=1.3588$ Å^{-1}, $r_0=2.8660$ Å, and $D=0.34290$ eV. Interactions within a cube of edge length $2a$ (where a is the lattice constant) with the subject atom at the center were considered, and thus J was 62. r_0 is, of course, not equal to d the distance between neighboring atoms in the crystal. d is in fact somewhat smaller than r_0. Moreover, the values of these constants are related to J. This was taken into account by minimizing the energy of the subject atom with respect to the 62 surrounding atoms in order to satisfy the Born stability criterion. The value r_0 was then found to be 2.7202 Å.

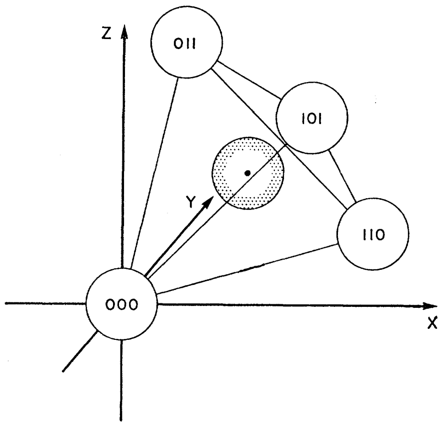

FIG. 2. Positions of the vacancies and the relaxing atom in the tetrahedral trivacancy. The three original vacancies are located at the corners of the triangle 011, 101, and 110, and the atom at 000 relaxes towards the center of the triangle as shown.

The copper crystal used in the calculations was a cube having an edge length of $8a$, containing 2457 atoms. Of these, only the central 365 atoms were allowed to move. It has been found previously that for vacancies and small vacancy clusters the volume change and its effect on the total energy of the defect are both negligibly small.[10] Because of this, the outer 2092 atoms were kept fixed. The four appropriate atoms were removed from the crystal, and the moving atoms were taken in turn and their relaxations (and accompanying energy changes) determined. No restrictions as to direction of relaxation were imposed on any moving atom. Each relaxation was achieved by a series of jumps in the positive and negative x, y, and z directions, starting with a jump length of $2.5\times10^{-3}\,a$ and gradually decreasing this length until the relaxed position had been determined to within a distance $5\times10^{-7}\,a$. The 365 moving atoms were arranged in order of priority of relaxation. This order was taken to be that of descending initial energy, $(E_i)_0$. All atoms were moved independently. There was no simultaneous movement of atoms in equivalent positions with respect to the vacancy cluster [i.e., with equal values of $(E_i)_0$]. Instead of relaxing all 365 moving atoms once before re-relaxing any atom a second time, the atoms were arranged in a series of cycles which moved the atoms close to the vacancies more frequently than those atoms which were further away. For instance, in the case of both the square and diamond configurations there are two atoms, very close to the four vacancies, which undergo quite

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[7] A. C. Damask, G. J. Dienes, and V. G. Wiezer, Phys. Rev. **113**, 781 (1959).

[8] L. A. Girifalco and V. G. Wiezer, Phys. Rev. **114**, 687 (1959).

[9] L. A. Girifalco and V. G. Wiezer, National Aeronautics and Space Agency Report No. R-5, 1959 (unpublished).

[10] R. A. Johnson and E. Brown, Phys. Rev. **127**, 446 (1962).

large relaxations and which therefore require many cycles to become stabilized. The computer was made to print out not only the new position of any atom but also its net energy change. Every time the 365th atom was moved, the computer printed out the net energy change of all 365 atoms in order and also the cumulative net energy change. As is discussed later, this latter quantity approaches a limiting value. Two stopping criteria were imposed upon the program. The first of these required that two successive limiting values of the cumulative net energy change be equal to within 0.1%. The second required that the positions of all the moving atoms change less than $1\times10^{-4}\ a$ between successive cycles. Both of these criteria had to be satisfied in order that the program be stopped. Typical numbers of cycles required for complete stabilization were 3 for the 365th atom, 8 for the 100th atom, and 80 for the first and second atoms.

In order to calculate the binding energy of a given cluster, one must know the energy of the corresponding perfect crystal, the energy of a single vacancy (including the relaxation energy, as determined by a method similar to the one described above for vacancy clusters), the initial energy of the cluster before relaxation, and and the net relaxation energy. The energies involved in the various stages of the calculation will now be defined. E_0 is the energy of any atom in the interior of the perfect crystal with respect to its 62 surrounding neighbors; E_S is the energy of an atom on the surface of the crystal. The energy of the ith atom after removal of the four atoms at the center of the crystal but before any relaxation has occurred is $(E_i)_0$. Clearly, $(E_i)_0$ will equal E_0 for any atom for which one of the removed atoms is not one of the 62 surrounding neighbors. $(E_i)_r$ is the energy of the ith atom after relaxation.

III. RESULTS

Details of the calculation of the single vacancy energy are given elsewhere.[11] The energy per atom in the perfect crystal E_0 was -6.947 eV. The energies, $(E_i)_0$, of some of the atoms close to the vacancies are given in Table I. The cumulative energy difference, $\frac{1}{2}\sum^{n}{}_{i=5}[(E_i)_0-E_0]$, is given as a function of n for each configuration in Fig. 3 (where the atoms are taken in the order discussed in Sec. II, and where the factor $\frac{1}{2}$ is used to allow for the double counting of bonds in the computation, as is discussed later). The cumulative energy difference after relaxation, $\frac{1}{2}\sum^{n}{}_{i=5}[(E_i)_0-(E_i)_r]$, is given as a function of n for each configuration in Fig. 4.

The value of $\sum^{n}{}_{i=5}[(E_i)_r-E_0]$, which is the quantity actually produced by the computer and which is given in Fig. 5, has been obtained by counting most of the bonds within the crystal twice. (A similar thing is true of Figs. 3 and 4, to which the following argument also

TABLE I. Positions and energies of some atoms before and after relaxation.

	Original positions			No. of equivalent atoms	$(E_i)_0$ Energy before relaxation (eV)	$(E_i)_r$ Energy after relaxation (eV)	Positions after relaxation		
Tetrahedral	1	−1	0	12	−6.1356	−6.1030	0.9697	−0.9481	0.0316
	−1	−1	0	12	−6.4809	−6.5041	−0.9794	−0.9794	0.0016
	0	−2	0	12	−6.6476	−6.7097	0.0016	−2.0121	0.0016
	2	−1	−1	4	−6.6790	−6.7816	1.9884	−0.9878	−0.9884
	2	−2	0	24	−6.8235	−6.8709	1.9906	−1.9909	0.0025
	−1	−2	−1	12	−6.8521	−6.8805	−0.9981	−1.9981	−0.9984
Square	1	−1	0	1	−5.9232	−6.1290	0.9988	−0.6963	0.0017
	1	1	0	1	−5.9232	−6.1304	1.0013	0.7009	−0.0013
	0	−1	1	8	−6.2622	−6.5113	0.0553	−0.8812	0.9450
	0	0	2	8	−6.4408	−6.4225	0.0172	0.0003	2.0097
	−1	1	0	8	−6.5183	−6.5734	−0.9750	0.9650	0.0003
	0	2	0	8	−6.5237	−6.6761	0.0263	1.9653	0.0000
	1	0	3	4	−6.7342	−6.7410	0.9991	0.0000	3.0244
	−1	1	2	8	−6.7743	−6.8573	−0.9863	0.9953	1.9863
	0	2	2	24	−6.8148	−6.8865	0.0100	1.9788	1.9784
Diamond	1	1	0	1	−5.9660	−6.9347	0.5934	0.7200	0.4094
	0	−1	1	1	−5.9660	−6.9345	0.4091	−0.7200	0.5922
	1	0	−1	4	−6.1355	−6.3770	0.9319	−0.0103	−0.8791
	−1	−1	0	4	−6.3050	−6.4159	−0.9641	−0.9850	0.0250
	2	−1	1	4	−6.3113	−6.4380	1.9369	−0.9813	0.9741
	0	2	0	4	−6.3916	−6.4342	0.0213	1.9903	0.0244
	−1	0	−1	2	−6.4809	−6.6690	−0.9597	0.0000	−0.9588
	−1	1	2	2	−6.5095	−6.6507	−0.9506	0.9791	1.9475
	0	2	2	4	−6.5674	−6.6479	0.0059	1.9747	1.9666
	1	0	3	8	−6.6476	−6.7250	0.9944	0.0034	3.0000
	2	1	−1	2	−6.6504	−6.7332	1.9388	0.9719	−0.9397
	0	3	1	2	−6.7342	−6.7551	−0.0006	3.0172	1.0006
	2	2	0	4	−6.7369	−6.6907	1.9669	1.9747	0.0081
	−1	2	−1	4	−6.7656	−6.8454	−0.9903	1.9934	−0.9916

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[11] R. M. J. Cotterill and M. Doyama, International Conference on Lattice Defects in Quenched Metals, Argonne, Illinois, June, 1964 (Academic Press Inc., New York, to be published).

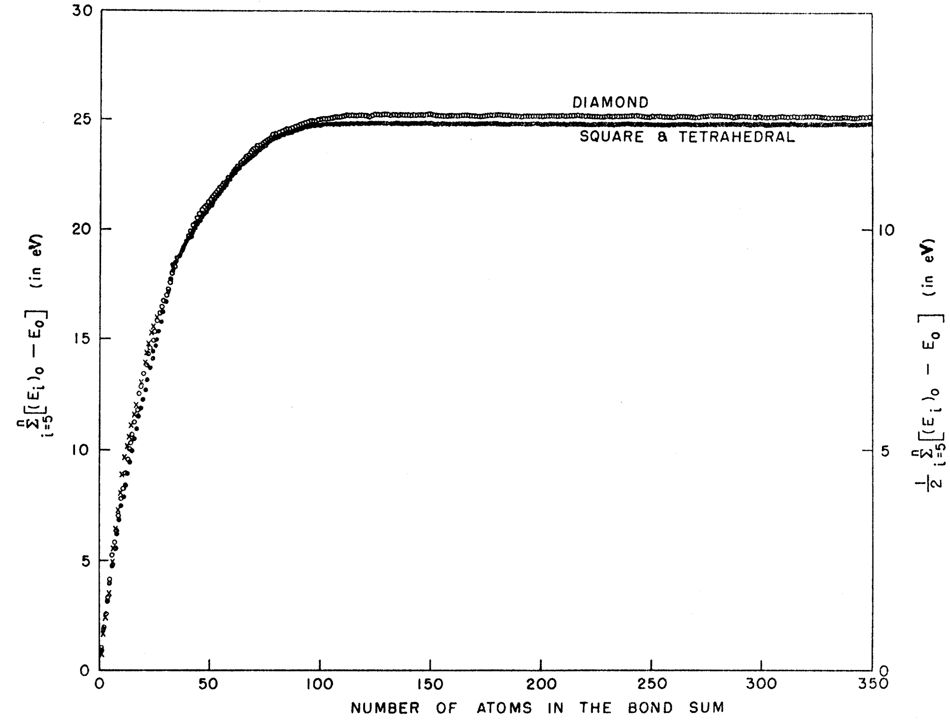

FIG. 3. The energies of the various tetravacancies, before relaxation, as a function of the number of atoms considered in the bond sum.

applies.) Atoms in the moving crystal whose 62 neighbors are all moving atoms have involved the counting of every bond twice. Atoms near the outer part of the moving crystal share some of their bonds with atoms of the outer crystal. Such bonds have been counted only once. There are two ways of correcting for this. One way, which would be exact, would involve a test built into the computer program to determine whether a given bond is with another moving atom of a fixed atom. It would divide the energy of the former by two, and leave the latter unaltered. The second way, which has been adopted here, involved the use of a number of moving atoms sufficiently large to ensure that the contribution of the energy change of bonds with fixed atoms was negligible. That the latter is true may be detected by the leveling off of the curves in Fig. 4. It is for this reason that the asymptotic value of Fig. 5 has simply been divided by two to give the net cumulative energy difference, $\frac{1}{2}\sum^{n}{}_{i=5}[(E_i)_r - E_0]$, and this latter quantity is given at the right-hand side of the figure. It reaches the asymptotic value when n becomes larger than about 200. The limiting value will be called E_{R4} (where the 4 denotes the four vacancies in the cluster).

Using the symbols defined in Sec. II, the initial energy of the perfect crystal containing N atoms is

$$E_{\text{init.}} = \tfrac{1}{2}\textstyle\sum^{N}{}_{i=1} E_i.$$

The final energy of the crystal with four atoms removed from the interior and deposited on the surface is

$$E_{\text{final}} = \tfrac{1}{2}\textstyle\sum^{N}{}_{i=5}(E_i)_r + 4E_S.$$

The net energy change is $E^F{}_{4V}$, the formation energy of the tetravacancy,

$$E^F{}_{4V} = \tfrac{1}{2}\textstyle\sum^{N}{}_{i=5}(E_i)_r + 4E_S - \tfrac{1}{2}\sum^{4}{}_{i=1}E_i - \tfrac{1}{2}\sum^{N}{}_{i=5}E_i.$$

The term E_i may be replaced by E_0 (by definition), so

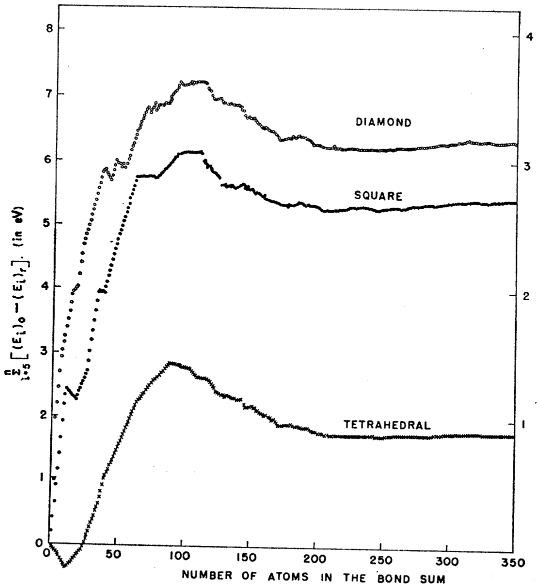

FIG. 4. The relaxation energies of the various tetravacancies, as a function of the number of atoms in the bond sum.

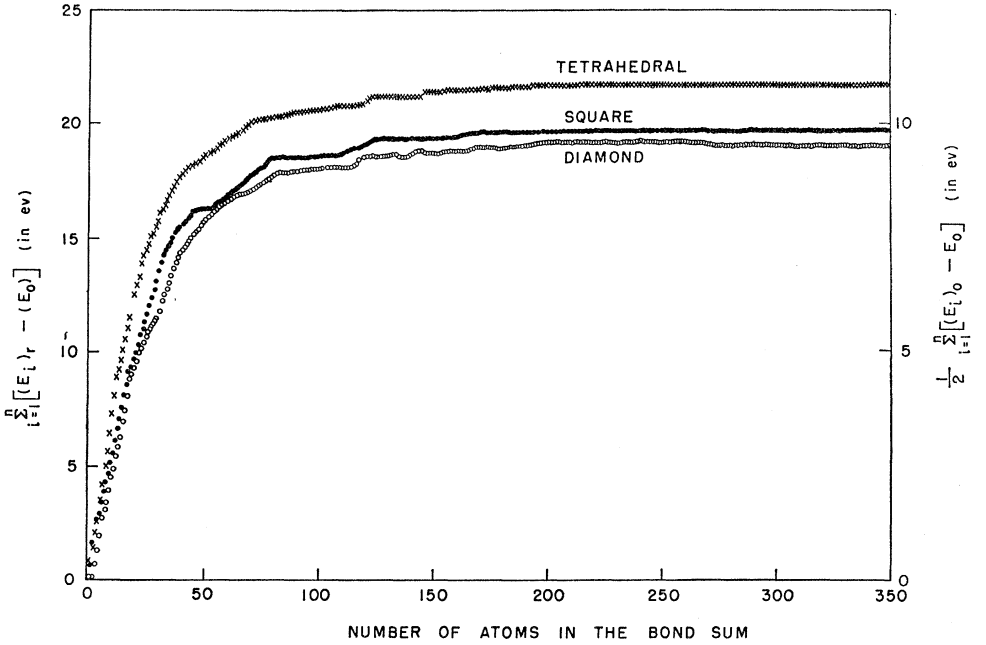

FIG. 5. The cumulative net energy changes of the various tetravacancies, as a function of the number of atoms in the bond sum.

that

$$E^F{}_{4V}=\tfrac{1}{2}\sum{}^N{}_{i=5}\{(E_i)_r-E_0\}+4E_S-2E_0$$
$$=E_{R4}+4E_S-2E_0. \quad (3)$$

(If $E_S=\frac{1}{2}E_0$, as is usually assumed, the second and third terms cancel out.) The binding energy of the tetravacancy against breakup into four isolated vacancies is

$$E^B{}_{4V}=4E^F{}_V-E^F{}_{4V}. \quad (4)$$

Where $E^F{}_V$ is obtained by a process exactly similar to that used to obtain $E^F{}_{4V}$, and

$$E^F{}_V=E_{R1}+E_S-\tfrac{1}{2}E_0. \quad (5)$$

Using (5) and (3) in (4), we have

$$E^B{}_{4V}=4E_{R1}-E_R\,. \quad (6)$$

E_{R1} was found to be 3.103 eV. The values of E_R and the corresponding values of $E^B{}_{4V}$ for each configuration are given in Table II.

The displacements of some of the atoms in the crystal are given in Table I. It is to be noted that these displacements are dependent upon the configuration. The displacements are relatively small for the case of the tetrahedral configuration.

TABLE II. Binding energies of the various tetravacancies.

	E_{R4}	$E^B{}_{4V}$
Diamond	9.4300 eV	2.982 eV
Square	9.8088	2.604
Tetrahedral	11.4435	0.969

IV. DISCUSSION

The present study establishes that the diamond tetravacancy is the lowest energy configuration of the tetravacancy. In this configuration, the atoms 110 and $0\bar{1}1$ do in fact move towards the centers of the triangles 000, 101, 011, and 000, 101, $1\bar{1}0$ as anticipated. The equilibrium positions of the moving atoms do not correspond exactly to the position of the central atom in the tetrahedral trivacancy, however, because these atoms interact with each other. The final arrangement of the two relaxed atoms, the four original vacancies, and the two partial vacancies left behind by the relaxing atoms is shown in Fig. 6 in which the plane of the paper is a {110} plane. It may be noted that both relaxed atoms lie in this {110} plane and that the final configuration thus has considerable symmetry. This symmetry is not carried to the extent that either relaxed atom is equidistant from vacancies $1\bar{1}0$ and $0\bar{1}1$, however (i.e., the atoms do not lie on the dashed line in the figure).

The square and tetrahedral configurations must be metastable. Had they been unstable, the computer program would have allowed them to degenerate to the diamond configuration. Their possible existence, as indicated theoretically by the present study, raises the interesting question as to whether these forms can be produced in practice. The tetrahedral form, for instance, involves very little relaxation and could eventually lead to the formation of uncollapsed voids in some metals. The present study does not rule out the possible existence of other metastable forms of the tetravacancy, but it seems quite unlikely that any of these could be more tightly bound than the diamond form because they would be much less compact.

As can be seen from the displacements given in Table I (and as is indicated in Fig. 6), the final distance between the two relaxed atoms is approximately equal to the nearest-neighbor distance in the perfect crystal. Moreover, the component of this separation distance along the $\langle 111\rangle$ direction normal to the plane containing the four original vacancies is approximately equal to the spacing between the $\{111\}$ planes, (i.e. the relaxed atoms lie close to the dotted lines in Fig. 6). This is interesting because it suggests that even for relatively small vacancy clusters there is a tendency for the relaxing atoms to move to the positions in the $\{111\}$ planes that they occupy in a Frank sessile dislocation loop. It appears, therefore, that the cluster can collapse at a very early stage and grow as a dislocation loop. Cotterill and Whelan[12] have recently shown that once a cluster has collapsed, vacancies will join the cluster at the outside edge, thus tending to confine the vacancy disk to the $\{111\}$ plane upon which collapse originally occurs.

Yoshida *et al.*[13] have recently discovered a new type of vacancy cluster in quenched aluminum. This cluster has the form of an octahedron bounded by $\{111\}$ planes. It is observed in highly pure aluminum when this metal is quenched from close to the melting point, at a relatively low quenching rate, and subsequently annealed at about 100°C. Yoshida *et al.*[13] believe that the defect is a hollow structure. It is interesting to note that the square tetravacancy also produces an octagonally shaped defect, when the two closest atoms have relaxed. It is not possible to say at this time whether the square tetravacancy would maintain its octahedral shape as further vacancies join it; but in view of the work of Yoshida *et al.*, the possibility does appear to warrant further consideration.

The absolute values of the binding energies given here should not be taken too seriously because the effects of the electron gas have been ignored. Moreover, the effect on the constants of the Morse potential due to the redistribution of the conduction electrons on forming the cluster is not known. Finally, it should be noted that the Morse function is only an approximation of the actual potential function. However, the relative values of the binding energies calculated here are thought to be quite reliable.

V. CONCLUSION

The most stable configuration of the tetravacancy is the one in which the four vacancies lie on a $\{111\}$ plane forming a rhombus made up of two equilateral triangles with a common side. The atom immediately above the center of one of the these triangles and the atom immediately below the other relax in the approximate direction of the center of these triangles. The final equilibrium positions of the atoms in this configuration are shown in Fig. 6 and Table II. The binding energy of this configuration against breakup into four isolated vacancies is 2.98 eV. The stability of this form of tetravacancy is taken to indicate that vacancy clusters can collapse to form dislocation loops at an early stage of their growth. Other compact configurations of the tetravacancy have been found to be metastable. The configuration in which the four original vacancies are arranged in a square on a $\{100\}$ plane has a total binding energy of 2.60 eV. This configuration may be the nucleus of the octahedral defect recently observed by Yoshida *et al.*[13] The tetrahedral form is found to produce only relatively small displacements and has a total binding energy of 0.97 eV. This latter result suggests that the tetrahedral tetravacancy is the elementary void, which, although having a higher energy, may be formed in some metals under certain circumstances.

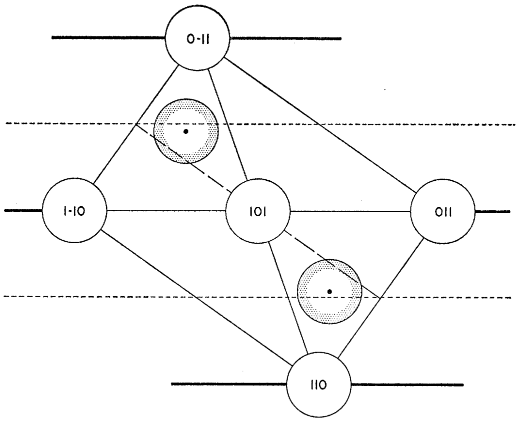

FIG. 6. The final arrangement of the vacancies and relaxing atoms in the diamond tetravacancy [compare with Fig. 1(c)]. All vacancies and relaxing atoms are in the plane of the paper, except for the vacancy 101, which is above, and the vacancy 000, which is below and which is hidden by 101.

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[13] S. Yoshida, M. Kiritani, and Y. Shimomura, International Conference on Lattice Defects in Quenched Metals, Argonne, Illinois, June, 1964 (Academic Press Inc., New York, to be published).