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Combined Pairs of Vacancies in Copper*

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An approximate theoretical calculation is given of the energy of dissociation of vacancy pairs in copper and of the activation energy required for the motion of associated pairs. If two atoms have been removed from neighboring lattice sites, the resulting double vacancy may be more stable than the configuration consisting of two single vacancies far apart. On the assumption that the lattice energy may be regarded as composed of contributions from pairs of atoms, the energy of dissociation of a double vacancy in copper has been estimated as about 0.6 ev. Furthermore, if the interatomic potential energy be represented by a Morse function, the activation energy for the motion of a double vacancy through any face-centered cubic metal crystal is about one-half that for a single vacancy. Double vacancies are, therefore, expected to be stable and highly mobile in such metals.

I. INTRODUCTION

LATTICE imperfections play an important role in many processes occuring in solids.[1] In this note attention is focused on vacancies and their possible aggregation into pairs and clusters. Studies of ionic crystals have shown that positive and negative vacancies tend to combine into stable pairs whose dissociation energy is about 0.9 ev in NaCl.[2,3] Theory indicates that such pairs are considerably more mobile than single negative vacancies.[4]

Similar studies have not yet been made for metals. Seitz[5] suggests that the energy of dissociation of a pair of vacancies in copper may be quite large and that, analogous to the alkali halides,[4] the pair may be very mobile because the number of repulsive interactions which must be overcome are reduced. Recent experiments on the annealing of lattice disturbances introduced by cold work[6–9] and fast particle irradiation[7,9,10] indicate that an appreciable amount of annealing takes place at quite low temperatures where single vacancies are not mobile enough to anneal out by diffusion out of the sample. Some of the low temperature annealing processes may possibly be attributed to the formation and/or motion of combined pairs of vacancies.[5]

The purpose of the present note is to describe some approximate theoretical calculations carried out in order to investigate the properties of pairs of vacancies. In particular, one wants to answer the following questions:

(a) Do vacancies in metals tend to associate into pairs?
(b) If the pairs are stable, what is their activation energy for migration?

II. THE ENERGY OF DISSOCIATION

The energy required to create isolated vacancies in copper is known theoretically from the work of Huntington and Seitz[11] and Huntington.[12] The energy of formation is about 1.4 ev, which is appreciably less than the cohesive energy, 3.52 ev, because of the rearrangement of the electrons and the atoms around a vacancy. In order to calculate the dissociation energy one has to inquire how much the energy of formation is reduced when a vacancy is created next to an already existing one rather than far away from it. In ionic crystals the major source of the energy of dissociation is the electrostatic attraction between positive and negative vacancies.[2,3] In metals, however, things are more complicated because of the homopolar type of bonding. An accurate calculation would probably use more involved methods than those of Huntington and Seitz, and would therefore be rather long, if indeed possible at present. Accordingly, we have used a fairly crude model, which is based on the assumption that the energy of the lattice can be regarded as composed of terms involving the interaction of pairs of atoms. This is a simple procedure and one which ought to be fairly reliable for obtaining a picture of the general situation.

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

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

where $E_f^{(1)}$ = energy to form an isolated single vacancy, E_c = cohesive energy = 3.52 ev for copper, and $W^{(1)}$

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[1] See, for example, the recent review by F. Seitz in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley and Sons, Inc., New York, 1952), pp. 3–77.

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[6] J. Molenaar and W. H. Aarts, Nature **166**, 690 (1950).

[7] Bowen, Eggelston, and Kropschot, J. Appl. Phys. **23**, 630 (1952); also paper given to the Society of Rheology at the Chicago anniversary meeting of the American Institute of Physics, October, 1951 (unpublished).

[8] Blewitt, Taylor, and Coltman, Phys. Rev. **82**, 769 (1951).

[9] For a review and discussion of this topic see G. J. Dienes, *Radiation Effects in Solids*, chapter in Annual Review of Nuclear Science, Vol. II (to be published).

[10] Marx, Cooper, and Henderson, Phys. Rev. **88**, 106 (1952).

[11] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942); **76**, 1728 (1949).

[12] H. B. Huntington, Phys. Rev. **61**, 325 (1942).

= energy regained by redistributing the electrons and atoms around the vacancy. From Huntington and Seitz[11,12] it is known that

$$E_f^{(1)}=1.4 \text{ ev, and therefore } W^{(1)}=1.7 \text{ ev.}$$

Let now a second atom be removed which is a nearest neighbor of the vacancy. One of the bonds of this atom is already broken, so that only 11 bonds have to be broken in removing it to the surface. Thus,

$$E_f^{(2)}=(11-6)(E_c/6)-W^{(2)}. \qquad (2)$$

The dissociation energy ΔE_d, is given by

$$\Delta E_d=E_f^{(1)}-E_f^{(2)}=\tfrac{1}{6}E_c-[W^{(1)}-W^{(2)}]. \qquad (3)$$

$W^{(1)}$ and $W^{(2)}$ are expected to be very nearly the same in magnitude. This is the case because the contribution to the dissociation energy arising from a reduction (by the association of two isolated vacancies) in the kinetic energy of the electrons is approximately canceled by the smaller polarization around the pair relative to two single vacancies. Further, simple calculations showed that the difference in repulsive energy arising from the relaxation of the neighbors is very small, of the order of 0.01 ev. On this basis the dissociation energy is estimated to be 0.59 ev. A somewhat lower value is obtained for this energy if $W^{(1)}$ and $W^{(2)}$ are not taken to be equal but are assumed to be distributed among the bonds in the same way as the cohesive energy. In this case the energy of dissociation is equal to $E_f^{(1)}$, which is 0.23 ev. Thus, ΔE_d is expected to be between 0.23 and 0.59 ev and is probably much closer to the 0.59-ev value. Even if the lower figure is the valid one, association is significant.

The relation between the number of combined pairs of vacancies n_2 and the number of isolated vacancies n_1 is given at equilibrium by[2]

$$n_2/n_1=12(n_1/N)e^{\Delta E_d/kT}, \qquad (4)$$

where N is the density of available sites and the factor 12 enters because the pair can be oriented in 12 different ways in the face-centered cubic lattice. For ΔE_d of 0.59 ev n_2/n_1 is small for a crystal in thermodynamic equilibrium. This is the case because at temperatures where the exponential is large the value of n_1/N is small. However, the fraction of pairs may be made appreciable by freezing in a nonequilibrium number of vacancies.

If thermal equilibrium can be assumed as approximately valid, then Eq. (4) may be applied in different ways to ascertain how vacancies actually tend to associate. If $n_1/N=10^{-7}$, $n_2=n_1$, and $\Delta E_d=0.59$ ev, then the temperature at which the number of pairs equals the number of single vacancies is 502°K. Recent work by Kauffman and Koehler[13] indicates that vacancies in gold may be quenched in to a concentration of the order of 10^{-4}, where the quenching is begun at 900°K and occurs in about 5 milliseconds. The average effective temperature will be lower than 900°K, but this value of T will give a lower limit for n_2/n_1. If $n_1/N=10^{-4}$, $T=900$°K, and $\Delta E_d=0.59$ ev, then Eq. (4) gives $n_2/n_1=2.4$. Since this is a lower limit for the ratio of pairs to singles, we suggest that the interpretation of experimental results must allow for the likelihood that vacancies will associate.

Dissociation of the vacancy pair may require not only the dissociation energy of about 0.59 ev but also a further activation energy to permit the pair to diffuse apart. A more careful examination is required for clarification of this point since one would have to determine the detailed form of the interaction potential of two vacancies as a function of their separation.

III. THE ACTIVATION ENERGY FOR THE MIGRATION OF COMBINED PAIRS OF VACANCIES

It was shown in the previous section that combined pairs of vacancies in copper are expected to be quite stable in any crystal in which an appreciable number of vacancies have been frozen in. It is pertinent, therefore, to inquire about the mobility of such pairs. A fairly simple comparative calculation can be carried out based on a Morse potential interaction between neighboring atoms. Such a calculation may be considerably in error as far as absolute magnitude is concerned. However, the comparison of the activation energies for the migration of pairs with that for the migration of single vacancies should be quite reliable when based on the same potential function.

Let the atomic interactions be represented by a Morse potential:

$$U=D[1-e^{-\alpha(r-r_0)}]^2, \qquad (5)$$

where r = interaction distance, r_0 = equilibrium interatomic distance, α = constant, D = dissociation energy per bond (atom-atom interaction), and U = potential energy per atom. In a face-centered cubic lattice,

$$D=\tfrac{1}{6}E_c, \qquad (6)$$

where E_c = cohesive energy. In copper $D=3.52/6$ ev $=0.59$ ev and a reasonable value for α is[14] 1.4A^{-1}. If a ratio of the two activation energies is taken for comparison, the final results turn out to be independent of the value of D, but are found to depend on the value of α.

Let the coordinates of any point in space be designated, in units of $a/2$ (where a = lattice parameter), by (xyz). These numbers are integers for the lattice points. Let the vacancies be located at (000) and (110). In order that the atomic jump should not dissociate the pair but permit it to move as a unit the moving atom must be a nearest neighbor of both vacant lattice sites. Let the initial position of the moving atom be at (011) and let (xyz) denote its position at any point within the triangle defined by these three lattice points. The total interaction energy was then calculated by means of Eq. (5) as a function of the position of the moving

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[13] J. W. Kauffman and J. S. Koehler, Phys. Rev. 88, 149 (1952).

[14] See, for example, J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), pp. 454–455.

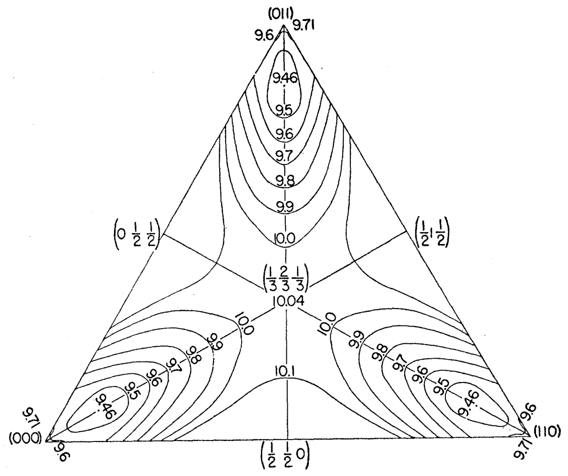

FIG. 1. Potential energy contours for diffusion of a combined pair of vacancy. Moving atom initially at (011), vacancies at (000) and (110).

atom. In this calculation the atom at (*xyz*) was assumed to interact with all the atoms at lattice points which were nearest neighbors of (000), (110), and (011). The energies were expressed in units of D, and the potential energy contours obtained are plotted in Fig. 1.

It is evident from the geometry of the lattice that the energy contours must be symmetrical with respect to the lines connecting the apex of the triangle to the midway point of the opposite side. As shown in Fig. 1 these lines represent the valleys directed toward the saddle point which was found to be at $(\frac{1}{3}\,\frac{2}{3}\,\frac{1}{3})$. Relaxation of the neighbors of the moving atom and of the vacancies was neglected prior to or during diffusion. In a comparative calculation the error introduced is expected to be small. However, because of the relaxation of the atom to be moved from (011) it really starts its climb over the potential barrier from a minimum at (1/12, 11/12, 5/6) which represents its relaxed position. The atom then travels up the valley toward the saddle point. The saddle point is seen to be a rather flat plateau. From the saddle point the atom may move either toward (110) or toward (000). The two paths are entirely equivalent, and the actual course of the particle will be determined by chance fluctuations. The activation energy for this jump, ΔE_2, given by the difference between the maximum and the minimum along the potential barrier, is $0.58D$. Calculations near the minimum and the maximum showed that the jumping atom has no tendency to move out of the plane defined by (000), (011), and (110).

An entirely analogous calculation was carried out for the motion of a single vacancy. In this case there is an atom at (110), the vacancy is at (000) and the atom to be moved is at (011). The motion is, therefore, along the line (011) to (000), and the saddle point is at $(0\,\frac{1}{2}\,\frac{1}{2})$. The minimum in energy was found to be $9.59D$ at (0, 0.91, 0.91) and the maximum $11.135D$, giving an activation energy ΔE_1, of $1.545D$. In this computation the same neighbors were taken into account as in the case of the double vacancy. For reasons of symmetry the noncommon nearest neighbors of (110) should be neglected. These atoms have very little influence on the activation energy, with the revised value being $1.640D$. This activation energy for the jump of a single vacancy is reasonable also in absolute magnitude. With D equal to 0.59 ev the activation energy amounts to 0.97 ev. This value is in good agreement with the estimate of Huntington and Seitz.[11,12]

The sensitivity of the results to variations in the α parameter was also investigated. The energies at the minimal and maximal positions were recalculated for $\alpha = 2.8\text{A}^{-1}$ (an extreme value). With this value of α, E_2 and E_1 were found to be $8.75D$ and $12.43D$, respectively. These figures are unreasonably large, of course. The point is that even at this extreme value of α the difference between ΔE_1 and ΔE_2 is significantly large.

The results are summarized in Table I where activation energies, differences, and ratios in activation energies are given for the various cases. The results show very clearly that the combined pairs of vacancies require a considerably lower activation energy for diffusion than the single vacancies. The ratio $\Delta E_2/\Delta E_1$ is probably the most significant quantity since its value is independent of the value of the bond strength D. The activation energy for the pair is 35 to 70 percent of the value for the simple vacancy, depending on what α is used. As pointed out, the lower α-value is the reasonable one. A conservative estimate for the activation energy for the motion of a pair is, therefore, about one-half of that for the single vacancy. The calculations fully confirm the physical arguments which indicated that a pair should be much more mobile than a single vacancy because of the more open structure of the combined imperfections.

TABLE I. Activation energies for the motion of single and double vacancies in copper.

α in A^{-1}	ΔE_1 in ev (single vacancy)	ΔE_2 in ev (double vacancy)	$\Delta E_1 - \Delta E_2$ in ev	$\frac{\Delta E_2}{\Delta E_1}$
1.4	0.97	0.34	0.63	0.354
2.8	7.33	5.16	2.17	0.705

These results are qualitatively valid for any face-centered cubic metal as long as a Morse function is a reasonable approximation to the actual potential function. Quantitatively, the ratio of the activation energies will depend on the value of α and the difference on both parameters, α and D.

The existence of stable pairs of vacancies in simple metals is strongly supported by the theoretical results. Furthermore, these results indicate clearly that pairs are much more mobile than single vacancies.

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