compared with the latter results. The reader is referred to the considerable literature for further details.

Very little theoretical work has been carried out on the properties of defects in covalent-bonded solids such as diamond, graphite, silicon and germanium. Swalin [29] has calculated the energies of formation and motion of vacancies in the tetrahedrally bonded elemental solids, diamond, silicon and germanium; his results, which are in agreement with experiment, are summarized in Table 2.3. Energies of formation and motion of the interstitial and vacancy in graphite have been calculated by Dienes [30],

TABLE 2.3
Calculated energies of formation and motion of point defects in covalent solids

Substance	Energies of formation (eV)		Energies of motion (eV)	
	E_{fi}	E_{fv}	E_{mi}	E_{mv}
Diamond	—	4·16	—	2·02
Silicon	—	2·32	—	1·06
Germanium	—	2·07	—	0·95
Graphite	9·9	10·7	0·016	—

Kanter [31], Coulson *et al.* [32] and Iwata and Suzuki [33]. Experimental determinations have been carried out of E_{mi} by Reynolds and Goggin [34] and E_{fv} and E_{mv} by Baker and Kelly [35]. The values are respectively 0·43 eV, 2·4–4·2 eV, and 2·6–3·7 eV, thus agreement with theory is not particularly good. Letaw [36] has measured the energy of formation of vacancies to be 2 eV in germanium, and thus deduced the activation energy for motion to be ~1 eV. Bemski [37] has measured E_{fv} to be 0·6 eV, and E_{mv} to be 0·8 eV for silicon.

This summary of theoretical and experimental determinations is necessarily brief and incomplete—it is hoped that it will serve as an indication of the available data on the various types of solid.

Long and short range forces exist between like and unlike defects which lead to the very important phenomena of defect clustering in solids bombarded at temperatures where one or both of the simpler types are mobile, and it is the nature of defect clusters which we now briefly consider.

2.1. AGGREGATION OF POINT DEFECTS

The simplest types of point defect clusters are the associated pair of interstitial atoms; the di-interstitial, and the associated pair of vacancies, the divacancy. Little is known of the di-interstitial; however, Corbett and Walker [38] have deduced their existence in low temperature electron bombarded metals. It is also possible that stable interstitial–vacancy pairs exist, but again the experimental and theoretical evidence is uncertain. Calculations have been made of the properties of divacancies in metals by Bartlett and Dienes [39], Seeger [40] and Lomer [41], and these authors find the binding energy to be 0·23–0·6 eV and the energy of formation to be 0·15–0·35 eV. It is found experimentally that the activation energy for motion of divacancies is lower than that of single vacancies in metals. Values of the activation energy for motion of divacancies given by Seeger [40] are:

Gold	<0·6 eV
Silver	0·57 eV
Copper	<0·58 eV

These values are deduced from the results of quenching experiments.

A further possible configuration for the interstitial is the "crowdion", in which an extra atom is fitted into a line of close-packed atoms, but it is not certain that this is a stable configuration; it is quite likely that the interstitial atom in such a case takes up a so-called "split" configuration. This is illustrated below in Fig. 17, together with some other defect configurations in the lattice.

The formation of trivacancies in metals has been discussed by Damask [42] and by Vineyard [43] and their collaborators.

The equilibrium form in copper has been found to be a tetrahedron of vacant sites with an atom at the centre. The binding energy of this configuration is calculated to be in the range 0·46–2·9 eV, and its migration energy to be 1·9 eV.

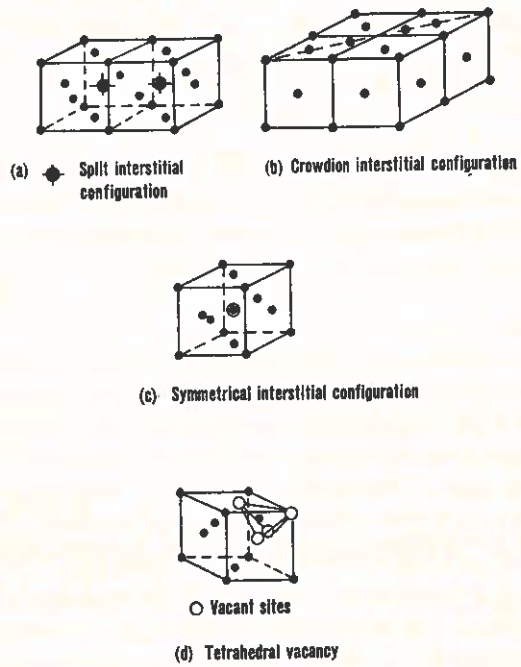

FIG. 17. Defect configurations in f.c.c. lattices.

In the ionic solids long range electrostatic forces exist between defects with charges of opposite sign, but little work seems to have been carried out on defect clustering in these conditions.

Most irradiations of technological interest are concerned with clusters of defects many times larger than those involving one-, two- and three-point defects, thus the properties of such clusters are considered next, the interstitial atom cluster first.

In any crystal lattice there are certain lattice planes which are most densely packed with atoms, and normal to which the lattice planes are more widely separated. In a situation in which interstitial atoms are able to aggregate, they will take up the minimum energy configuration which is in the form of a platelet one atom thick lying between the adjacent close-packed planes. The form of such a cluster is illustrated in Fig. 18, and for clusters containing more than about 100 atoms this may be considered as a ring of edge dislocation with Burgers vector normal to the close-

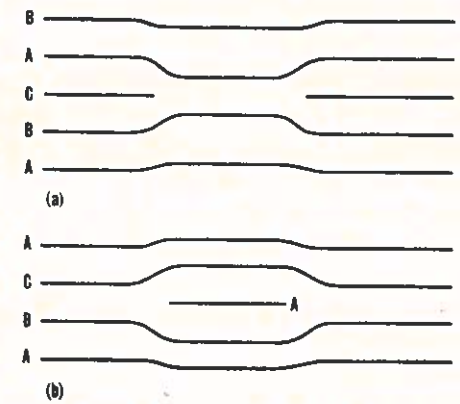

FIG. 18. (*a*) Vacancy, and (*b*) interstitial condensation in f.c.c. crystals.

packed plane, the actual nature of the loop depending upon the crystal lattice.

In the f.c.c. lattice the interstitial loop [44] has a Burgers vector $a/3$ (111) and constitutes a stacking fault. The stacking fault can be removed if two partial dislocations sweep across the loop, one on the glide plane above the loop plane, and the other in the plane below the loop. Figure 18 shows the condensation of interstitials and vacancies in the f.c.c. lattice.

The stacking fault is removed if the energy E_p of the perfect loop is smaller than that of the faulted one E_f. The energies of the

loops, considered as discs of radius R, are given by:

(*a*) Faulted loop:

$$E_f = \frac{2}{3}\frac{1}{(1-\nu)}.Gb^2R\left[\ln\frac{4R}{r_o}-2\right]+\pi R^2\gamma \tag{2.4}$$

(*b*) Perfect loop:

$$E_p = \left[\frac{2}{3}\frac{1}{(1-\nu)}+\frac{1}{3}\left(\frac{2-\nu}{2(1-\nu)}\right)\right]Gb^2R\left[\ln\frac{4R}{r_o}-2\right] \tag{2.5}$$

In these expressions G is the shear modulus, b the Burgers vector of the loop, γ the stacking fault energy and ν the Poissons ratio. It is found that the stability criterion is

$$\gamma \geqq \frac{Gb^2}{3\pi}\left[\frac{2-\nu}{2(1-\nu)}\right]\frac{1}{R}\left[\ln\frac{4R}{r_0}-2\right] \tag{2.6}$$

This kind of reaction may be expected to happen in the case of hexagonal materials, where the interstitial loop is once more in a stacking fault location, taking up a *c*-position between the usual layer positions which may be denoted by *ABAB* [45], if the loop grows to sufficient size.

The case of vacancy condensation is a little different for small numbers of vacancies; the form of an aggregate with least energy is the spherical void. If the surface energy of the solid is σ, the energy of the spherical void of radius r is

$$E_S = 4\pi r^2\sigma \tag{2.7}$$

As the number of vacancies in the cavity increases, the least energy configuration is that of the planar dislocation loop. In this case, the energy is the same as that for the interstitial loop (2.4). In order to achieve this planar configuration, however, the sphere has to pass through the form of a disc-shaped cavity for which the energy is

$$E_C = 2\pi a^2\sigma \tag{2.8}$$

where a is the radius. If Ω^3 is the atomic volume then the number

of vacancies in the void is

$$n_V = \frac{4}{3}\frac{\pi r^3}{\Omega^3} \tag{2.9}$$

For the same number of vacancies, $E_c > E_s$, and therefore an activation energy is required for the transformation.

The disc-shaped configuration collapses to the closed ring of dislocation loop if it grows to sufficient size. The energy of the loop is approximately given by

$$E_L = Gb^2\pi r_0+\pi r_0^2\gamma \tag{2.10}$$

(The last term applies only if there is a stacking fault.) It is obvious that $E_C > E_L$ if

$$r_0 > \frac{Gb^2}{(2\sigma-\gamma)} \tag{2.11}$$

It is thus reasoned that the vacancy agglomerate is spherical for a small number of vacancies, and then if the activation energy is available becomes a planar cluster. When the number of vacancies is increased the planar cluster becomes a closed ring of vacancy loop. It is easily seen that in substances with a large surface energy small voids may remain.

One further type of defect formed by vacancies is the tetrahedral void, which has been observed by Silcox and Hirsch [46] in quenched gold; this is referred to again later.

In the f.c.c. lattice the vacancies precipitate in planar sheets on the (111) plane, the close-packed planes; the cavity formed collapses as discussed above. Once more there is a stacking fault which can only be eliminated by the passage of a partial dislocation with Burgers vector $a/6$ (111). The resulting dislocation loop is then a perfect prismatic dislocation with Burgers vector

$$a/3[111]+a/6[11\bar{2}]\rightarrow a/2[110]$$

which is inclined with respect to the original loop plane. It is interesting to observe that the interstitial and vacancy loop cases are not equivalent. The motion of a single partial dislocation removes the stacking fault from the vacancy loop, whereas two

partial dislocations are required in the case of the interstitial loop. It is possible that there is insufficient energy available in some substances to nucleate the two partial dislocations required for the interstitial case and then it would be expected that the stacking faults would be removed from the vacancy but not the interstitial loop [47].

The observed formation of tetrahedral voids by vacancies in gold is believed to occur when vacancies condense into triangular sessile loops on a (111) plane, with the edges parallel to the $[1\bar{1}0]$, $[10\bar{1}]$, $[01\bar{1}]$ directions. The partial dislocations around the loop limits are able to split on the different (111) planes intersecting the edges of the loop with a gain in energy. A sequence of dislocation reactions then leads to the formation of the tetrahedron [46]. An alternative formation process has been proposed by De Jong and Koehler [47] in which the tetrahedral trivacancy acts as a nucleus which grows by accretion of vacancies into a tetrahedron. The interested reader is referred to these papers for further details of tetrahedra, which have been observed in silver [48] and nickel–cobalt alloys [49] as well as gold.

There do not as yet seem to be any observations of defect clusters in b.c.c. metals.

In hexagonal materials such as magnesium, zinc and graphite it is to be expected that vacancies would condense into loops in the basal plane. The normal stacking in hexagonal crystals is *ABAB*. If part of a layer is removed, the stacking of the adjacent layers is *AA*. The collapse of layers when the loop reaches sufficient size must therefore require the slip of one layer with respect to the other to reduce the stacking fault energy. A more detailed discussion is given in the book by Read [45].

We pass now to the kinds of damage produced by various bombarding particles.

2.2. DEFECT FORMATION DURING BOMBARDMENT

The simplest type of irradiation damage is expected to be produced when those atoms which interact directly with the

irradiation receive energy only slightly in excess of the displacement energy E_d at a temperature too low for either the interstitial atom or vacancy to be mobile. In this case the damage consists of simple interstitial atoms and vacancies for total bombardments which displace only a small fraction of the atoms. In order to achieve non-mobility of the interstitial atom it is generally necessary to irradiate at very low temperatures, $\sim 20°K$ for instance for metals. Uniform simple damage of this kind may be produced in thin samples by electron bombardment or by γ-ray or X-ray bombardment in rather larger samples. Experimental studies on the metals aluminium, silver, copper, iron and nickel have been carried out by Lucasson and Walker [50] using electron bombardments, and many other authors have carried out similar experiments. This type of experiment is invaluable for the study of the properties of the simplest defects, that is the activation energies for motion of the interstitial and vacancy and the effect they have on the physical properties of the solid. The numbers of interstitials and vacancies are essentially equal in this case and may be simply calculated.

The next case for consideration is that in which atoms are displaced homogeneously through the solid, corresponding to the simple cases of electrons and γ-rays of low energy and also the bombardment of solids such as graphite composed of very light atoms with fast neutrons. This latter case occurs because the primary knock-on atoms have low cross-sections for collisions with lattice atoms. If an irradiation of this type is now carried out at temperature where one type of defect only, usually the interstitial, is mobile, then defect clustering will be able to occur, as well as mutual annihilation by interstitial vacancy recombination, during the irradiation.

If we at present forget the recombination of point defects and consider the way in which clusters can form, then two possibilities present themselves. The first possibility is that a point defect diffusing through the solid will encounter another similar defect and form a bound pair which is immobile, and this pair then constitutes a nucleus for condensation of further similar defects.