2 November 1962, Volume 138, Number 3540 SCIENCE

The Effects of Irradiation on Metals

Insight concerning interstitial atoms and vacant sites is obtained from studies of bombarded metals.

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The fact that atoms may be dislodged from crystals by fast particles became of considerable interest about 20 years ago when the first reactors were developed (*1*). It was anticipated that the displaced atoms would lodge in interstitial positions, producing both vacant lattice sites and interstitial atoms, as well as other possible types of disorder. The effect (*2*) achieves its purest form in substances, such as graphite and metals, in which there are many conduction electrons to dissipate the effects of purely electronic excitation. In such materials, particularly in the metals, one may expect the primary changes in physical properties to be associated with atomic displacements, at least for lower levels of irradiation. Once the problem of displacement is recognized, innumerable questions arise —for example, those concerning the effectiveness of the displacement process which leads to the production of interstitial atoms and vacancies, and those relating to the changes in such physical properties as electrical and thermal conductivity, dimensions, stored energy, and the like. In this survey (*3*) I focus primary attention upon the close-packed noble metals, of which copper, silver, and gold are the prototypes, since they have been studied most extensively. Copper in particular has been the object of much concentrated attention.

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Theoretical Treatments of Bombardment

Several calculational techniques (*2*) have been developed to estimate the effectiveness of incident radiations in producing displacements of atoms from normal lattice positions. One of the most useful approaches, which frequently serves as a standard of reference, is based on the simplifying assumption that each atom in the solid is held in a potential well of depth E_d with a steplike boundary, and that the atom becomes permanently displaced if it is struck in such a way as to receive a kinetic energy greater than E_d (see Fig. 1). Actually, the well holding an atom in position should have a less discontinuous slope; moreover, it is most likely that the probability of ejection varies continuously with energy between zero and unity in some such manner as that shown schematically in Fig. 2. Nevertheless, the simple model can be treated quantitatively under a variety of circumstances and yields much valuable information when combined with an empirically determined value of E_d. Such values range between about 15 and 40 electron volts (ev) for typical solids of the type normally studied. It is feasible to correct the results in part for continuous variations of the probability of ejection of the type shown in Fig. 2.

In recent years, Gibson, Goland, Milgram, and Vineyard (*4*) have used digital computers to attempt to consider the course of events near the threshold energy in small rectangular blocks of somewhat idealized crystals containing up to 1000 atoms. Fairly realistic assumptions are made regarding the interaction between pairs of atoms, and the entire system is considered as a single dynamic entity. I shall discuss later some of the results obtained in these investigations.

Three types of bombarding particles are used commonly—electrons with energies in the neighborhood of 1 Mev, charged nucleons such as protons or deuterons, and neutrons. Electrons with energies in the vicinity of 1 Mev have momenta close to the threshold value needed for transferring the energy E_d to typical atoms in the most favorable collisions. In fact, by varying the energy of such electrons and studying the changes in a physical property of the material, such as its electrical resistivity, one may obtain an appropriate value of the parameter E_d for the metal. The most accurately determined value is that for copper—namely, 22 ev. It was determined by Corbett, Denney, Fiske, and Walker (*5*), using electrons with energies lying in the range from 0.7 to 1.4 Mev.

Table 1 shows typical results obtained from the simple square-well theory for three typical bombardments. When a 1.4-Mev electron strikes an atom of copper, it transfers 28 ev on the average. This *primary* struck atom may also displace 0.25 other, or *secondary*, atoms to within a few atomic distances. Of the 28 ev transferred to the primary atom, about 22 will produce agitation, resembling heat motion,

Table 1. Displacement calculations for copper. E_d = 22 ev.

Particles	Primary kinetic energy (ev)	Atoms displaced per primary (No.)	Vibrational energy per primary (ev)
1.4–Mev electrons	28	1.25	22.5
9–Mev deuterons	170	6.2	150
Reactor neutrons (~0.8 Mev)	2.5×10^4	500	2.2×10^4

in the vicinity of the collision. The remainder will reside as energy stored in the interstitial atoms and vacancies, if they do not recombine. The thermal energy diffuses away in a time of the order of 10^{-11} second.

In the case of 9-Mev deuterons, the displaced atom receives 170 ev on the average and displaces 5.2 secondary atoms on the average. The primary energies actually are distributed as $1/E$, in accordance with Rutherford collisions. In the average collision of the type illustrated, about 150 ev emerge in the form of agitation.

A typical fast-fission neutron with an energy of 0.8 Mev produces a primary displaced copper atom with an energy of 2.5×10^4 ev. The primary produces about 500 secondary atoms, according to the simple displacement theory, and about 2.2×10^4 ev of the energy of the primary emerges as heat. The energy of the primary atoms is uniformly distributed from zero to the maximum value for a head-on collision under neutron bombardment.

The contrasting situations for the three types of radiation are shown schematically in Fig. 3. The electrons with energies near the threshold produce the simplest type of displacement pattern, consisting principally of isolated vacancy-interstitial pairs more or less randomly distributed if the electron energy is not degraded in the specimen. The charged nucleons produce small groupings of pairs, whereas the fission neutrons produce large groupings containing several hundred pairs. It is difficult to make an accurate estimate of the effect of thermal agitation associated with the deposition of energy. We might expect it to promote migration of the interstitial atoms and vacancies. It is evident, however, that the effects of thermal agitation should be least for electron bombardment near threshold and most for neutron energies near 1 Mev.

Silsbee (*6*) has pointed out that one may expect "focusing collisions" along densely packed rows of atoms in a well-ordered lattice when one atom in the row has received an appropriate amount of energy directed within the appropriate solid angle. Such focusing collisions always transfer energy, but they may also transfer matter if circumstances are right. Their effect has been explored by Leibfried (*7*) and by Vineyard (*4*) and his colleagues, using the model of a crystallite with several hundred cells described previously. The focusing collisions undoubtedly play some role in determining the course of events following the displacement of the primary atom. The fact that such collisions provide a means for transferring a fraction of the energy over very long distances may explain the observation that damage sometimes appears (*8*) to concentrate at existing imperfections, at least during the early stages of bombardment. It also provides an explanation of the highly directed patterns of ejected atoms during the sputtering (*9*) of metals under ion bombardment.

Before entering into a discussion of irradiation effects in metals, I shall consider an important related topic on which information has developed in recent years—namely, the thermally induced defects in metals.

Thermally Induced Defects

Thirty-five years ago, Frenkel (*10*) predicted that all solids should exhibit defects on an atomic scale at sufficiently high temperatures as a result of the effects of thermal fluctuations. In general, the lattice should possess vacant-lattice sites or interstitial atoms, or both, whose fractional density N/No should vary with temperature in accordance with the Boltzmann factor of the form

$$N/No = C \exp(-E/kT) \qquad (1)$$

Here No is the number of atoms per unit volume, E is closely related to the energy required to form the defect, C is nearly constant, T is the absolute temperature, and k is Boltzmann's constant. Viewed in a simple way, vacancies may be formed when atoms near the surface jump to the surface layer, whereas interstitials may be formed when atoms on the surface force their way into interstitial positions. In general, one would expect the defects to be mobile at sufficiently high temperatures and to contribute to such physical processes as atomic diffusion and electrolysis. The principles which determine the presence of these point defects are the same as those which determine the presence of a vapor over a liquid or solid. In general, the thermally generated defect which will be present in greatest density will be the one having the lowest value of E in Eq. 1.

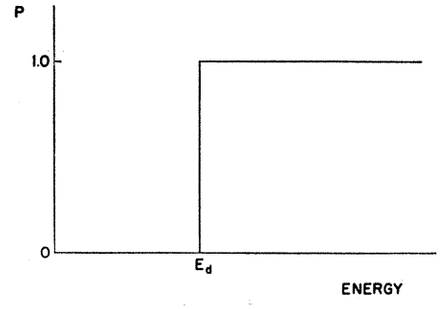

Fig. 1. The approximate form of the curve-giving probability of displacement as a function of energy used in a simple treatment of the topic. The probability is zero until the atom obtains the threshold energy E_d, and then it jumps abruptly to 1. Actually, the curve probably has a form more nearly like that shown in Fig. 2.

In the discussion that follows I shall focus attention on vacant lattice sites and interstitial atoms, first, because they appear to be the most prominent defects observed in solids, and second, because they have a bearing on the interpretation of the problem of radiation effects in solids. As may be readily seen in Fig. 4, a mobile vacancy imparts mobility to the atoms around it. Similarly, an interstitial atom in a close-packed metal usually moves by forcing a neighboring atom of the same

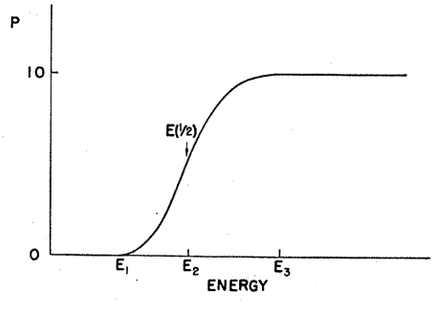

Fig. 2. Schematic diagram showing the variation of the probability of atomic displacement as a function of the energy the atom receives. The probability is zero until the true threshold E_1 is reached. It climbs toward unity for higher energies; E_2 is the value at which the probability reaches 0.5, whereas E_3 is the value at which the probability reaches unity. Actually, the curve is dependent upon the direction in which the atom moves relative to the lattice.

kind into an interstitial site and taking its place. Thus, the interstitial *pattern*, rather than a given interstitial atom, migrates during motion. The motion of the point defects is a thermally activated process also governed by a Boltzmann factor of the form appearing in Eq. 1, the energy E now being related to the activation energy for migration, usually designated E_m to distinguish it from the formation energy of the defect, usually designated E_f.

Prior to 1940, much work on the interpretation of the thermally induced point defects was carried out (*11*) on salts such as NaCl and AgCl. In such cases, one may enhance the defects by appropriate chemical additions. For example, if $CaCl_2$ is dissolved in solid NaCl, each ion of Ca^{++} will replace two Na^+ ions and hence produce one vacant site in the lattice of Na^+. Investigations based on the use of this principle have shown that the normal thermal defects which appear in NaCl are vacancies which occur in equal number in the Na^+ and Cl^- lattices. Similarly, the prominent defects in AgCl below 300°C have been demonstrated to be Ag^+ vacancies and interstitial Ag^+ ions.

The methods of analysis which prove so effective for salts are not applicable to metals, since the latter do not obey the simple rules of ionic binding. Other techniques must be employed. About 20 years ago, before adequate experimental methods had been developed, Huntington and I (*12*) attempted to obtain a reasonable picture of the factors affecting the formation and migration of point defects by carrying through theoretical calculations based on the quantum mechanical theory of metals. We focused attention on copper as the simplest of the noble metals and employed empirical parameters in cases in which it proved too difficult to derive quantities from first principles. This work showed that the energy of formation of vacancies is substantially less than that of interstitial atoms, being near 1.0 ev, so that vacancies should be the prominent thermally induced defect in this metal and in those close-packed metals which resemble it. Calculations also showed that the energy of migration of vacancies should be in the vicinity of 1.0 ev. Huntington (*13*) extended the calculations and eventually demonstrated that the activation energy for migration of interstitial atoms in copper probably is very low, of the order 0.1 ev, even though the energy of formation probably is

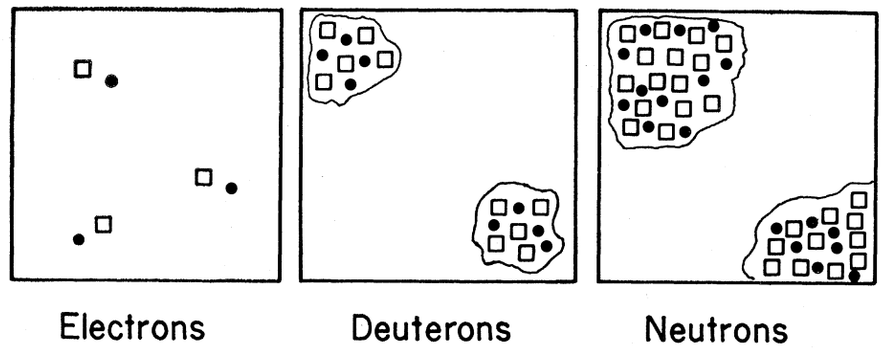

Fig. 3. Schematic diagram showing the differences in displacement effects to be expected for electrons near threshold; for charged nucleons, such as deuterons with energies well above E_d; and for neutrons. In the case of electrons near threshold, relatively simple vacancy-interstitial pairs are produced. The pairs are isolated and are essentially randomly distributed. In the case of charged nucleons, clusters containing, on the average, about six pairs are produced. The energy received by the primary atom in each cluster is distributed as $1/E$, so that there is a statistical distribution in size. In the case of fast fission neutrons, the clusters produced by a given primary atom may have several hundred pairs.

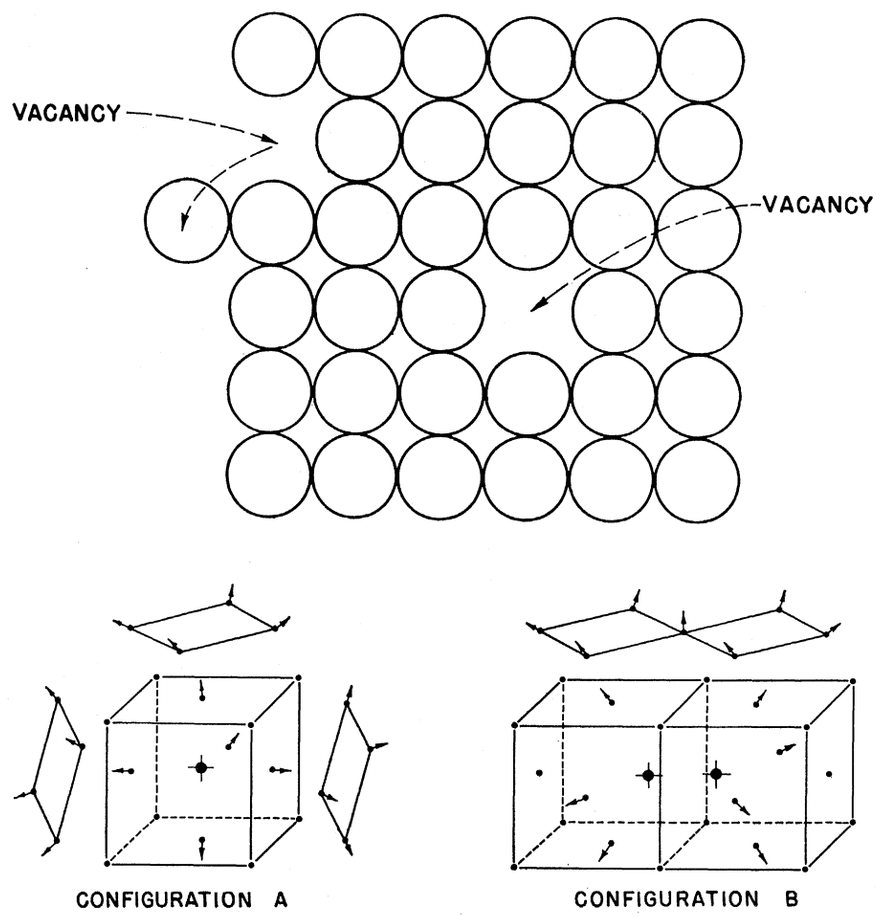

Fig. 4. (Top) Schematic representation of lattice vacancies in a monatomic lattice. Vacancies may be produced near the surface as a result of atoms jumping to the surface, or they may be produced internally near dislocations. The motion of the vacancies imparts mobility to the atoms in the lattice. (Bottom) Two configurations for interstitial atoms in a face-centered cubic lattice. In configuration A, the extra atom is at the center of the cube and the neighboring atoms are displaced as shown. In configuration B, the extra atom is divided between two sites symmetrically disposed relative to the dividing line shown. Present calculations indicate that B may be slightly more stable than A, by an amount of the order of 0.1 electron volt. In this case, configuration A corresponds to the activated state.

Table 2. Comparison of vacancy densities and related properties.

Property	Cu	Ag	Au	Al
$\Delta N/N$ (mp)	1.9×10^{-4}	1.7×10^{-4}	7.0×10^{-4}	9.4×10^{-4}
E_f	1.17 ev	1.09 ev	1.0 ev	0.76 ev
Q	2.05 ev	1.91 ev	1.81 ev	1.4 ev
$E_m = Q - E_f$	0.88 ev	0.82 ev	0.81 ev	0.6 ev
kT_m	0.117 ev	0.107 ev	0.115 ev	0.081 ev
E_f/kT_m	10.0	10.2	8.7	9.5
E_f/Q	0.5_7	0.5_7	0.5_4	0.5_4
$\Delta\rho/(\Delta N/N)$			1.5 ± 0.3 μohm/at 1%	3 μohm/at 1%

near 5.0 ev. In brief, he found that the two interstitial configurations shown in Fig. 4 (bottom), one of which presumably is the normal and the other the activated state of motion, have the same energy to within about 0.1 ev. If this low value of E_m for interstitial migration is correct, one would expect interstitial migrations at temperatures near 50°K, whereas vacancies should not be mobile in a practical sense much below room temperature (300°K).

The calculational techniques used to estimate the energies of formation and migration of the defects have also been used to determine the change in volume (*14*) associated with introduction of defects and their contribution to the electrical resistivity (*15*).

Although most of the early calculations were carried out in a reasonably dispassionate atmosphere, they ultimately became the center of much discussion and controversy as more investigators became interested in the problem. The use of empirically determined parameters allowed much room for manipulation of the models and hence permitted considerable diversity. Ultimately it became clear that experimental methods would have to be used to place the question of the nature and properties of the defects beyond reasonable doubt.

Comparison of Lattice and Macroscopic Expansion

Let us assume that vacant lattice sites are the defects which are generated most easily when the crystal is heated. As long as the total number of atoms remains fixed, it will be necessary for a given specimen of the metal to increase the number of unit cells in order to compensate for the vacant sites. It may do this, for example, by adding extra atomic planes at the surface. Exactly the converse situation will prevail if the prominent defect is an interstitial atom; that is, a given specimen will lose unit cells as the atoms wander into interstitial spaces—for example, from the surface. Should vacancies and interstitial atoms be formed in exactly equal numbers, the total number of cells would not be affected by the number of defect pairs.

In other words, the macroscopic dimensions of the specimen expand by a larger fraction than the dimensions of the unit cell with increasing temperature if vacancies are formed, whereas the converse is the case if interstitial atoms are formed. The fractional changes are equal if vacancies and interstitials are formed in equal numbers. Figure 5 shows the two types of fractional expansion—that for the lattice cell and that for the entire specimen—in the case of aluminum. The measurements were made by Simmons and Balluffi (*16, 17*). To date, similar measurements have been made for copper, silver, and gold, with the same qualitative result. It may be seen that the macroscopic coefficient is greater than the coefficient for the lattice cell, so that vacancies are the predominant thermal induced defect. It is possible to determine the energy of formation of vacancies, E_f, by comparing the difference in the two curves with a function of the type given in Eq. 1. Table 2 contains the observed values of E_f for copper, silver, gold, and aluminum, determined in this way (row 2), along with the fractional concentration of vacancies at the melting point (row 1).

Table 2 contains other quantities as follows. Row 3: Q, the activation energy for self-diffusion in the metal—that is, the diffusion of a tracer; Q is the sum of E_f and E_m, the energies of formation and migration of the vacancy. Row 4: $E_m(= Q - E_f)$. Row 5: kT_m, where k is Boltzmann's constant and T_m is the melting temperature. This product provides a measure of the energy of melting. Row 6: the ratio E_f/kT_m. Row 7: the ratio E_f/Q. Row 8: the estimated ratio of the extra component of electrical resistivity associated with vacancies to the fraction of vacancies; it has become conventional to express this in terms of the resistivity for 1 percent of vacancies. The last ratio has thus far been determined with reasonable experimental accuracy only

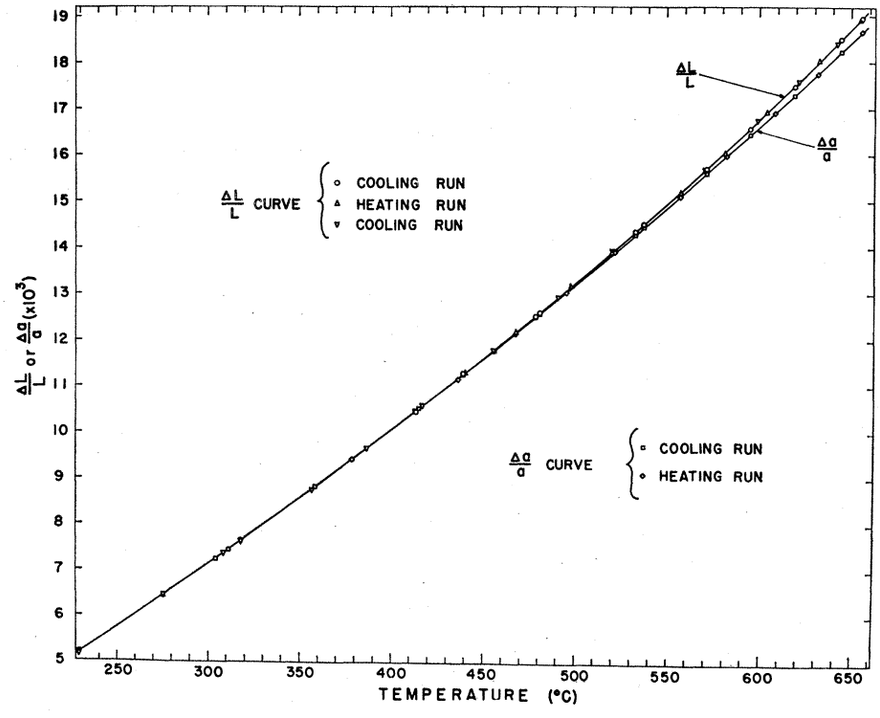

Fig. 5. Measured values of the fractional change in length and lattice parameter as a function of temperature in the case of aluminum. The specimen expands more rapidly than the unit cell, as is to be expected if vacancies are the predominant defect. [After Simmons and Balluffi (*16*)]

in the case of aluminum. It may be noted that E_f/kT_m is much less constant than E_f/Q. This suggests that the appearance of vacancies alone is not a critical factor in determining the melting temperature of the metals—in particular, it suggests that silver melts at a temperature substantially lower than copper or gold.

The values of the energies of formation and migration are in the general range expected from the theoretical treatment that Huntington and I developed.

Quenching-In of Vacancies

During the mid-1950's, Koehler, Kauffman, and Bauerle (*18*) developed techniques for cooling wires of gold, and ultimately of other metals, so rapidly that the density of vacancies at the temperature T_q from which the quenching starts is frozen in. The presence of such frozen-in vacancies has been detected by several methods: (i) by their contribution to the electrical resistivity at low temperatures (for example, 80°K); (ii) by their contribution to the macroscopic volume of the specimen; (iii) by the energy released when they are allowed to migrate and coagulate.

Figure 6 shows the logarithm of the extra resistivity $\Delta\rho$ when plotted as a function of $1/T_q$. The linear relation in the diagram, which is the standard Boltzmann plot, supports the view that the equilibrium density of vacancies at temperature T_q is governed by a function of the type given in Eq. 1. The slope of the line provides a value for E_f, the energy of formation.

Figure 7 shows the exponential decay with time of the extra resistivity at 60°C in a specimen which has been quenched from 700°C. This behavior of the decay is found in all specimens quenched from temperatures below 700°C and shows that, for the material used, the vacancies die at fixed sinks when the density of vacancies is low. Such decay is not found in specimens which are quenched from higher temperatures—that is, when the concentration is higher; instead, the decay is more rapid. This result shows that the vacancies no longer die at fixed sinks but condense to form clusters, which ultimately collapse. In other words, the vacancies generate their own sinks. The annealing occurs at a convenient rate for experimental work near room temperature in gold, as one might expect from the fact that the activation energy E_m is near 1 ev (see Table 2). Incidentally, the value of E_m as determined from Fig. 6 agrees with that given in Table 2 to within the limits of experimental error.

Measurements made by Bauerle (*18*) on the contraction of specimens when the vacancies are annealed make it possible to determine the ratio $\Delta\rho/\Delta V$ for vacancies. Here ΔV is the volume expansion which occurs when an atom is taken from the interior of the lattice to the surface to form a vacancy. Similarly, DeSorbo (*19*) has measured the heat evolved during the annealing of vacancies in gold and thereby has been able to determine the ratio $\Delta\rho/E_f$, employing other investigators' values of $\Delta\rho$. Table 3 shows the values of $\Delta\rho$ and ΔV obtained from these ratios when the value $E_f = 1.0$, given in Table 2, is used. It may be seen that the lattice expands by only about 0.57 times the atomic volume V_a when a vacancy is formed by taking an atom to the surface of the crystal. In other words, the lattice contracts by a volume of about 0.43 V_a when an atom is plucked out of a normal site and taken away from the crystal.

The value for the resistivity associated with 1 percent of defects, given in Table 3—namely, 1.8 μohm-cm per 1 percent, is in the general range estimated by Jongenburger and by Blatt (*15*), using relatively simple models.

Table 3. Coefficients for vacancies determined from DeSorbo's stored energy measurement in quenched gold using $E_f = 0.97$ ev.

$\Delta E/\Delta\rho$ (cal/g μohm-cm)	$\Delta\rho$ (μohm-cm/1% vacancies)	ΔV (V_a)
0.63	1.8	0.57

A careful comparison of the absolute density of defects quenched-in with those determined by equilibrium methods, as discussed earlier, shows that the former sometimes tends to be somewhat smaller than the latter, or at least gives the appearance of being smaller when values of resistivity or stored energy are used in making the comparison. The results suggest that during the cooling process a fixed *fraction* of the vacancies, essentially independent of temperature, are sometimes transformed into a state in which they do not contribute in full measure to the resistivity. The effect seems to be sensitive to the impurity content but has not yet been adequately explained. In any event, the existence of the effect causes one, at the present time, to place somewhat more reliance on the parameters determined from the equilibrium method than on those determined from the quenching experiments. On the whole, the results obtained for gold by the two methods are in close agreement.

Jackson and Koehler (*20*) have studied the rate of generation of vacan-

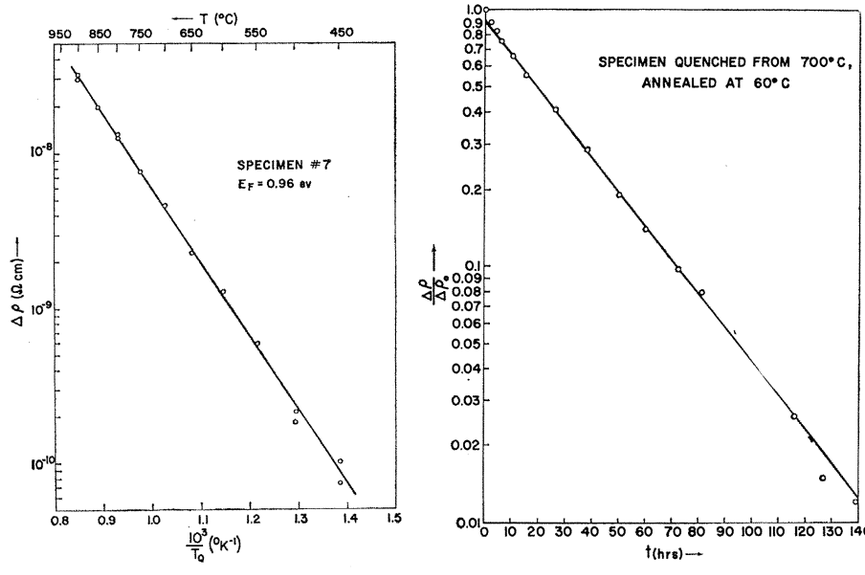

Fig. 6 (left). The electrical resistivity associated with quenched-in vacancies as a function of the temperature from which the specimen is quenched. The vertical scale is logarithmic, so the extra resistivity is governed by a Boltzmann function. Fig. 7 (right). The annealing of the quenched-in resistivity is a function of time in a specimen quenched from 700°C. The vertical scale is logarithmic, so the decay varies exponentially with time. This simple dependence is not found in specimens quenched above 700°C.

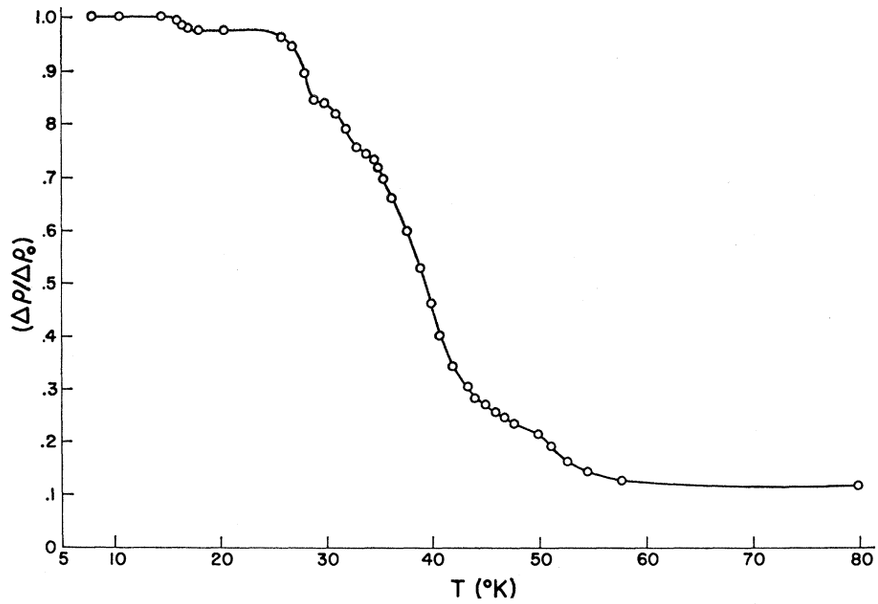

Fig. 8. The variation of the resistivity induced by electron bombardment near helium temperatures as a function of the annealing temperature. The temperature is kept at each of the points shown for a fixed time [after Corbett, Denny, Fiske, and Walter (*5*)]. This type of annealing near liquid-helium temperatures was first observed in deuteron-bombarded specimens by Cooper, Koehler, and Marx (*36*).

cies in gold in the temperature range between 650° and 800°C. Wires about 0.05 millimeter in diameter and resting in helium gas were heated to temperature electrically in a time of the order of 0.1 millisecond, held at temperature for varying times, and cooled by natural convection in a time of the order of 10 milliseconds. The investigators observed the growth of the component of electrical resistivity associated with the generation of vacancies at the elevated temperature. The rise of resistivity showed a strong, probably predominant, component which varied as $t^{1/2}$ at the start and which may arise from the diffusion of vacancies from the surface of the specimen. One would expect a linear term from internal sources if E_f/E_m is near unity or greater. It should be emphasized that the wires used in these experiments had a diameter nearly 10 times smaller than the specimens used in the quenching experiments from which the data shown in Figs. 6 and 7 were obtained. Thus, one might expect the surface to play a more important role. Nevertheless, the predominant role played by surface sources suggests that, at least in the specimens used, the density of active internal sources in the range between 650° and 800°C is much less (*21*) than the density of sinks near room temperature. The latter appears to be near 10^{15} per cubic centimeter; the former seems to be 10^{13}, or less, per cubic centimeter. The relatively low value for the density of sources at high temperatures implies that only a few points along the internal dislocation lines may act as sources in the specimens used.

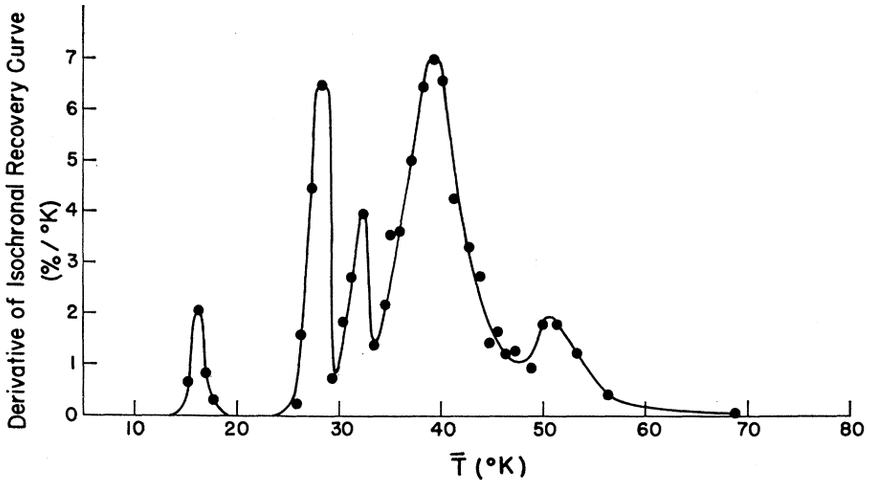

Fig. 9. The derivative of the curve of Fig. 8. The three peaks below 33°K anneal in accordance with a monomolecular reaction. The two peaks above 33°K do not. See also Fig. 10 for deuteron-bombarded specimens in which the upper two peaks are fused.

Experimental Aspects of Radiation Bombardment

As stated earlier, one may expect qualitative differences when metals are bombarded (i) with electrons near threshold, (ii) with deuterons or protons, and (iii) with neutrons. Although, in a historical sense, most of the definitive work on bombardment of a quantitative nature was first carried out with charged nucleons and neutrons, I will first describe the changes produced by electrons, since the results have relative simplicity and purity. Most of the experiments with electrons to be described have been carried out at the General Electric Research Laboratory, by Corbett and Walker and their colleagues (*5, 22*).

Electron bombardment. Figure 8 shows the annealing of the additional resistivity induced in a specimen of copper which was bombarded near liquid-helium temperature with 1.4-Mev electrons and was subsequently warmed by stages, being held at successively higher temperatures for times of equal length. It may be seen that there are several distinct annealing stages, corresponding to relatively sharp steps in the curve of Fig. 8. Figure 9 shows the derivative of Fig. 8 and accentuates the annealing steps. It should be added that some of the key features of this structure were first observed (*2, 23, 24*) in deuteron-bombarded specimens.

The three annealing peaks of Fig. 9 below 33°K are associated with simple monomolecular rate processes—a finding which suggests very strongly that they arise from the direct recombination of close vacancy-interstitial pairs, each peak belonging to a pair separated by a well-defined interatomic distance.

The two peaks above 33°K in Fig. 9 are not associated with monomolecular

decay processes. Moreover, the peak at higher temperature is very sensitive both to the purity of the specimen and to the amount of prior irradiation. It is presumed to be associated with the relatively free migration of an interstitial atom. The migration terminates when the interstitial atom meets either a vacancy, another interstitial atom with which it combines, or a foreign atom. The activation energy associated with this free migration of the interstitial is in the vicinity of 0.12 ev, as proposed by Huntington. The peak near 40°K is much less sensitive to purity and to prior irradiation. It is believed to be associated with a correlated migration of an interstitial atom about its vacancy pair which terminates when the two combine. The activation energy for this migration is the same as that associated with the peak near 50°K. The temperature at which it is observed is lower, because the interstitial makes many fewer jumps before annihilation. Clearly, the upper two peaks are closely coupled. In one case (the upper peak) the rather freely migrating interstitial "escapes" from its vacancy; in the other (the peak near 40°K) it does not. Granato (*25*) believes that the peak near 40°K exhibits structure, indicative of several types of close pairs.

It may be seen in Fig. 8 that about 90 percent of the extra resistivity has annealed by the time the temperature has reached 60°K. Sosin (*26*) has studied the structure shown in Fig. 9 as a function of the bombarding energy down to the threshold E_d, near 22 ev. As might be expected, he has found that the fraction of the total area associated with the three peaks which anneal below 33°K increases with decreasing bombarding energy, as if relatively close pairs were favored in comparison to more widely separated ones for which complete separation is possible. On the other hand, the relative amplitude of the peak farthest to the left, which anneals at the lowest temperature, *decreases* with decreasing energy and is nearly zero at threshold. He concludes that the least stable pair, which presumably is that having the smallest separation, is formed in a somewhat indirect way—for example, by an atom which is not struck in a direction for which the well-height is least.

It may be added that the annealing behavior of gold bombarded by electrons (*27*) or deuterons (*2*) appears to be somewhat different from the annealing of copper in a quantitative, if not qualitative, sense. The annealing is distributed more diffusely. This topic deserves further study.

Deuteron bombardment. Specimens which have been irradiated with deuterons to achieve a much higher density of vacancy-interstitial pairs than that achieved in the experiments with electrons display the same pronounced set of annealing peaks below 48°K. Figure 10 shows the annealing peaks for copper and silver obtained by Palmer, Magnuson, and Koehler (*23*) in a scale in which the activation energy rather than the temperature is used for the horizontal coordinate. The peak associated with the completely free migration of interstitials, to be found near 54°K in Fig. 9, is not separable in the experiments with deuterons because of the higher density of defects and hence the shorter range of migration before capture.

Additional investigations with deuteron-bombarded specimens of copper have revealed the following facts.

1) The macroscopic and lattice expansion coefficients change by the same fractions during irradiation to within the limits of experimental error (*28, 29*). Thus, interstitial atoms and vacancies are produced in equal numbers. The corresponding contractions are the same during the annealing stages to temperatures near 100°K. It follows that the two defects disappear pairwise in this range.

2) The measurements of the fall in resistivity and of the recovery of expan-

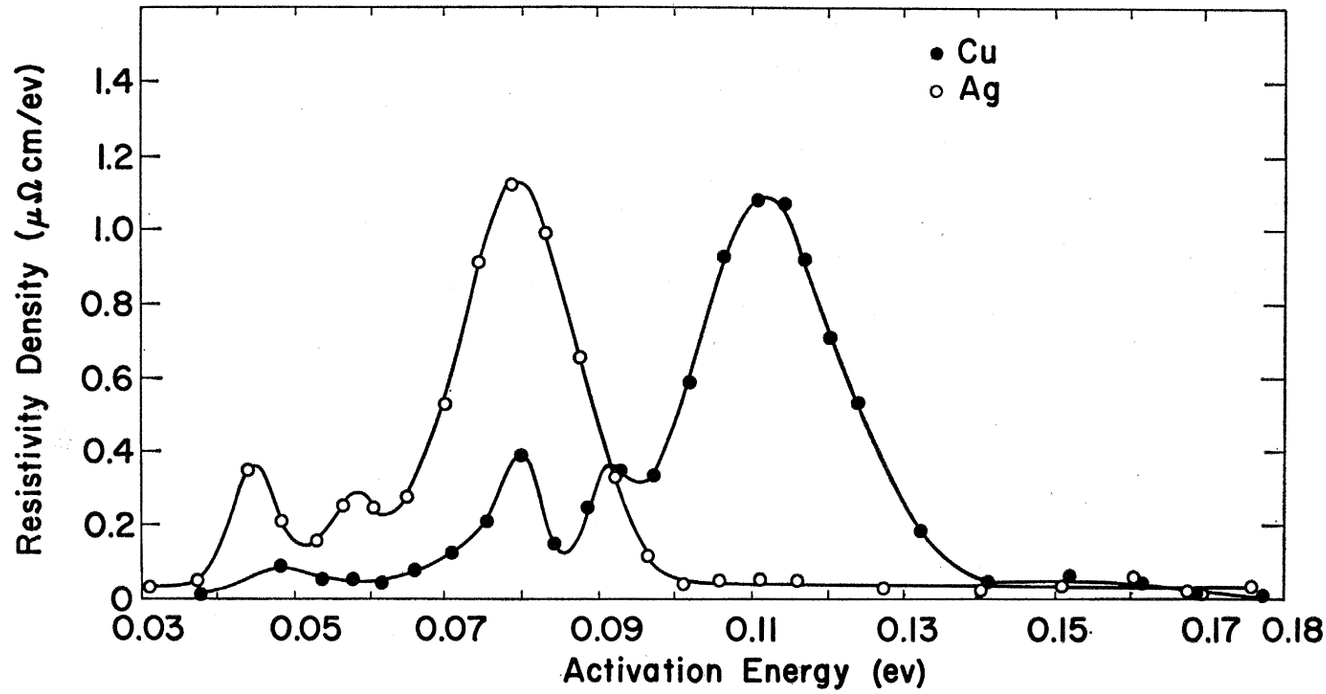

Fig. 10. The activation peaks for deuteron-induced electrical resistivity produced near liquid-helium temperatures (see also Fig. 9). The two curves are for copper and silver. [After Magnuson, Palmer, and Koehler (*23*)]

sion during annealing are correlated to within the limits of experimental error (see Table 4). This shows that the agent which anneals out affects both quantities in the same relative way below 60°K.

3) The energy released during annealing after bombardment with deuterons at liquid-helium temperatures has been measured by Nilan and Granato (*30*). It is found that the stored energy is released in a stepwise manner and yields peaks which coincide almost exactly with those shown in Fig. 10. Moreover, the ratio of the stored energy to the resistivity is found to have the value 7.1 calories per gram per microohm-centimeter. This may be compared with the value 0.63 for vacancies in gold, given in Table 3. Assuming that the value for vacancies in copper is similar to that in gold, we may conclude that the ratio $\Delta E/\Delta\rho$ for interstitials is considerably larger than the value for vacancies.

Table 4. Observed fraction of damage during annealing at temperatures below 60°K in investigations with deuteron-bombarded specimens of copper.

Lattice parameter (Simmons and Balluffi, *16*)	$\frac{\Delta a}{\Delta a_o} = 0.62 \pm 0.02$
Length (R. Vook and Wert, *29*)	$\frac{\Delta L}{\Delta L_o} = 0.65 \pm 0.04$
Resistivity (Magnuson, Palmer, and Koehler, *23*)	$\frac{\Delta \rho}{\Delta \rho_o} = 0.64 \pm 0.06$

Table 5. Estimate of resistivity of displacement pairs in copper from stored energy and from volume change.

$\Delta E/\Delta\rho$	= 7.1 cal/gm per μohm-cm
$\Delta E/\Delta V$	= 4.2 ev per V_a
If E_p	= 5.0 ev, $\Delta\rho_p$ = 2.5 μohm-cm per 1%
If ΔV_v	$= -0.5\ V_a$
ΔV_i	$= 1.7\ V_a$
ΔV_p	$= 1.2\ V_a$
$\Delta\rho_p$	= 2.5 μohm-cm per 1%

Table 6. Observed and calculated fractions of atoms displaced in copper, when $\Delta\rho$ (1 percent) is assumed to be 3.0×10^{-6} ohm-cm. Density of bombarding particles in each case, 10^{17}/cm^2.

Bombarding particles		C_{obs}
Kind	Energy (Mev)	
Electrons	1.4	$2.2 \times 10^{-6} = C_{calc}/\ 2.7$
Deuterons	9	$6.7 \times 10^{-4} = C_{calc}/\ 6.0$
Neutrons	~0.8	$4.0 \times 10^{-6} = C_{calc}/18$

These measurements make the analysis given in Table 5 possible. If it is assumed that the energy required to form a vacancy-interstitial pair is about 5.0 ev (a reasonable calculated value), it is found from the measured ratio of the stored energy to the electrical resistivity that the electrical resistivity associated with 1 percent of pairs is about 2.5 μohm-cm. The same value is found if it is assumed that the change in volume associated with production of a pair is 1.2 V_a. In this connection Tewordt (*14*) has estimated, on theoretical grounds, that the shrinkage which occurs in copper when an atom is removed from the lattice lies between 0.45 and 0.53 V_a, whereas the expansion which occurs when an external atom is forced into an interstitial position lies in the range from 1.67 to 2.01 V_a. Thus, according to his calculations, the expansion associated with production of a vacancy-interstitial pair should lie in the range from 1.0 to 1.5 V_a. Taken as a whole, the combination of experimental and theoretical analyses implies that the electrical resistivity associated with 1 percent of vacancy-interstitial pairs is about 3.0 μohm-cm, a value of the magnitude derived by Blatt (*15*) through simple theoretical analysis.

It may be added that over 60 percent of the extra resistivity produced by deuteron bombardment at liquid-helium temperature anneals by the time a relatively pure specimen has been heated to 60°K.

During bombardment with deuterons, the increase in electrical resistivity varies linearly with flux when the density of defects is in the vicinity of 10^{-5}. However, the resistivity curve appears to bend over when the density of defects becomes substantially larger. This effect, known as radiation annealing, has not yet been adequately explained and merits further study. Recent work by Herschbach (*31*) and Koehler, using deuterons with gold and aluminum foils, suggests that the annealing effect actually may be a purely thermal one.

Neutron bombardment. A group at Oak Ridge National Laboratory has made careful studies (*32*) of copper bombarded with neutrons at liquid-helium temperatures. The recovery does not show the same sharp steps that are found in specimens bombarded by electrons or deuterons. The annealing is more nearly continuous and more gradual. Moreover, the fraction which can be annealed at a temperature of 60°K is only of the order of 40 percent. Furthermore, the ratio $\Delta E/\Delta\rho$—the ratio of the energy released to the decrease in resistivity—is substantially lower than the value found for deuterons, being between 2.5 and 3.8 calories per gram per microohm-centimeter instead of 7.1. In fact, the value is very close to that found in specimens which have been irradiated with deuterons near 100°K, where the interstitial should be mobile as soon as it is formed. The results strongly suggest that the migration of interstitial atoms and presumably other rearrangements occur in the relatively large heated zone formed by each primary displaced atom (see Table 1 and Fig. 3). In this connection, Brinkman (*33*) has proposed that the region of the crystal in which the primary atom displaced by a typical fission neutron deposits its energy is radically rearranged, and that part of the disorder is quenched-in during the cooling.

Table 6 compares the concentrations of vacancy-interstitial pairs produced by equal fluxes of three types of particles. Comparison is made on the assumption that the electrical resistivity of a pair is 3.0 μohm-cm and that the resistivity retains its initial linear relation with respect to the flux curve (that is, that it corrects for possible radiation annealing). These "observed" values are also compared with the values calculated from the simple theory described in the discussion of bombardment. It may be seen that the calculated value is about 2.7 times too large for electrons, about 6 times too large for deuterons, and about 20 times too large for neutrons. The overestimate of the number of displaced pairs for electrons implies that the probability of ejection is substantially less than unity when the best threshold value, E_d, of 22 ev is exceeded, in keeping with the supposition of Fig. 2. On the other hand, the relatively lower value of C_{obs} for deuterons suggests that, in addition to the effect observed for electrons, there is an additional annealing produced by the thermal agitation which accompanies the production of displacements (see Table 1). This effect presumably is much more accentuated for neutron bombardment; in fact, the relatively close similarity of the deviations between the observed and the calculated values for deuterons and for neutrons probably is a coincidence since, as we saw above, there is substantial evidence that the residual dam-

age is qualitatively different in the two cases. It is by no means evident that the observed resistivity in the neutron-bombarded specimens can be ascribed primarily to pairs of interstitials and vacancies.

Problems of the Future

There are a number of problems which provide interesting and important avenues for future investigations. Three of these are as follows:

1) *The role of focusing collisions.* There is little doubt that such collisions can produce highly interesting effects even if they do not play a major role in the normal damage properties described earlier. It would be useful to study the disordering produced in ordered lattices of atoms having nearly equal mass, such as CuZn, when they are bombarded with electrons near the threshold energy.

2) *Factors governing the clustering of interstitial atoms.* The fate of freely wandering interstitial atoms provides interesting food for speculation. Experiments on the annealing of deuteron-bombarded material imply quite strongly that such wandering interstitials can combine with other interstitials to form diatomic pairs and, ultimately, larger interstitial clusters. It would be highly desirable to know more about the properties of such diatomic clusters. In this connection it may be noted that Seeger (*34*) has proposed that the highly mobile interstitial is not that shown in Fig. 4 but is a unit obtained by crowding an extra atom into a densely packed row of atoms extending along a (110) row of atoms. Such a unit is sometimes called a "crowdion." Apparently it is Seeger's opinion that one of the interstitial configurations shown in Fig. 4 is stable relative to the other by an energy near 0.6 ev. The crowdion is metastable relative to this more stable interstitial configuration but eventually reverts to it, producing an interstitial which is not mobile below 100°K. The evidence for this viewpoint is quite indirect, arising from studies of plastically deformed metals which probably contain a wide variety of defects. Granato (*35*) has shown that the observed concentration-dependence of the high-temperature peak in Fig. 9, presumably associated with the wandering interstitial, corresponds to a random walk in three dimensions but not in one dimension.

3) Experiments show that ordered lattices such as Cu_3Au disorder much more during deuteron and neutron bombardment than can be explained by the simple theory of displacements alone. Several explanations of this effect have been given—for example, that it is due to the influence of dislocations generated in the heated zone about a dislocation, to focusing collisions, or to the migration of interstitials or vacancies in the thermal pulse accompanying the production of a primary displacement.

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