experimental results rule out crowdion migration, as had been done in the literature.

Even if we leave aside the case of nickel, where we have fairly direct evidence for interstitial migration in stage III, I feel that the observed kinetics after electron bombardment and cold-work do not allow any simple explanation other than interstitial migration. *E.g.*, in gold we have analysed the kinetics quantitatively, and have found the right magnitude for interstitial-vacancy recombination cross-section. I do not think that these results could be explained by the break-up of interstitial clusters or by divacancy migration. None of these processes would give second-order kinetics. This has been concluded earlier by R. Walker, who had felt compelled to attribute stage III to vacancy migration. Of course, this possibility is now ruled out by the assignment of vacancy migration to stage IV.

Hasiguti, R. R.: It is almost certain that an interstitial is trapped by an impurity atom. Where do you assign the annealing of trapped interstitials?

Seeger, A.: For interstitial impurity interaction, I should like to refer to a paper by P. Simson and R. Sizmann: Z. Naturforschung **17a** (1962) 596. These authors show for nickel that in pure material stage III is large and stage IV very small, whereas the opposite is true for impure material. The interpretation is that in impure material the interstitials get trapped before they reach vacancy. Annihilation occurs by the migration of the vacancies. I believe that this explanation is true in general.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

The Interstitial Configurations in the Noble Metals

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The annealing spectrum observed in the region from 10 to 60°K in deuteron irradiated copper and silver are similar, that in silver being displaced towards lower temperatures. Recent experiments show that the annealing spectrum in electron irradiated gold is qualitatively different from that of copper and silver. It is therefore suggested that the interstitial which takes part in annealing in copper differs from that in gold. More specifically it is suggested that the interstitial is a cube centered interstitial in copper and a split (100) interstitial in gold. Reasons for this assignment and consequences of it are examined.

In spite of considerable experimental and theoretical work, the equilibrium configuration of the interstitial defect is not definitely established in the noble metals. Recent experiments by Ward and Kauffman[1] and by Bauer, de Ford, Kauffman and Koehler[2] have established that the annealing peak structure observed in gold is different from that found in copper and silver (see Magnuson, Palmer and Koehler[3], also Nilan and Granato[4] and Corbett, Smith and Walker[5]). This experimental information

* Research supported by the United States Atomic Energy Commission.

suggests that the equilibrium configuration of the interstitial is different in gold from its configuration in copper and silver.

In the present note we would like to suggest that the arrangement of the interstitial which forms one of the members of a close interstitial vacancy pair in copper and silver is the cube centered interstitial shown in Fig. 1a. In gold we suggest that the configuration associated with the close pair peaks is the split configuration shown in Fig. 1b. These arrangements were first described by Huntington[6].

Consider first the IV pairs which use cube centered interstitials. In this case (see Fig. 2) the interstitials at increasing distance from the vacancy are labelled I_1, I_2, I_3, I_4, etc. The distance between the interstitial and the vacancy is given in Table I together with the number of such equivalent interstitial locations which exist for each vacancy. In Table I, a is the cube edge. There are several notable features of this sequence. Suppose that the activation energy required for the recombination of a given close IV pair is a monotonically increasing function of the IV separation. Then the annealing spectrum would probably split into groups, each group containing three annealing peaks. The detailed calculations of Tewordt[7] and of Bennemann and Tewordt[9] suggest that the first group of three is likely to be un-

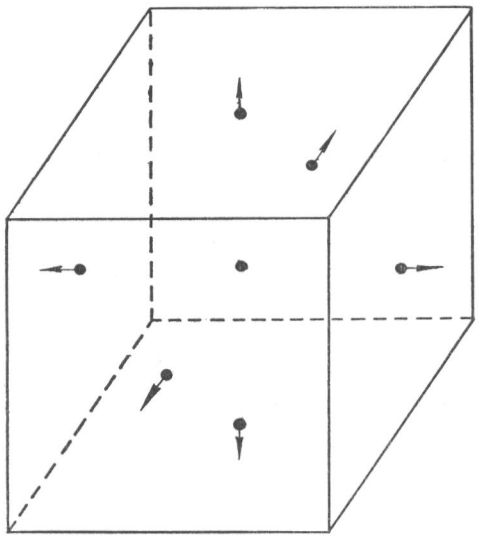

Fig. 1a. The cube centered interstitial.

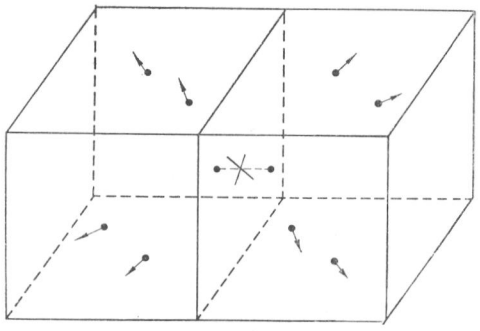

Fig. 1b. The split interstitial (after Huntington[6])

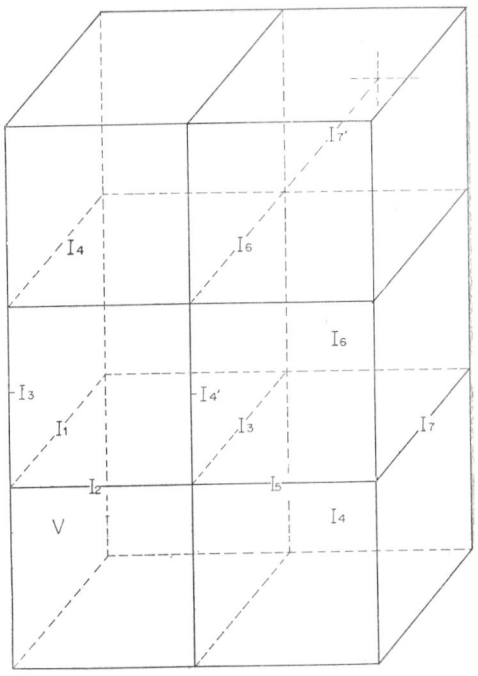

Fig. 2. Cube centered interstitials near a vacancy in a face centered cubic metal.

Table I. Spacings and degeneracy of IV pairs using a cube centered interstitial

	IV Distance	Number of Equivalent I_i Positions
I_1	$a\sqrt{1/4} = 0.50a$	6
I_2	$a\sqrt{3/4} = 0.866a$	8
I_3	$a\sqrt{5/4} = 1.119a$	24
I_4 and I_4'	$a\sqrt{9/4} = 1.500a$	4 and 24
I_5	$a\sqrt{11/4} = 1.660a$	24
I_6	$a\sqrt{13/4} = 1.803a$	24
I_7 and I_7'	$a\sqrt{17/4} = 2.062a$	24 and 24
I_8	$a\sqrt{19/4} = 2.179a$	48
I_9	$a\sqrt{21/4} = 2.291a$	48
I_{10}	$a\sqrt{25/4} = 2.500a$	

stable. If so, I_4V, $I_{4'}V$, I_5V, and I_6V form the group of three peaks observed in copper below 35°K. Note that I_4V and $I_{4'}V$ have the same separation, but (see Fig. 2) the two have a different local configuration and need not have the same activation energy for annealing. One would of course expect that the two annealing energies would probably not be very different. The same situation occurs at I_7V and $I_{7'}V$. The gaps in the spectrum occur because 7, 15, 23, 31, etc. cannot be obtained by adding the squares of three integers. Nilan and Granato[4] showed that the large peak (peak D) has structure in copper and recently Herschbach[9] has reanalyzed the Magnuson, Palmer and Koehler[3] data to show that the large peak in both copper and silver has fine structure. Granato[10] has pointed out that peak D should probably be regarded as a superposition of several close pair peaks since its position is not a function of concentration, since it shows structure, and since it is too wide for a single first order peak. Thus peak D could well arise from the recombination of I_7V, $I_{7'}V$, I_8V and I_9V. Note that the change in separation in going from one such pair to the next is less than 6% of the pair separation itself so that the activation energies for annealing are probably not very different. The increase in separation in going from I_9V to $I_{10}V$ is 8.4% and the $I_{10}V$ separation is 9.0 Å for copper. Conceivably I_{10} is a free interstitial and moves at random when thermally activated.

Consider next the spectrum associated with split interstitials. Table II gives the spacings and the degeneracies of the various IV pairs if the split interstitial is used. In this case the locations available for the center of gravity of the split interstitial are all of the lattice points of the f.c.c. lattice in contrast to the previous case in which the interstitials can occupy the lattice points of a b.c.c. lattice. Notice that in the case of the split interstitial there are no missing members in the sequence. In addition since for each location of the center of gravity of the split interstitial there are three possible orientations of its axis the multiplicity of possible annealing energies is considerably increased. We have supposed that the activation energy for annealing is some function of the separation of the IV pair and also the angle ϕ_i which the axis of the split interstitial makes with the line joining the vacancy and the center of gravity of the interstitial. Hence the last column of Table II gives the number of different activation energies for recombination for each pair separation.

Suppose that one assumes that first three separations correspond to unstable IV pairs; then in the split interstitial spectrum there are 23 different annealing processes associated with separations less than $2.5a$ whereas in the case of the cube centered interstitial there are only 6 close pair recombination peaks or at most 8 if I_4V differs from $I_{4'}V$ and I_7V differs from $I_{7'}V$. This difference

Table II. Spacings degeneracy and different orientations of IV pairs using the split interstitial

	IV Spacing	Number of Equivalent I_i Positions	Different Orientation at Each Site
I_1	$a\sqrt{1/2}=0.707a$	12	2
I_2	$a\sqrt{2/2}=1.000a$	6	2
I_3	$a\sqrt{3/2}=1.222a$	24	2
I_4	$a\sqrt{4/2}=1.414a$	12	2
I_5	$a\sqrt{5/2}=1.580a$	24	3
I_6	$a\sqrt{6/2}=1.732a$	8	1
I_7	$a\sqrt{7/2}=1.870a$	48	3
I_8	$a\sqrt{8/2}=2.000a$	6	2
I_9 and $I_{9'}$	$a\sqrt{9/2}=2.122a$	12 and 24	2 and 2
I_{10}	$a\sqrt{10/2}=2.237a$	24	3
I_{11}	$a\sqrt{11/2}=2.343a$	12	2
I_{12}	$a\sqrt{12/2}=2.447a$	24	3

in the number of peaks and also the existence of gaps in the cube centered spectrum are features in qualitative agreement with the existing data for copper, silver and gold.

The suggested interpretation is not in disagreement with Sosin's[11] and Chaplin and Shearin's[12] measurements of the changes in the relative amounts of the various close pairs in copper with energy of the incident electrons. Sosin found that as the bombarding energy increases from 0.46 MEV to 0.97 MEV peak C decreased from 34% of the total damage to 10% indicating that peak C is associated with a defect which is easily produced near threshold. The above interpretation assigns peak C to the recombination of I_6V. In this case the interstitial is located nearly along a (110) direction relative to its vacancy; hence focussing collisions should be effective for the production of I_6V. Gibson[13] and coworkers have given calculations which demonstrate the importance of (110) focussing in damage production in f.c.c. crystals for energies near the threshold for displacement. I_4V, $I_{4'}V$ and I_5V are not as likely to be made by focussing at low energies since the line joining the interstitial and the vacancy is not along or near the (110) direction. The I_4V pair should be sensitive to (100) focussing.

Physically one would expect the split interstitial to be more likely in gold than in copper and silver. The ratio of half the smallest interatomic distance d to the Pauling ionic radius r_0 is 1.33 for copper, 1.14 for silver and 1.05 for gold. Thus in gold the closed shells associated with nearest neighbors nearly touch even in the perfect crystal. Hence introducing an interstitial into gold should produce larger distortions and a larger energy increase than in copper. One would expect that for large values of d/r_0 (say for copper) the cube centered interstitial would be the interstitial configuration of lowest energy but as d/r_0 decreases, *i.e.* as the degree of local distortion increases, one should arrive at a situation in which the split interstitial is the most stable configuration. This speculation is in agreement with the detailed calculations of Huntington[6] who used a soft potential (a) and a hard potential (b). Table III shows first the closed shell repulsive energy for the cube centered and the split interstitial and then the total energy including terms resulting from electronic interaction. Note that in both cases the split interstitial tends to become more stable as the potential is changed from soft to hard. A calculation of Tewordt[7] shows that the largest volume increase of the specimen occurs in the case of the hard potential thus justifying our association of the hard potential with gold.

It should be noticed that in considering close IV pairs the presence of a vacancy near the interstitial will of course introduce an asymmetry into the surroundings which should favor at least one of the split interstitial configurations over the cube centered arrangement. Hence, in the case of gold even though a portion or all of the annealing spectrum is associated with split interstitials it is not certain that an *isolated* interstitial in gold is a split interstitial. In fact it is possible that the interstitials in the closest pairs in gold are split whereas those in the ones having large IV separation are cube centered.

Even the fact that the recombination energies in silver are lower than the corresponding energies in copper is consistent with the present suggestion since in silver d/r_0 is smaller than in copper and hence the difference between cube centered configuration and the split configuration should be smaller than in copper. Note that this energy difference is associated with the migration energy in the case of the cube centered interstitial[6].

The annealing experiments on irradiated

Table III. The influence of the repulsive potential of the interstitial configuration (after H. B. Huntington[6])

Potential	Repulsive Energy (ev)		Total Energy (ev)	
	Cube Centered	Split	Cube Centered	Split
Soft (a)	4.34	4.43	5.14	5.07
Hard (b)	4.85	4.74	6.09	5.82

noble metals definitely show a different annealing spectrum for gold than for copper and silver. This unexpected result demonstrates that small changes in the nature of the material can have a very real influence on the nature of the defects produced by irradiation. It is this surprising sensitivity which makes detailed calculations so very difficult.

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DISCUSSION

Blewitt, T. H.: I should like to agree with Dr. Koehler's remark that the annealing of gold should be treated with caution. R. Coltman of Oak Ridge has recently found that appreciable annealing occurs as low as 3.8°K in neutron irradiated gold. It would therefore seem somewhat dangerous to assume that the first 4 peaks are I A thru I E when additional peaks may exist.

Koehler, J. S.: Concerning the behavior of pure gold during Stage I one would like to have the following data:

(a) The minimum energy E_d required to displace a gold atom.

(b) The concentration dependence of the Stage I peaks during isochronal annealing. The Bauer and de Ford data shows that many of the peaks occur at nearly the same temperature as the Ward and Kauffman data although the concentration of damage was larger in the Bauer and de Ford case by a factor of 24. There is good agreement between the temperature at which the largest annealing rates occurred for most peaks, but in a few cases one group observes a peak missed by the other group.

Bauer and de Ford	Ward and Kauffman
$\Delta\rho_0 = 8.5\times10^{-9}$ ohm-cm	$\Delta\rho_0 = 3.5\times10^{-10}$ ohm-cm
T_0=(not observed)	T_0=14.5°K
T_1=17.0°K (large)	T_1=18.3°K (large peak)
T_2=20.5°K	T_2=(not observed)
T_3=22.5°K	T_3=22.5°K
T_4=26.0°K	T_4=28°K
T_5=40.0°K	T_5=42°K

$\Delta\rho_0$ is the total resistivity increase introduced by irradiation.

Thompson, D. O.: How does nickel fit into the relative scheme given for copper, silver, and gold?

Koehler, J. S.: In the case of nickel, the electronic structure differs from the noble metals in that holes exist in the *d* shell. At present we do not know how these holes influence the properties of lattice vacancies or interstitial atoms. Therefore, I do not know how the properties of nickel containing defects are related to those of the noble metals. It would be of value to find this out.

Seeger, A.: I should like to mention that the postulate of a different stable interstitial configuration in copper and gold is highly speculative. While I agree that if there were really a difference, it would be in the sense Prof. Koehler proposed, our own calculation, (Seeger, Mann and v. Jan: J. Phys. Chem. Solids (1962)) have failed to

show the postulated effect. We considered a series of possible potentials, both soft and hard ones, and always found the dumb-bell configuration to be the more stable one.

I should further like to ask what stage and what activation energy the Urbana school ascribes for the free migration of interstitials in gold?

Koehler, J. S.: The initial calculations on lattice vacancies in copper by Huntington and Seitz and on the interstitial by Huntington were so well supported by the experimental data that one hoped that further calculations would give all of the properties of the point defects in the noble metals. Unfortunately this is not true. Actually, the calculations are able to give a rough idea of what the major features of point defects are but at present they can give none of the fine details. For example, all calculations on copper give the migration energy of the interstitial to be smaller than the migration energy of a lattice vacancy, but there are wide variations in the resulting value of the interstitial migration energy. Huntington (Phys. Rev. **91** (1953) 1092) gave $E_M{}^I = 0.17 \pm 0.10$ eV Seeger, Mann and Jan (J. Phys. Chem. Solids **23** (1962) 639) found $E_M{}^I = 0.50 \pm 0.05$ eV.

There are good reasons for being rather cautious about the accuracy of the calculation of the properties of point defects at present. Some of these reasons are listed below:

(a) The best calculation to date of the cohesive energy of copper gives a result which is too low by about 30% (Kambe: Phys. Rev. **99** (1955) 419).

(b) The closed shell repulsive potential is not well known. Even if one assumes a certain form for the potential, then the constants which appear in the expression are not completely determined by the experimental data. (E. Mann and A. Seeger: J. Phys. Chem. Solids **12** (1960) 314).

(c) Most of the calculations do not consider the electronic contributions to the energy very carefully. Huntington did attempt to consider electronic contributions to the formation energy of interstitials of various shapes. Assuming a uniform electron distribution, he found that electrical interactions added 0.80 eV to the closed shell repulsive terms in the case of the cube centered interstitial; the electrical interactions added 0.64 eV in the case of the ⟨100⟩ split interstitial. Huntington also found that the contributions from the electrical interactions dropped by 0.89 eV if the electrons were allowed to redistribute themselves in the cube centered case. He did not perform such a calculation for the split interstitial. Thus far no one has done a self-consistent calculation in which both the ions and the electrons are allowed to move in seeking the defect configuration of minimum energy.

Finally the formation energy of an interstitial is so large that to obtain any accuracy on a calculation of $E_M{}^I$, one must have extremely high accuracy in the formation energy. For example, Seeger, Mann and Jan calculate a formation energy for the split ⟨100⟩ interstitial of 2.74 eV and a migration energy of 0.50 eV. This means that if the migration energy is to be accurate to 50%, then the two formation energies have to be accurate to 4.6%, which is a difficult requirement.

In gold thus far no one has located a peak in Stage I annealing whose position (in temperature) is concentration dependent. We believe that a concentration dependent peak will be found somewhere below 80°K. Thus we believe in gold that the migration energy associated with free migration of an interstitial is probably less than 0.3 eV.

Lazarus, D.: It may be significant to note that reasonably non-controversial studies of diffusion and quenched resistivity in copper, silver, and gold reveal that the formation energy of a vacancy in gold is significantly less than that in copper and silver. Since the electronic contributions to the formation energy would be expected to be almost identical, particularly for Au and Ag, where the lattice are almost identical, the difference might be mostly attributable to a larger negative contribu-

tion for gold due to elimination of a larger closed-shell repulsion term on formation of a vacancy. Thus, as suggested by Professor Koehler, the closed-shell terms may indeed be more important for gold than for copper or silver.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE
JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT III, 1963

Theory of Point Defect Annealing in Metals*

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The kinetics of the annealing of point defects, either by migration to sinks or by recombination, is complicated by the occurrence of a variety of simultaneous reactions. An extensive theoretical study of annealing processes is in progress at Brookhaven based on the isolation and combination of simple kinetic steps. When analytic solutions could not be found, computer solutions have been used to obtain useful approximations and to determine their regions of validity. Two migration reaction schemes have been studied; the simultaneous annealing of single and divacancies, and the annealing of single vacancies with impurity trapping. Three recombination reactions have been investigated; vacancy-interstitial annihilation with interstitial migration to sinks, di-interstitial formation, and interstitial trapping at impurities.

Introduction

Point defects tend to anneal out of any crystal that contains more defects than the thermodynamic equilibrium concentration, provided they have sufficiently high mobility to do so. Vacancies and interstitials can anneal out by migration to sinks and by recombination with each other. It is also known that single point defects can cluster or become attached to impurity atoms. The investigation of the kinetics and the measurement of the corresponding activation energy for the annealing of point defects are therefore complicated by the occurrence of a variety of simultaneous reactions. An extensive theoretical study of annealing processes is in progress at Brookhaven based on the isolation and combination of simple kinetic steps. When analytic solutions to the rate equations could not be found, computer solutions have been used to obtain useful approximations and to determine their regions of validity. The various migration and recombination reactions that have been studied are listed in Table I.

* Supported in part by the U. S. Atomic Energy Commission.

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Migration Reactions

If a defect of only one type is present, recombination reactions do not take place and annealing occurs by migration to sinks. Although the kinetic formulations to be discussed are valid for any defect, the discussion will be given in terms of vacancies because there is a great deal of experimental information on quenched-in vacancies.

In quenching experiments only vacancies and their simple clusters are introduced. The simplest idealized model of the subsequent annealing process involves the simultaneous migration of single and divacancies and the formation and decomposition of the divacancies (Case I, Table I). The overall annealing process is kinetically complex and exhibits five regions of different kinetic behavior as a function of annealing temperature, as illustrated in Fig. 1. The different regions arise from the different temperature dependence of the various K's. The range