73-85

Note: This is a draft of a paper being submitted for publication. Contents of this paper should not be quoted nor referred to without permission of the author(s).

COMPUTER STUDIES OF REPLACEMENT SEQUENCES IN SOLIDS
ASSOCIATED WITH ATOMIC DISPLACEMENT CASCADES

D. K. Holmes and M. T. Robinson

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION
Oak Ridge, Tennessee 37830

September 1973

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

COMPUTER STUDIES OF REPLACEMENT SEQUENCES IN SOLIDS
ASSOCIATED WITH ATOMIC DISPLACEMENT CASCADES*

D. K. Holmes and M. T. Robinson

Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830, U.S.A.

ABSTRACT

Focussed sequences of replacement collisions have been studied, especially in association with radiation damage cascades. Radiation damage events are simulated using a computer program based on the binary collision approximation. The results are averaged over a complete set of initial directions of the primary knock-on atom for each primary energy to obtain quantities of physical interest for which the effects of replacement sequences may be made explicit. The calculations are compared with recent experimental results.

*Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

1. INTRODUCTION

The concept of a focussed sequence of collisions along a close-packed row of lattice atoms was introduced by Silsbee¹ in 1957. Since then the theory has been discussed by many investigators^{2,3,4,5} but until very recently there has been no firm establishment of this physical phenomenon on an experimental basis (at least, not in metals). The purpose of the present work is to extend the theoretical study of the effects of such focussing sequences (especially those which involve mass transport along the line, i.e. replacement sequences) in association with radiation damage cascades, and to attempt to compare the results with recent experiments.

The calculations reported here are based on a computer simulation of radiation damage events. This computer program (called Marlowe) has been discussed in greater detail elsewhere.^{6,7} The most important features of the program for the present discussion are: (i) the full symmetry of the crystalline lattice is used but (ii) only binary collisions between moving atoms and stationary lattice atoms are allowed. The first point is clearly necessary if replacement sequences are to be studied; on the other hand the restriction to binary collisions makes the approximation poorer for such sequences of collisions. It is in the low energy range in which focussed replacement sequences are important; these are energies of motion of the order of 10-50 eV. In this energy region the lattice atoms have a strong interaction over distances of the order of the equilibrium lattice distance, so that a moving atom will, in general, experience significant

forces from several stationary atoms at once. Nevertheless, it is felt that with careful treatment the binary collision approximation can give valuable insight into the role of focussing events. The advantage of the binary collision approximation is that the full detail of relatively large displacement cascades in the lattice can be treated. The new feature of the Marlowe computer program which has been incorporated to assist in the present study is a statistical analysis of replacement sequences accompanying each radiation damage cascade.

A brief outline of the use of the Marlowe program for these calculations follows. For a given substance the lattice geometry is specified and the interatomic potential is chosen. Generally the latter is the Molière approximation to the Thomas-Fermi potential with an appropriately chosen screening radius. For each binary collision an inelastic energy loss is also permitted (based on the Firsov model⁸). One atom, the primary, is started with a given kinetic energy from a lattice site and the full development of the subsequent collision cascade is followed until all energies of motion have fallen below a specified value. This process is repeated for a number of cascades with the starting direction of the primary allowed to vary randomly over the full unit sphere. For the present calculations the number of such initial directions for each primary energy was usually taken to be one thousand. After the set of cascades has been calculated the program presents as output a statistical summary of the important results. For the present the most significant quantities are: (i) the total number of vacancies and interstitials produced, along with

the distribution of the separations of vacancy-interstitial pairs, (ii) the total number of replacement events (both proper and improper, see later discussion), and (iii) the distribution of lengths of replacement sequences along the principal lattice directions.

Some results of these calculations will now be discussed along with possible implications for experimental observations.

II. THE TOTAL LENGTH OF REPLACEMENT SEQUENCES AS A FUNCTION OF PRIMARY ENERGY

In the Marlowe program a replacement event is said to occur for a collision in which the energy of the moving atom falls below a certain value while the energy transferred to the stationary atom is above a specified value. These two limiting energies are not necessarily the same, but have been taken to be the same in the present calculations. The value of that energy, called the displacement energy, E_d , has mostly been taken as 5 eV for the calculations reported here. If the momentum is sufficiently low and is fairly well directed along a close-packed lattice row, a sequence of replacement collisions will result which the computer program follows in detail. The sequence terminates when the energies of both of the colliding atoms falls below E_d after the collision. At this point in the lattice the final atom in the sequence becomes an interstitial. The replacement sequences discussed in the present work are generated under very favorable circumstances. Both fcc (copper) and bcc (iron) lattices have been used, with potentials leading to good focussing along $\langle 110 \rangle$ and $\langle 111 \rangle$ rows, respectively. Qualitatively, the results reported here apply

equally well for both substances. The parameters chosen for the calculations are such that the interaction with lattice rows neighboring the given replacement sequence is neglected. The energy loss to neighboring rows has been separately calculated, and is about one-tenth of an electron volt per collision in the replacement chain. Further, the lattice is taken as perfectly static for these calculations (except for special purposes to be discussed later, for which very large thermal vibrations were introduced.) Again the effect of thermal vibration has been calculated separately; it is estimated that as much as 1.5 eV may be lost per collision in the chain due to zero-point vibrations alone.

As the cascade of displaced atoms develops from a given primary event a number of replacement sequences may result, moving in various lattice directions, mostly away from the region containing the vacancies produced. This is illustrated schematically in Fig. 1 which shows a two-dimensional array of atoms containing the displacement cascade and some resulting replacement sequences. Such replacement sequences carry an atomic mass down the close-packed lattice line, and when the sequence terminates an interstitial is formed at the end of the chain. Thus, these events carry interstitials far from the vacant lattice sites. The replacement sequences produced will vary in length depending on the energy and direction of motion of the first atom in the chain. One of the quantities which can be calculated is, then, the total length (in total number of replacement events) of such replacement sequences associated with a given cascade. When the result is averaged over a statistical distribution of primary

directions, the value calculated is characteristic of the primary energy alone (for the chosen crystal). The total length itself is not, of course, physically observable in a monatomic lattice, but the discussion of this quantity brings out some of the important aspects of replacement sequences associated with cascades, and, further, the quantity itself is of importance in consideration of order-disorder alloys. For the present discussion the "total length" will be taken to mean the total length of all sequences which involve more than two atoms. This is an attempt to concentrate on those sequences which are definitely focussed along a lattice row.

The dependence of the total length of replacement sequences on the primary energy is presented in Fig. 2. The example chosen is copper (fcc) with a screening radius⁶ of $0.0738 \text{ \AA}$ for the Molière potential. The length reported in this case is mostly (98.6%) due to $\langle 110 \rangle$ type sequences. From the results plotted it may be seen that there are two regions in energy on each side of a distinct minimum at about 50 eV. A closer examination of the details of individual cascades shows that the high and low energy regions do, indeed, involve different sets of replacement sequences. In the regions below 50 eV the principal events will be called here, for convenience, "primary replacement sequences." These sequences result directly from the action of the primary knock-on atom on a close-packed row which contains the original position of the primary. Such an event is schematically presented in Fig. 1 which shows one replacement sequence directly stemming from the primary. In the energy range above

50 eV the replacement sequences arise from collisions between moving cascade atoms and stationary lattice atoms, as represented in Fig. 1 by all of the sequences shown except the "primary replacement sequence." These secondary replacement sequences will be called here "cascade replacement sequences."

The processes occurring in the energy range below 50 eV are just those which have been extensively discussed in the literature in connection with focussing events.⁹ The primary event tends to produce a single replacement sequence and not much of an associated cascade. The most favorable energy region for long sequences is in the general region of the focussing energy which is about 13 eV for the present choice of potential for copper (for the screening radius chosen for iron, 0.0781 Å, for the calculations reported later, it is about 17 eV). In the upper part of the low energy range (20-50 eV) the sequences are initially defocussed and thus lose a large portion of their energy in the early collisions with a consequent reduction in the total length. In the lower part (below 15 eV) the initial energy is so low that the primary replacement sequence is cut off by the energy criterion before it achieves much length.

In the energy region above 50 eV it may be seen that the total length tends to rise linearly with the initial energy of the primary. This is simply a reflection of the fact that the higher energies produce larger displacement cascades with more resulting cascade replacement sequences. A simple analytical theory for this region may be constructed by assuming that the energy distribution of collisions in the cascade is essentially

that for the hard sphere model ($\sim \frac{2E_0}{E^2}$) and that a cascade replacement sequence has a certain (low) probability of being produced whenever a struck lattice atom is given an energy below, say, 50 eV. This theory shows the expected linear behavior, and may be fitted to the computer results by the choice of the probability for production of a cascade replacement sequence and of its total length.

The minimum near 50 eV results from the facts that in this energy region the primary replacement sequences are defocussing and short, while the cascades are small resulting in few cascade replacement sequences. The minimum calculated by the computer program is, in fact, much lower than would be predicted by the simple analytical model fitted to the linear high energy portion of the curve of Fig. 2. This is due to a physical effect which is not taken into account in the analytical theory. When a moving cascade atom approaches a close-packed lattice row, the very close-packed positions of the atoms makes it difficult for the moving atom to produce a cascade replacement sequence. At the higher energies, (say 100 eV or above) this merely means that the probability for sequence production is low. However, when the energy gets down near the focussing energy range, the loss of energy, which is a consequence of the interaction of the moving atom with the atoms of the row, makes it impossible to produce long sequences. This is illustrated in Fig. 3 which shows in the upper part the easy production of a long cascade sequence by a moving 50 eV atom when one atom is missing from the row. On the other hand for a perfect row, as shown in the lower part of the

figure, the same moving atom loses too much energy to be able to initiate a long sequence.

III. THE TOTAL DAMAGE AS A FUNCTION OF THE PRIMARY ENERGY

Focussed replacement sequences also have an effect on the total damage remaining as a result of a radiation damage cascade. The damage remaining, for purposes of discussing this effect, will be taken to be the number of vacancy-interstitial pairs. In order to make the results physically more realistic it is important to allow for the collapse of close pairs which will not be counted in the total damage remaining (see reference 7 for a discussion of this point). For this discussion we will concentrate on the Fe (bcc) lattice and allow the collapse of all vacancy-interstitial pairs within a radius, r_v , which is taken, for this case to be three lattice distances (cubic cell edges). The resulting damage as a function of primary energy is shown in Fig. 4 as the curve labeled "total". It may be seen that the results again show different behaviors on either side of a minimum, this time located at about 25 eV. (The different positions of the minima in energy in Figs. 2, 4, and 5 is not completely understood.) The higher energy range shows the expected behavior in that the damage rises linearly with primary energy. If the relationship is taken to be of the form $\frac{E_0}{2E_d}$, at very high energies, then $E_d \approx 33$ eV. On the other hand the damage does not fall smoothly to zero at low energies. Below 25 eV there is a distinct maximum in the damage remaining. From the previous discussion it may be suspected that this effect is due to primary replacement sequences. This is confirmed by the results shown in the second curve of Fig. 4. In

order to generate a damage curve without the effects of long replacement sequences, very large thermal vibrations were introduced into the Marlowe program (see reference 7 for a discussion of thermal vibrations as used in the computer simulation). The parameters were chosen so that the effective RMS thermal amplitude was 0.3 lattice distances. As a result of this high amplitude the lattice rows were effectively destroyed and no replacement sequences as long as three lattice distances were possible. The resulting curve in Fig. 4 shows that the damage below 25 eV is almost completely eliminated. This indicates that the onset of residual damage in the low primary energy range can be due to long (primary) replacement sequences which carry the interstitial far away from the vacancy at the lattice site of the primary atom. The difference between the two curves in the energy range above 25 eV indicates that the cascade replacement sequences are effective in adding to the stable damage produced by separating pairs to distances greater than the collapse radius. (It is to be noted that the remaining damage in either case in the low energy range is well below one pair per primary atom.)

IV. THE AVERAGE SEPARATION OF VACANCY-INTERSTITIAL PAIRS AS A FUNCTION OF PRIMARY ENERGY

As mentioned above, the Marlowe program gives a statistical analysis of the separations of the vacancy-interstitial pairs resulting from a given primary atom. This is of special interest because of recent experimental results obtained by Becker et al.¹⁰ As in the case of the total

damage, pairs below a certain separation radius, r_v , were allowed to collapse and thus were not counted in the final results. Fig. 5 shows the average pair separation as a function of primary energy. For this case the calculations were made using the Fe (bcc) lattice and the collapse radius was taken as two lattice distances. The upper curve of Fig. 5 shows the average pair separation when long replacement sequences are allowed. As before, it may be seen that the results are different in the two energy ranges above and below a minimum at about 75 eV. Again it is reasonable to suppose that the pronounced maximum in the low energy range is due to primary replacement sequences which carry the interstitial far from the vacancy. This is confirmed by the lower curve in Fig. 5 for which large amplitude (0.2 lattice distances) thermal vibrations were introduced so that replacement sequences larger than three lattice distances did not occur. As may be seen, destroying the primary replacement sequences greatly reduces the average pair separation in the low energy range. Again there is also a reduction in the average separation in the high energy range indicating that the cascade replacement sequences contribute some well separated pairs to the total damage remaining.

The results shown in the upper curve of Fig. 5 agree well with the conclusions of Becker et al.¹⁰ from their experimental work (using electron irradiation of copper crystals). (As previously mentioned the differences between the results for copper (fcc) and iron (bcc) are believed to be negligible, at least qualitatively, for the potentials used here.) These are (i) the average pair separation increases greatly as the maximum

primary energy is reduced below 30 eV. (ii) The average pair separation rises very slowly (or not at all) with rising primary energy in the range above 75 eV. (iii) The large separations observed in the vicinity of 20 eV are due to the production of long focussed replacement sequences.

V. REPLACEMENT SEQUENCES IN ORDER-DISORDER ALLOYS

In the ordered state of an order-disorder alloy a focussed replacement sequence can produce disorder by being directed along a lattice line which is itself an ordered arrangement of more than one atomic species. Such replacement disorder can add to the observed damage produced by irradiation. Again such events are of special interest because of recent experimental work on Ni_3Mn by Becker et al.¹¹ and Blewitt et al.¹² The damage events were simulated in Ni_3Mn using the Marlowe program. The damage calculated (after allowing pair collapse within two lattice distances) falls into three categories: (i) the surviving vacancy-interstitial pairs, (ii) "improper" replacements, i.e. replacements of a nickel atom by a manganese atom or vice versa, which occurred during the development of the cascade, and include single and double replacement events as well as longer replacement sequences, and (iii) the "improper" replacements which result from the pair collapse process when the "wrong" type of interstitial atom falls into a vacant lattice site. For a simplified approach, remaining pairs and "improper" replacements were taken to give equal contributions to the observable damage (e.g. electrical resistivity) (see the discussion on this point by Becker et al.¹¹). Also the weighting given to each atomic

type for purposes of starting them as primary atoms was taken to be just their atomic percentages in the lattice. This does not quite correctly reflect the experimental situation, especially in the case of thermal neutron capture damage (Blewitt et al.¹²). With these assumptions the Marlowe program can be used to calculate the ratio of the damage expected in ordered Ni_3Mn to the damage expected in pure nickel. Under the conditions of the calculation (no thermal vibrations, no interaction of replacement sequences with neighboring rows, and interatomic potentials and lattice spacing the same as for copper [fcc]) large effects of long replacement sequences may be expected.

In order to compare the calculational results with the experimental data two different primary energies were used. Becker et al.¹¹ irradiated with 1.0 to 3.0 MeV electrons; to simulate events in this range a primary energy of 50 eV was chosen. Blewitt et al.¹² used thermal neutron irradiation with a reported average recoil energy of 400 eV; for comparison with this experiment, then, a 400 eV primary was chosen. As may be seen from Fig. 2 these two primary energies correspond to quite different total lengths of replacement sequences. A 50 eV primary is near the minimum and gives a total length of about two atoms, while a 400 eV primary is well up in the "cascade replacement sequence" region and gives a total length of about 50 atoms.

The resulting damage ratios, however, do not differ so greatly. For a 50 eV primary the damage ratio (ratio of damage in Ni_3Mn to that in Ni) is about 2.6. This value agrees well with the results reported by Becker

et al.¹¹ For a 400 eV primary the ratio is about 4.7. This result does not agree well with that reported by Blewitt et al.¹² who give a damage ratio of 60. Consider an arbitrary increase in the total length of all cascade replacement sequences of length two atoms or more for the 400 eV cascade as an attempt to obtain a damage ratio of 60. The total length required would be of the order of 1000 atoms instead of the 50 atom total length calculated. (If the resistivity contribution of a vacancy-interstitial pair is taken to be twice that of an improper replacement, as may be suggested by the discussion in reference 11, a total length of the order of 2000 atoms would be required.) This is particularly striking when it is recalled that the 50 atom length was calculated under very favorable conditions for long replacement sequences; namely no losses to neighboring rows or thermal vibrations were taken into account.

REFERENCES

1. R. H. Silsbee, J. Appl. Phys. 28, 1246 (1957).
2. G. Leibfried, J. Appl. Phys. 30, 1388 (1959).
3. P. H. Dederichs and G. Leibfried, Zeit. f. Physik 170, 320 (1962).
4. J. B. Sanders and J. M. Flint, Physica 30, 129 (1964).
5. C. Erginsoy, G. H. Vineyard, and A. Englert, Phys. Rev. 133, No. 2A, A595 (1964).
6. (a) I.M. Torrens and M. T. Robinson in Radiation Induced Voids in Metals, edited by J. W. Corbett and L. C. Ianniello (U.S.A.E.C., CONF-710601, 1972) p. 739.
(b) idem, in Interatomic Potentials and Simulation of Lattice Defects, edited by P. C. Gehlen, J. R. Beeler, Jr., and R. I. Jaffee (Plenum Publ. Corp., New York, 1972) p. 423.
7. M. T. Robinson and I. M. Torrens, to be published.
8. O. B. Firsov, Zh. Eksperim. Teor. Fiz. 36, 1517 (1959) [English translation: Soviet Phys.-JETP 36, 1076 (1959)].
9. G. Leibfried, Bestrahlungseffekte in Festkörpern, B. G. Teubner, Stuttgart, 1965, Section 7.2.
10. D. E. Becker, F. Dworschak, and H. Wollenberger, Rad. Eff. 17, 25 (1973).
11. D. Becker, F. Dworschak, C. Lehmann, K. T. Rie, H. Schuster, H. Wollenberger and J. Wurm, Phys. Stat. Sol. 30, 219 (1968).
12. T. H. Blewitt, A. C. Klank, T. L. Scott, and S. T. Macrander, private communication.

FIGURE CAPTIONS

- Fig. 1. Schematic representation of a radiation damage cascade including vacancies ☺, interstitials ☻, and replacement sequences (shaded lines of atoms). At the end of each replacement sequence (not shown) is an interstitial atom.
- Fig. 2. The total length of replacement sequences associated with cascades resulting from primaries of various energies. The total length is measured in total number of atoms replaced and is given for all sequences greater than two atoms in length. The results are for copper (fcc).
- Fig. 3. The collision of a moving cascade atom with a close-packed line of lattice atoms. (a) The chain is incomplete and a long replacement sequence results. (b) The same conditions but with a complete chain and no focussed replacement sequence results.
- Fig. 4. The total damage remaining as a function of primary energy. The particular case chosen is iron (bcc) with a pair collapse radius, r_v , of three lattice distances (cubic cell edges). The damage is measured in terms of vacancy-interstitial pairs per cascade. The upper curve is for the perfect lattice, while the lower curve is for the disordered lattice (large amplitude thermal vibrations).
- Fig. 5. The average vacancy-interstitial pair separation as a function of primary energy. The particular case chosen is iron (bcc) with a pair collapse radius, r_v , of two lattice distances (cubic cell edges). The separation is measured in lattice distances. The upper curve is for the perfect lattice, while the lower curve is for the lattice disordered by large amplitude thermal vibrations.

FIG 1

FIG 2

(a) COLLISION WITHOUT PREVIOUS ATOM
IN FOCUSING CHAIN

(b) COLLISION WITH PREVIOUS ATOM
IN FOCUSING CHAIN

FIG 4

ORNL-DWG 73-8745

FIG 5