LATTICE DEFECTS in NOBLE METALS

A conference report by ***A. Sosin, J. A. Brinkman, C. J. Meechan***

ON October 16–17, 1958, an international round-table meeting on "Lattice Defects in the Noble Metals" was held at the laboratory of Atomics International in Canoga Park, California. The meeting was sponsored by the Metallurgy and Materials Branch of the Division of Research, US Atomic Energy Commission, and was chaired by Dr. George Vineyard of the Brookhaven National Laboratory.

The main purpose of the conference was to compare the various proposed models for the recovery of the physical property changes which result from the presence of lattice defects in metals. These defects are introduced into the materials by such treatments as high-energy particle irradiation, quenching, and plastic deformation. If the production of defects occurs near 4°K in copper, say, and the temperature is subsequently increased, the physical property may tend to return to its original value, i.e., *recover* in a manner such as that shown schematically in Figure 1. Five separate recovery stages occur above 20°K in such metals as copper, silver, and gold at approximately 100°K intervals. These stages have been labeled in an obvious manner.

Figure 2 schematically shows the various lattice defects which are presently believed to exist in the damaged lattice. The number of different kinds of defects has grown in recent years in a manner similar to the growth of the number of fundamental particles in nuclear physics. It is therefore not surprising that considerable controversy has arisen in the attempts to interpret these recovery stages in terms of the available defects.

Initially it was believed that the only defects which were required to explain the observed phenomena were interstitial atoms (*interstitials*), vacant lattice sites (*vacancies*), and dislocations. However, as the accumulated data increased, as the number of identified recovery stages also increased, and as the detailed character of these stages was further explored, it became clear that the final model would probably require the inclusion of more complex defects. Despite these difficulties, the number of proposed models has narrowed so that only two principal schools of thought now exist.

To appreciate the problem further, it will be helpful to look at the individual defects in more detail. Interstitials and vacancies are the simplest of the many defects. To produce these in copper one might irradiate with 0.5-Mev electrons. Consideration of the dynamics of the situation shows that electrons with energies in this range can transmit about 25 ev to an atom in a head-on collision. This usually turns out to be sufficient to knock the struck atom out of its lattice site into a nearby interstitial lattice site, leaving a vacancy behind. The details of the journey of the interstitial to its final destination are still not entirely clear. It seems correct to suppose that the atom which eventually becomes the interstitial frequently is different from the initial knocked-on atom and that a chain of billiard-ball-like collisions occurs. Each

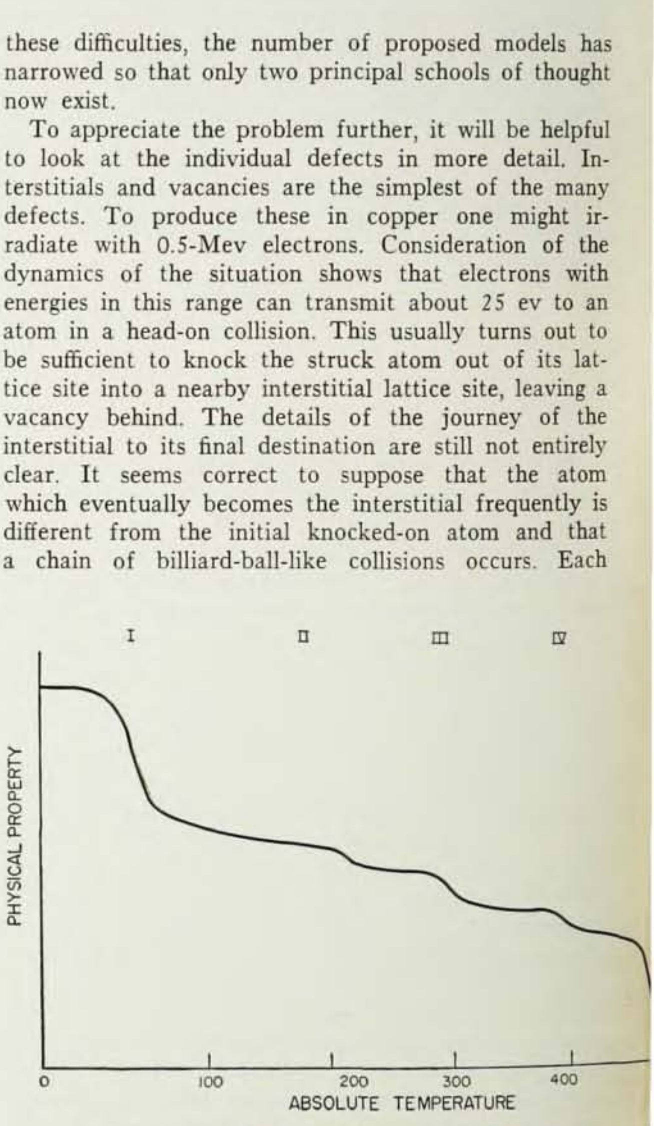


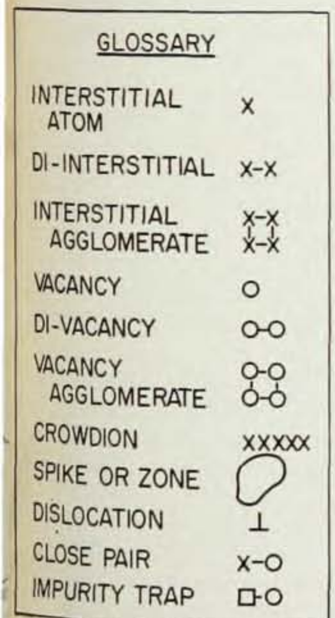
Fig. 1. Schematic representation of the recovery of a physical property of a noble metal following a sufficiently low-temperature damaging treatment. The actual details of the recovery will vary depending on the metal being considered and the type and amount of damage imposed.

The authors of this report are all members of the staff of Atomics International, Canoga Park, Calif., where the round-table meeting was held.

atom travels only one interatomic distance, transfers its momentum to the next, and replaces it on its lattice site. Such collisions are called *replacement collisions*. While the occurrence of a series of simple replacement collisions results in the production of only a single interstitial at the end of the chain and a vacancy at the beginning, an appreciably larger number of atoms exchange lattice sites. The mechanism therefore tends, for instance, to disorder ordered alloys which are irradiated with fast particles.

A somewhat more complex defect is referred to as a *crowdion*. The crowdion is visualized as N atoms approximately equally spaced along (N-1) lattice sites in a straight line, where N is, perhaps, between five and ten. There is a growing awareness of the possible importance of this defect. The conferees agreed on the need to consider *dynamic crowdions*. Dynamic crowdion motion is not too different from the billiard-ball-like chain of replacement collisions just described. The essential feature distinguishing the two is the cooperative character of the crowdion motion rather than a succession of two-body collisions. While this difference may seem rather subtle, the energy losses suffered by this crowdion travelling through the lattice are appreciably smaller so that the static defect which eventually results is more removed from the vacancy than the interstitial atom resulting from the billiard-ball-like collisions. This static defect may be an interstitial atom too; it is possible that a *static crowdion* will persist. The conferees were divided in their opinions on this matter. While it was agreed that the interstitial is a defect configuration of lower energy than the static crowdion, it still seems possible that the static crowdion may be metastable.

Interstitials and vacancies also arise in other ways. In fact, one expects equilibrium concentrations of each to be produced thermally at elevated temperatures. The reason for this is clear from thermodynamics. The equilibrium state of a system, the metal lattice in this case, is one of minimum free energy, $F = U - TS$. While the internal energy, U, is raised by the presence of any lattice defects, the entropy, S, is increased as well. The lattice defect contribution to U is proportional to the defect concentration; the contribution to S increases rapidly with concentration at very small concentrations but goes up more slowly at somewhat higher concentrations. The equilibrium concentration, i.e., that at which F has its minimum value, turns out to have a temperature dependence given by a Boltzmann factor, $e^{-Q_f/RT}$, where Q_f represents the formation energy of the particular defect. Due to the sizable strain energy associated with interstitials, the equilibrium interstitial concentration in noble metals probably never becomes appreciable. This is not true for vacancies, however, and considerable work in recent years has shown that one can



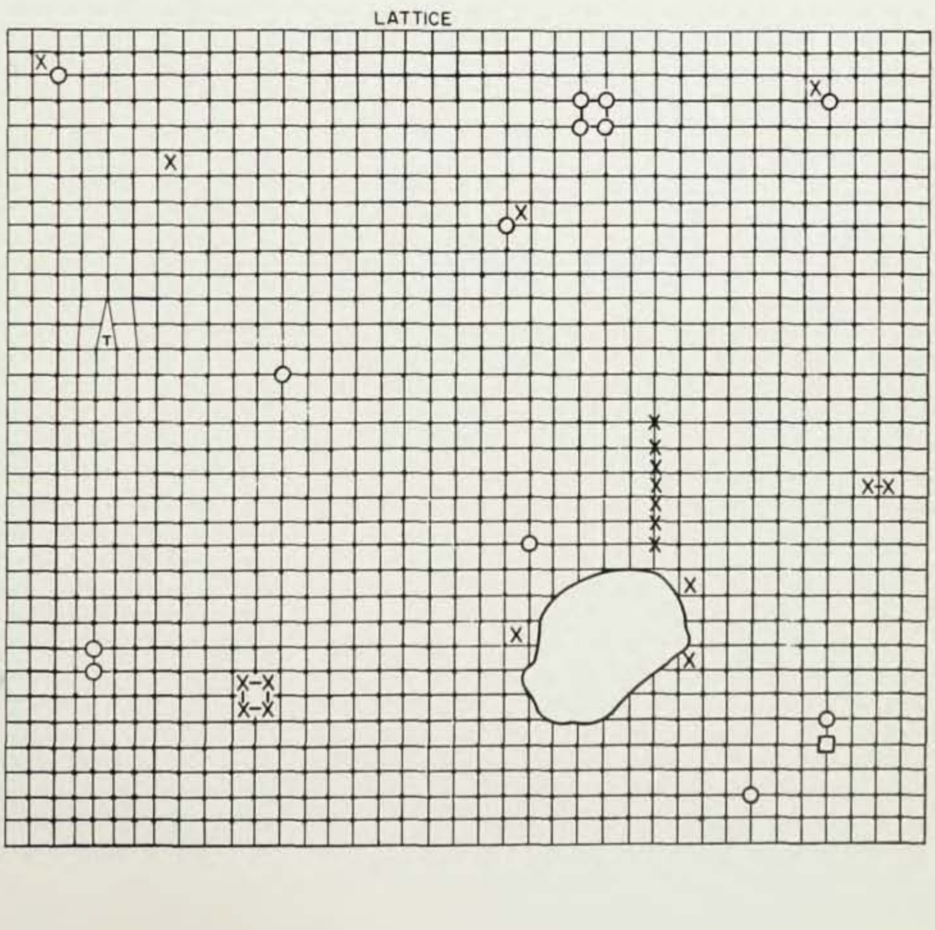


Fig. 2. Schematic diagram of various lattice defects resulting from damaging treatment. Defects may become more mobile at elevated temperatures to produce recovery shown in Fig. 1.

achieve an appreciable nonequilibrium number of vacancies near room temperature by raising the temperature of a sample to the range of high concentrations, then quenching the temperature quickly, typically in milliseconds. Originally, it was believed that only single vacancies are quenched in by this method, but it is evident now that multiple vacancies (*divacancies*, *trivacancies*, etc.) also are very much present. These vacancy complexes pose as fascinating new members of the growing defect family.

There is still a third way of manufacturing these various lattice defects—by plastic deformation, the simplest way experimentally. The greatest concentrations of defects may be generated by this method. Unfortunately, the fact that a profusion of many types of defects is produced is also a disadvantage of plastic deformation as a tool in defect studies, since interpretation of data on plastic flow is extremely difficult.

The defects of most importance in plastic deformation are *dislocations*. An adequate description of dislocations here would lead too far afield. However, one feature of dislocations of interest here is that dislocations will move through the lattice in response to a stress greater than some fixed value, called the yield stress. Vacancies, interstitials, and various multivacancy and multiinterstitial agglomerates can be produced when these dislocations cross each others' paths. Our two-dimensional schematic diagram fails to illustrate this phenomena. It must suffice to note that dislocations, being line defects in nature, can "intersect". There are several possible consequences of this intersection. A simple interstitial or vacancy may be created, a row of spaced interstitials or vacancies may extend away from the point of intersection, or, in some cases, no *point defects* (interstitials and vacancies) are created at all.

It is also of interest to note that, while thermodynamics predicts nonzero equilibrium concentrations of point defects, it does not say where or how these defects are created or destroyed. There is little doubt that dislocations play this vital role of sources and sinks for interstitials and vacancies. In this case, no stress-induced motion of dislocations is necessary. Instead, point defects are emitted and absorbed from regions along the dislocation where the dislocation line "jogs" from one lattice plane to the next. This process proceeds in a manner quite analogous to electron emission from a metal surface in the Richardson effect.

To complete this compendium of defects, it is necessary to return to radiation effects, this time those produced by heavy-particle rather than electron irradiation. Deuterons and neutrons have been the particles most frequently used. These enjoy an advantage over 1-Mev electrons as a defect investigation tool, in that their damaging ability per incident particle is considerably higher. They produce vacancies and interstitials, as do electrons; however, they also create more complex defects as well, at least in some of the heavier metals. The nature of these defects is by no means agreed upon and the conferees devoted some time to this matter. These defects have been referred to as *displacement spikes* or *depleted zones*. They result from an extremely localized release of a rather large amount of energy ($10^4 - 10^5$ ev) when a high-energy knocked-on atom is brought to a stop in the lattice.

Suppose we now take a sample, a copper wire for example, and subject it to one or more of the above damaging treatments. To make our experiment more definite, perform this experiment in a bath of liquid helium. The result is chaos of a sort: a profusion of defects of various types are created. One might hope that at such a low temperature these defects would be stable, and we shall assume this to be so. Now warm the sample slowly. The wire does indeed respond to the therapy; the damage is gradually healed because, as the temperature is increased, the various defects in turn become mobile. The problem which obviously presents itself is this: in what order, as the temperature is raised, do the defects become mobile, and where do they go?

Considering the sizeable number of possible defect configurations, it is not surprising that more than one model has been proposed to identify the mobile defects with the observed recovery processes. The situation is even more complicated, since one mobile defect may choose any of several other defects as "sinks". Furthermore, it is now clear that the five recovery stages in copper are composed of substages. The study of this "fine structure" is still being explored. Preliminary evidence was presented indicating that Stage I recovery following neutron irradiation begins as low as 8°K.

Despite these imposing difficulties, a considerable amount of agreement was achieved in the conference. It is very generally agreed, for instance, that the energy of migration of an interstitial is less than that for a vacancy; the interstitial should, therefore, be mobile at temperatures at which the vacancy remains frozen. In its migration, the interstitial may encounter a vacancy. The result will be the annihilation of both defects, in a manner analogous to electron-positron annihilation.

A process very similar to this occurs if the interstitial finds itself very close to its original vacancy. The energy required for the interstitial to migrate to its own vacancy is reduced by the action of the attractive force between the defects to the extent that such recombination is fairly inevitable. This is the most frequent defect configuration produced by 1-Mev electron irradiation and it is also produced to a lesser extent by irradiation with heavier particles. It is this *close-pair recombination* that is rather definitely to be assigned to the low-temperatures substages in Stage I.

The higher temperature substages of Stage I were discussed in greater detail. The most important data bearing on these come from electrical resistivity and elastic moduli measurements following irradiation, both of which indicate that the mobile defect roams an

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appreciable distance in the lattice before being annihilated or trapped. The simplest interpretation is that interstitials are undergoing free migration in this temperature region. Note that even if one assumes that interstitials migrate at these lower temperatures, it does not follow that all interstitials and vacancies have left the lattice. A certain amount of data points to the possibility that many interstitials are trapped by impurity atoms or dislocations, thereby leaving an equal number of vacancies which have not been annihilated (in the case of electron irradiation).

The conferees were able to reach some tentative agreement concerning the nature of Stage II. This stage shows fine structure also. It seems acceptable, based primarily on internal friction measurements after plastic deformation, to assign these substages to migration of small vacancy or interstitial agglomerates, e.g., divacancies. The exact assignment must await more investigation.

Rather than proceed up the temperature scale, it may be most profitable to turn next to the highest temperatures. Stage V is clearly due to recrystallization, a process which involves the reduction of the dislocation concentration. Recrystallization is, in itself, an important phenomena but the conferees did not discuss it.

An interpretation for Stage IV was not agreed upon by the conferees. Many felt confident that it is to be associated with vacancy migration and there is a considerable amount of data which supports this interpretation. Some of these data discussed in the conference were electrical resistivity and stored energy measurements in copper and nickel and quenching measurements in gold.

This leaves Stage III for interpretation, and here the biggest disagreement exists. This is somewhat surprising, since electrical resistivity data on electron-irradiated copper and nickel show that the recovery of this stage proceeds in a manner which originally seemed to imply the free migration of either interstitials or vacancies. But, as we have seen, these are the defects which are assigned to Stages I and IV by many of the conferees. What other possibilities remain? While no firm conclusion was reached, one new possibility was discussed. It is possible that either Stage III or the higher temperature substages of Stage I are to be associated with "static" crowdion migration, the other being associated with interstitial migration by the *interstitialcy mechanism*. While this possibility is not devoid of objections, it does fulfill an important requirement imposed by data on lattice parameter and density measurements following deuteron irradiation. The other possibility is that Stage III is associated with vacancy migration, leaving Stage IV to be explained in terms of a more complex defect.

Before adjourning, the conference considered the matter of conference records. It was decided to publish an AEC report of the full proceedings after editing to the approval of all conferees. This report should be published sometime in 1959.

The conferees did unanimously agree on one conclusion. The small, informal, round-table conference method is desirable and efficient and is to be recommended wherever applicable. There is little doubt that the future efforts in the field of lattice defects in noble metals will be influenced by this particular conference.