Mendelssohn, K.: Do the values of negative specific heat traced in your diagram correspond to equilibrium conditions in the metal at each temperature?

Blewitt, T. H.: I don't know for sure, but I certainly hope so. The fact that negative specific heat curve approximates the shape of the differential isochronal annealing curve would offer some evidence in support of equilibrium. Furthermore some measurements have been made at different reactor power levels which seem to support this view also.

Hasiguti, R. R.: You mentioned that you found I_B, I_C and I_D sub-stages in your stored energy spectrum. I understand the reason why I_A is missing. But how about I_E?

Blewitt, T. H.: Since a long bombardment was used it is probable that stage I_E is submerged in stage I_D.

Schmid, E. K. H.: I should like to make a short comment to the interesting results of Dr. Blewitt. It concerns the irradiation of Cu- and Ag-whiskers with α-rays. Ivoboda in our Institute in Vienna has found that the resistivity is raised with the dose of irradiation and that creep resistance was lowered. Whereas non irradiated samples did not show any creep, they began to elongate immediately after approaching the Po target. Elongations more than 1% could be detected.

Recovery Stages in Noble Metals

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In this paper the recovery processes occurring in the temperature range of stage III and IV after irradiation, deformation, and quenching will be discussed. A comparison of the activation energies measured in this temperature range and a consideration of the kinetics during recovery suggest the migration of interstitials in stage III and the migration of vacancies in stage IV.

Point defects, which are created in metals either by irradiation or deformation at low temperatures, or by quenching from high temperatures anneal out with increasing temperatures in five different recovery stages[1]. Stage V, where recrystallisation and recovery of hardening occurs, will not be discussed here. Numerous experimental and theoretical works have been published in the past ten years, dealing with the identification of point defects and their attribution to particular recovery stages. There is considerable disagreement in the interpretation of results, especially as far as interstitial migration is concerned, which has been attributed to stage I (at very low temperatures) and to stage III (just below room temperature) by different authors (c.f. (2) to (6)).

According to the calculations by Huntington[7], the migration energy of an interstitial in copper amounts to 0.1–0.3 eV. Activation energies of this order are found in stage I (20° to 70°K), so that the migration of interstitials was frequently attributed to stage I (I_E in copper). This, however, leads to contradictions in the interpretation of the remaining recovery stages[2],[3]. Recent calculations[8] yield a value of 0.5 eV for the migration energy of interstitials (dumb-bell configuration) in copper, which is in good agreement with the experimental value of

0.6 eV[5].

The assumption that interstitials are migrating below stage III, would require an attribution of another defect to this stage. The attribution of vacancies, divacancies, diinterstitials and the release of interstitials either trapped by impurities or by dislocations, to stage III is discussed in the literature[9]. The annihilation of the mentioned defects can be excluded by the results of the quenching experiments, by the comparison of the activation energies, found in the temperature range of stage III and IV (−40 to 200°C) after irradiation, deformation and quenching and from our knowledge of the recovery kinetics.

Part 1

For an analysis and interpretation of the results, only values which are precise to a few 1/100 eV can be used, since the activation energies, measured in this temperature range differ frequently by less than 1/10 eV. Results on copper, gold and some results on silver have been obtained with a high degree of precision ($\sim$ 1/100 eV). Nearly all of them were obtained from measurements of the electrical resistivity in connection with a method to determine the activation energy proposed by Meechan and Brinkman[5].
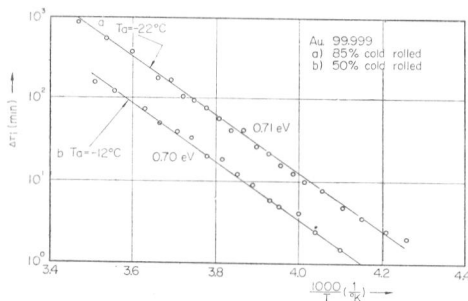

Fig. 1. Activation energy of stage III in gold (Ref. (10)).

The accuracy with which activation energies after deformation can be determined is shown in the case of gold (Fig. 1). From the fact that only one straight line is observed, we conclude that the recovery process has a single activation energy. From the slope of the straight line an activation energy of 0.71 eV is calculated with an error range of 0.01 to 0.02 eV. Lowering the degree of deformation the same ac-
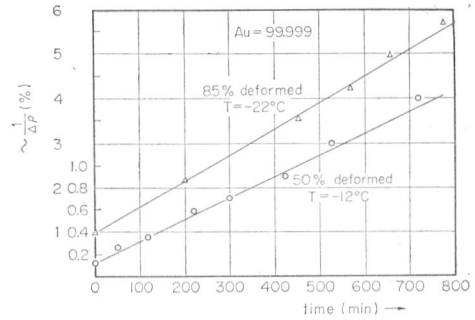

Fig. 2. The reciprocal change of resistivity in percentage for 85% and 50% cold-rolled gold (Stage III) (Ref. (10)).

tivation energy is found, although with a lower precision, due to the fact that the recovery of the resistivity after a smaller predeformation is smaller than after a higher one. In Fig. 2 the reciprocal change of resistivity during stage III recovery is drawn against the recovery time. Since a straight line is found, which is very well established, the reaction of the recovery process is of the second order. A comparison of the activation energies of stage III measured after deformation and after irradiation with electrons (Table I) shows that

Table I. Activation energies (values in eV) and order of reactions of stage III.

	Irrad.	Order of reaction	Deform.	Order of reaction
Cu	0.60±0.01[5]	2[5] [18]	0.64±0.05[6]	2[6]
Ag		2[18]	0.60±0.05[6]	2[6]
Au	0.72±0.04[19]	2[18]	0.71±0.02[6]	2[6]

the agreement in both copper and gold is very good. On silver no determination of the activation energy after irradiation is available. The order of reaction (Table I) after irradiation as well as after deformation is two. From both the agreement of the activation energies and that of the second order reaction, it must be concluded that after deformation and after irradiation in stage III the same defects are migrating and it is obvious that the annihilation occurs by recombination with another type of defects, due to the second order reaction.

As it is well known, after deformation, stage I in copper is absent, and after irradiation with electron, stage II is absent

in copper and stage III is observed in both cases. If one agrees with the assumption that after irradiation with electrons mainly Frenkel pairs and independent interstitials and vacancies are created, and that the concentrations of divacancies and diinterstitials are very small compared to the concentration of the other defects, then the attribution of interstitials or vacancies to stage III are the only possibilities. In fact, the attribution of different close Frenkel pairs to stage I is commonly assumed. According to theoretical calculations[7],[8] interstitials have a lower activation energy than vacancies. We conclude therefore that the recovery in stage III is due to the migration of interstitials and their recombination with vacancies. The results on gold by Ward and Kauffman[19] confirm this interpretation, because in gold, there is no evidence for recovery stage I_E, which is frequently attributed to the interstitial migration and annihilation. Stage I_E, which is pronounced only in copper is attributed to crowdions[3].

Part II

The concentration of interstitials after quenching from high temperatures compared to that of vacancies is very low because of the differences in the formation energies of both defects. Hence, the activation energies determined after quenching from high temperatures can only be attributed to single vacancies or to vacancy clusters, formed during quenching by the migration of single vacancies.

In Figs. 3 and 4 it is shown, how precisely the migration energies for single vacancies in gold and in copper are determined.
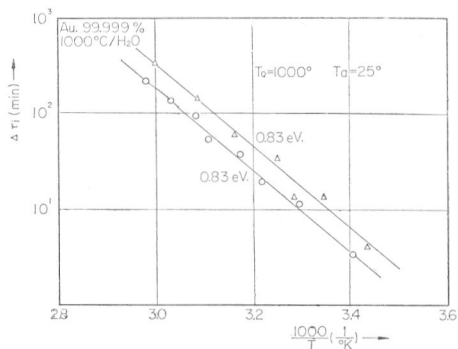

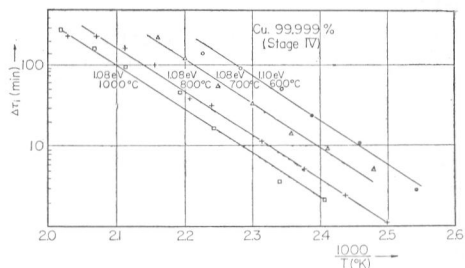Fig. 3. Activation energy of stage IV in gold (Ref. (10)).

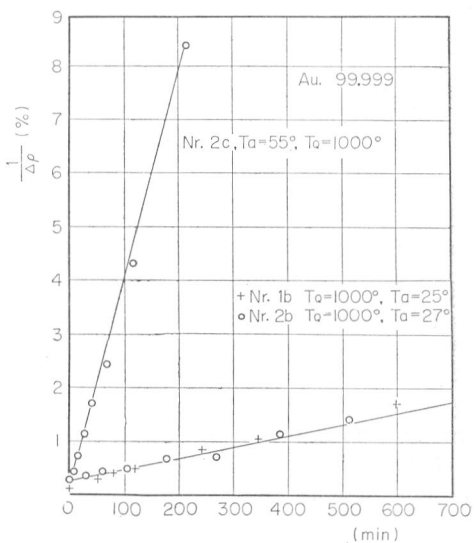Fig. 4. Activation energy of stage IV in copper (Ref. (11)).

Fig. 5. The reciprocal change of resistivity in percentage for isothermal recovery (Stage IV) (Ref. (10)).

The reaction of the recovery process is of the second order since the plot of the reciprocal of the change of resistivity during recovery against the recovery time is a straight line (Fig. 5). During annealing single vacancies form divacancies which are annihilated immediately because their migration energy is lower than that of the single vacancies. With decreasing quenching rate the concentration of the quenched-in vacancies decreases because more and more vacancies are annihilated during quenching. In addition, the ratio of the concentration of single vacancies to that of vacancy clusters decreases with decreasing quenching rate. According to Bartlett and Dienes[12], divacancies have a lower migration energy than single vacancies, so that the decreasing activation energy measured with decreasing

quenching velocity (by quenching from 1000°C) is due to the relative increase of the concentration of divacancies. The smallest value of the activation energy measured by a low quenching rate is 0.6 eV for gold[13],[10]. This is an upper limit for the migration energy of divacancies, since the single vacancies may influence the measured activation energy. In copper and silver[6],[11],[14] the migration energies for single vacancies, determined after quenching, are essentially higher than in gold (Table II). On the other hand there is no

Table II. Activation energies (values in eV) of stages III and IV.

	III	IV	Divac.
Cu	0.60±0.01[5]	1.08±0.02[6]	0.58[6]
Ag	0.60±0.05[6]	0.88±0.03[6]	0.57[6],[15]
Au	0.71±0.02[6],[19]	0.83±0.02[6]	0.60[6]

recovery stage or only a weak indication of a stage below room temperature[11],[14], after quenching in water, *i.e.* with a low quenching rate. It must be concluded, that the migration energy for divacancies for these two metals is less than 0.58 eV if the weak indication of a stage is attributed to divacancies. If the migration energy for divacancies would be in the range of 0.60 to 0.64 eV as the values found in stage III after irradiation and after deformation, then it should be possible to measure their migration energy in copper and silver, too, by using the same quenching method as in gold. For silver the migration energy for divacancies was determined with different methods[15],[16] and a value of 0.57 eV seems well established.

The sum of migration and formation energy of vacancies agrees very well with the activation energy for self diffusion, as it should be for face centered cubic metals. The migration energy for vacancies in gold is about 15% smaller than the formation energy, and in copper the formation energy is 45% smaller than the migration energy. This is in agreement with the results of thermal diffusion measurements[17].

From Table II it can be seen that the migration energies for single vacancies for these metals are essentially higher than the value determined for stage III. Even the

temperature range, in which the single vacancies are annihilated is about 100°C higher than the temperature range of stage III. The annihilation of single vacancies is therefore attributed to recovery stage IV. The activation energies for divacancies are below those of stage III, though only in gold the error limits do not overlap. The second order reaction, which is found after deformation as well as after irradiation in stage III recovery is not compatible with the migration of divacancies in stage III. Also the annihilation of divacancies by dislocations or by the formation of clusters requires a reaction order lower than two. The migration of divacancies can be attributed, therefore, to stage II. But this defect is not the only one responsible for stage II[3].

Part III

The release of trapped interstitials from impurities or dislocations and their annihilation in stage III can finally be excluded by the following considerations. The change of defect concentration of impurities in 99.999% pure material is by two orders of magnitude smaller than the change of defect concentration during annealing. Therefore, it is not probable that in stage III the release of point defects by impurities and their following annihilation is of any importance. Further confirmation for this argument can be drawn from the investigations on copper, silver and gold doped with different amounts of impurities. By adding different amount of different impurities to copper[20] and gold[10], the amount of recovery in stage III relative to the other recovery stages is changed and stage III and IV in copper[11] become less distinguishable, but no change of activation energy is found. The influence of impurities on recovery stages II and III can be seen from measurements of the release of stored energy after deformation at −195°C[21]. The temperature range of the substages of stage II and the release of stored energy is changed by adding impurities. But the release of stored energy in stage III is only changed by adding more than 0.01 at. % impurities and no shifting of the temperature range is visible. Parallel to the decrease of stored

energy, another substep III$_B$ above stage III appears. Only this substep may be attributed to the release of interstitials trapped by impurities, and to their following annihilation.

Also, the release of interstitials trapped by dislocations in stage III can be excluded from the experiments. In fact in copper and gold after different grades of plastic deformation as well as after electron irradiation, the same activation energy is measured in stage III (Table, I), although the dislocation densities differ considerably.

Summary:

a) The agreement between the activation energies and the second order reaction which are found in copper and gold after electron irradiation and plastic deformation support the view that free interstitials migrate in stage III.

b) From the results of further experiments the attribution of defects, which were considered by other authors to explain stage III recovery, can be excluded. Quenching experiments make it clear that single vacancies migrate in stage IV and divacancies in stage II, even if the last mentioned defect is not the only one responsible for the recovery occurring in stage II.

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DISCUSSION

Müller, E. W.: I am very much concerned about the influence of oxygen in the atmosphere during quenching of copper and silver. An oxygen content of a few parts per million in the argon would suffice to introduce oxygen in the surface of the specimens, which may cause severe resistance changes. As the quenching is done in water, oxydation by water vapor is even more probable. Oxide films many atomic layers thick would not be visible on the specimen, but would have a severe effect on the data measured.

Schüle, W.: Unfortunately it is not possible to quench metals in water from vacuum, and we are forced to anneal and quench metals from an atmosphere. Of course a few parts per million oxygen in copper or silver give rise to resistivity changes, but they can be neglected so long as the concentration of defects (vacancies) after quenching is much larger than the oxygen concentration.

Brinkman, J. A.: I would like to mention the results of theoretical calculations, presented in a paper by A. Sosin and myself at the Berkeley Nuclear Conference in 1961, on the maximum divacancy concentration which can be produced relative to the concentration of single vacancies by 1 MeV electron irradiatian. These results indicate that the observed magnitude of Stage III following electron irradiation is far too large to permit its association with divacancies.

Nowick, A.S.: Would it be possible to resolve some of the conflict in this field by attributing Stage III in Au to interstitials but Stage III in Cu to divacancies? This assignment would not be inconsistent with your Table, and would agree with the existence of a low-temperature migrating defect in Cu but not in Au.

Schüle, W.: 1) The attribution of divacancies to stage III only in copper is not compatible with the second order reaction, which is found in copper as well as in gold and silver.

2) If divacancies would migrate in stage III where an activation energy of 0.60 eV is measured, it should be easy to detect after quenching in water as in Au or in Ag. 3) Prof. Seeger informed me recently, that they found a value of 0.55 eV after quenching copper, which they attribute to divacancy migration. This value does not agree with that one found in stage III. 4) At least I would like to refer to the comment given by Dr. Brinkman.

Simmons, R. O.: How do you identify the defects which are responsible for the annealing you observe in what you call Stage IV? It appears, for example, that the resistivity increments you quench into silver and copper are too large, by a factor 5 or more, when compared to the values one would expect for monovacancies from equilibrium vacancy concentration measurements.

Schüle, W.: After quenching copper we found one stage in the temperature range of 130°–200°C and a small indication of a stage below room temperature. We attribute the activation energy found in the upper stage to the migration energy of vacancies because the sum of the migration and formation energy agrees well with the activation energy for self diffusion. There is also agreement with thermal diffusion measurements made by Meechan and Lehman. A further point is, that the recovery process in this stage follows a second order reaction. If one would attribute this stage to the release of impurity trapped vacancies (for example oxygen), then we would expect at least a small stage between room temperature and 130°C indicating vacancy migration. With our technique we were able to detect concentration changes of 4×10^{-7}. Deformation experiments with oxygen free copper (99.999) show in the temperature range of 130°–200°C a small stage too, as you can see from our experiments and from Berghout's one (Acta Met. **6** (1958) 613). This stage is the first stage formed above stage III and in both cases after quench and after deformation, the same activation energy (1.10 eV) is found.

Seeger, A.: In answer to Dr. Simmons' question I should like to reply as follows: 1) The quenched-in resistivities in our experiments on silver are compatible with both the equilibrium measurements and the determination of the energy of formation in silver. However, a question as to the identification of the quenched-in defect arises in the experiments of Doyama and Koehler. In these experiments the quenched-in resistivity in the specimen used for the annealing studies was considerably higher than the resistivities of the specimen quenched from the same temperature in the determination of the energy of formation. 2) I do not think that the divacancies would actually influence the self-diffusion activation energy in copper. If the binding energy for divacancies is assumed to be 0.2 eV, the energy of formation is $(2 \times 0.97 - 0.2)$ eV = 1.74 eV. Adding the measured value 0.55 eV for divacancy migration energy gives us for self-diffusion by divacancies about 2.3 eV, which is sufficiently larger than the experimental value 2.05 eV.

Tomizuka, C. T.: May I ask whether or not you measured the quenching rate of

the copper foil you used. If you did what was your quenching rate? I understand that the quenching rate obtained by the Illinois group is $5\times10^{4\circ}$C/sec.

Schüle, W.: The quenching rate was measured. We got values between 9000°C/sec and 17000°C/sec, using copper-constantan thermo-couples. The wires of the thermo-couple were soldered at different points of the specimen to be sure that the temperature change of the specimen is measured. I would like to mention that we found a higher concentration of quenched-in vacancies after quenching from 1000°C as the Illinois group, although they measured an essentially higher quenching rate than we. After quenching from 1000°C we found the migration energy for vacancies in gold, a second order reaction, and a quenched-in resistivity, which is only a little smaller than that one, which is found by equilibrium measurements.

Koehler, J. S.: How did you quench copper? We had great difficulty in keeping our copper pure.

We have recently measured the energy of migration of divacancies in gold. We find $E_M{}^2 = 0.65 \pm 0.04$ eV.

Schüle, W.: We quenched copper foil from a very pure argon atmosphere in water. For one experiments we conclude that the oxygen content after quenching was so low, that no interaction between oxygen and vacancies was detectable. Airoldi, Bachella and Germagnoli found no stage in the same temperature range as we. They have to anneal the specimens at much higher temperatures. It is possible that they measured the annihilation of oxygen trapped vacancies. I think that 0.60 eV for the migration energy of divacancies is an upper limit as mentioned in my paper, a value, which you found in earlier experiments. I think that stage II recovery in gold found after deformation can be attributed to divacancy migration. If this is so, one can calculate from the temperature range of stage II an activation energy of 0.54 eV using the activation energy found in stage III (or IV) ($T_1/T_2 = Q_1/Q_2$), assuming that the order of reaction on both stage (II and III) is two. The value 0.54 eV measured after quenching was found in earlier experiments, reported by you and a Russian group.

Lücke, K.: By rationalization of modulus measurements in the low kilocycle range Granato, Hikata and myself established 6 years ago the existence of a defect migrating with an activation energy of about 1 eV. As pointed out in my paper for the Tokyo Symposium this value has recently been reconfirmed by damping measurements in the megacycle range. However this number from 0.95 to 1 eV for copper does not show up in your table. I feel that it is unjustified to neglect this value on the grounds that it is obtained by a less direct type of measurement than in the case of the numbers listed in your table; the details of the process of recovery of resistivity are certainly not better established than those for the recovery of internal friction data. I would like to have your comment on this point.

Schüle, W.: On the recovery stage measured after deformation by Smith, where you and your coworkers have established point defect migration with an activation energy of about 1 eV 6 years ago, recrystallisation and recovery of hardening is found, too. So I have some doubt, whether this activation energy of 1 eV can be connected with a single defect migration. Nevertheless in the limited accuracy of this activation energy it is in agreement with our value of 1.08 eV found for vacancy migration in copper. D. O. Thompson, Oak Ridge, found after irradiation with modulus measurements in copper a value of 1.06 eV, which is in good agreement with the value of 1.08 eV in our table.