Stage IV Recovery of Platinum after Electron Irradiation*

WALTER BAUER
Atomics International Division of North American Aviation, Canoga Park, California
AND
A. SOSIN
North American Aviation Science Center, Thousand Oaks, California
(Received 27 December 1965)

The activation energy of the stage IV resistivity recovery after electron irradiation of platinum has been measured to be 1.36±0.08 eV. The recovery is due to the migration of single vacancies. A model of diffusion to inexhaustible internal sinks, complicated by a vacancy-impurity trapping interaction, is found to describe the platinum recovery data. In addition, the stage IV recovery of deformed nickel is found to follow the same recovery model.

I. INTRODUCTION

SEVERAL electrical resistivity recovery stages occur in metals as a result of the annihilation of vacancies, interstitials, and higher order complexes produced by irradiation, quenching, or plastic deformation. Of these, plastic deformation is generally accepted as the most complex for interpretation. (Interpretation here signifies identification of the defect which migrates in a particular stage and the eventual disposition of this defect.) In principle, it should be possible to associate vacancy or interstitial migration with a particular recovery stage by a simple comparison of recovery following quenching and irradiation. This should be particularly true if samples are quenched from a temperature which is not too high so that only single vacancies are frozen into the crystal and if electron irradiations are used such that $T_d \leq T_m \leq 2T_d$, where T_d is the threshold displacement energy and T_m is the maximum energy imparted to a lattice atom. Under these conditions of irradiation, the resulting damage consists of an equal number of single vacancies and single interstitials.

Despite its apparent simplicity, identification based on this approach—even in the most intensely studied metals, copper and gold—has been only partially successful.[1] In contrast, the recovery above room temperature of the transition metals, nickel and platinum, which are next to copper and gold, respectively, in the periodic table offers a much better opportunity for interpretation. In platinum, stage III and IV recoveries after electron irradiation are well separated in temperature, and reliable quenching data are available.[2-5] In nickel stage IV recovery after electron irradiation is not well defined, but the stage III and IV recoveries after deformation are well separated and defined.[6-8] We discuss previous results in nickel alongside the new results in platinum in this paper to emphasize the parallel nature of the recovery of these two transition metals. That is, we show that the mechanism for the stage IV recovery in platinum applies equally well to the stage IV recovery of deformed nickel.

II. EXPERIMENTAL PROCEDURE

The specimen preparation, holder, and irradiation procedure near 80°K are the same as that used by Bauer and Sosin for gold.[1] The specimens used for electron irradiation were 0.004-in. wires, with a residual resistivity in the range from 3.1 to 4.5×10^{-9} Ω-cm, based on a room-temperature resistivity of 10^{-5} Ω-cm. The electron energy for the irradiation was such that $T_m=66$ eV. The value of $T_d\approx36$ eV has been recently measured in this laboratory.

The relatively high-annealing temperatures (250–450°C) for the recovery measurements were attained by pulsing a known current to resistively heat the specimen. This procedure does not, of course, result in a completely uniform temperature distribution across the specimen. This uncertainty in the temperature has been minimized by placing the potential leads close together near the center of the specimen. However, a considerable part of the uncertainty in the value of the activation energy is due to this problem. It should be pointed out that all anneals were carried out in either a helium or a nitrogen atmosphere, since annealing in air occasionally caused anomalous resistivity increases.

III. EXPERIMENTAL RESULTS

Although the recovery region of interest begins around 200°C, we chose to irradiate near liquid-nitrogen temperatures in order to utilize a high electron flux without appreciable heating effects. The equipment used for this type of irradiation does not lend itself to

* Based on work sponsored by the Metallurgy Branch, Division of Research, U. S. Atomic Energy Commission, under Contract AT-(11-1)-GEN-8.

[1] W. Bauer and A. Sosin, Phys. Rev. **136**, A474 (1964).
[2] J. J. Jackson, in *Lattice Defects in Quenched Metals* (Academic Press Inc., New York, 1965), p. 467.
[3] A. Ascoli, M. Asdente, E. Germagnoli, and A. Manara, J. Phys. Chem. Solids **6**, 59 (1958).
[4] G. L. Bachella, E. Germagnoli, and S. Granata, J. Appl. Phys. **30**, 748 (1959).
[5] G. R. Piercy, Phil. Mag. **5**, 201 (1960).
[6] A. Sosin and J. A. Brinkman, Acta Met. **7**, 478 (1959).
[7] P. Simson and R. Sizman, Z. Naturforsch. **17a**, 596 (1962).
[8] D. Schumacher, W. Schule, and A. Seeger, Z. Naturforsch. **17a**, 228 (1962).

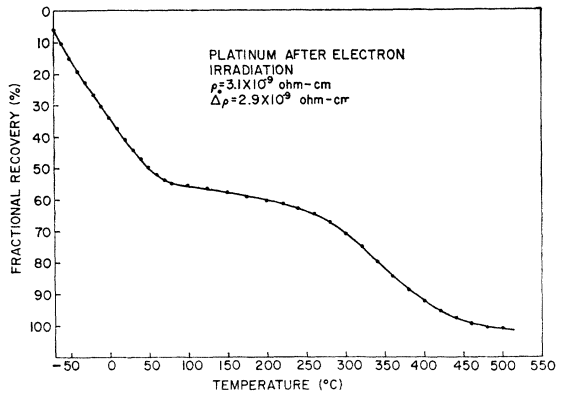

FIG. 1. Fractional recovery of platinum after 30-min anneals at the indicated temperatures.

precise measurements of electron flux. Therefore, no attempt was made to measure the damage rate [(resistivity increase)/(unit electron flux)] precisely. However, we observed a definite saturation effect—a decrease of the damage rate as a function of electron flux. Recovery measurements after electron irradiation at 4°K currently in progress in our laboratory show that a considerable amount of recovery occurs in the temperature region below 80°K in platinum. The most natural explanation for this effect is the occurrence of long-range migration below 80°K. Then the instantaneous sink concentration (vacancies) is increased at larger fluxes, with a corresponding increase in the probability of interstitial annihilation.

Both isochronal and isothermal annealing treatments have been carried out after irradiation. The result of one of the isochronal anneals is shown in Fig. 1. The separation of the stage III and stage IV recovery regions are clearly apparent. We present the results of a typical isothermal anneal in Sec. III where its discussion is more appropriate.

A. Activation Energy

We have chosen the Meechan and Brinkman,[9] (MB) analysis for the activation energy. Aside from the arguments advanced as to the utility of the MB method by Bauer and Sosin,[1] the method is applicable to processes which do not necessarily obey a simple chemical rate equation. The major experimental requirement is that the specimens used for the isochronal and isothermal anneals have closely identical histories. This was achieved by introducing equal resistivity increases in the same specimen in succeeding runs.

The results of applying the MB method for the activation energy to the recovery data after electron irradiation are shown in Fig. 2. An explanation of the MB method and the symbols used in the figures can be found in Refs. 1 and 9. Upon a careful examination of Fig. 2 one notes that two straight lines with slightly different slopes can be drawn through the data points. This is reminiscent of the state IV recovery in nickel after deformation as originally investigated by Sosin and Brinkman[6] where activation energies of 1.0 and 2.5 eV were found. Subsequent work by Schumacher *et al.*[8] and by Bell[10] did not reveal this break-up into two activation energies. (They reported a unique activation energy of approximately 1.5 eV.) We were unable to reproduce this break-up into two lines in platinum in additional irradiation experiments. We, thus, conclude that the recovery in stage IV after electron irradiation is uniquely activated over approximately 75% of the stage with an activation energy of 1.36±0.08 eV. Piercy[5] has studied the resistivity recovery of 99.99% pure platinum after deformation, quenching, and neutron irradiation. Recently extensive quenching studies on 99.999% pure platinum were carried out by Jackson.[2] These results, our results, and the proposed identity of the migrating defect are summarized in Table I.[11]

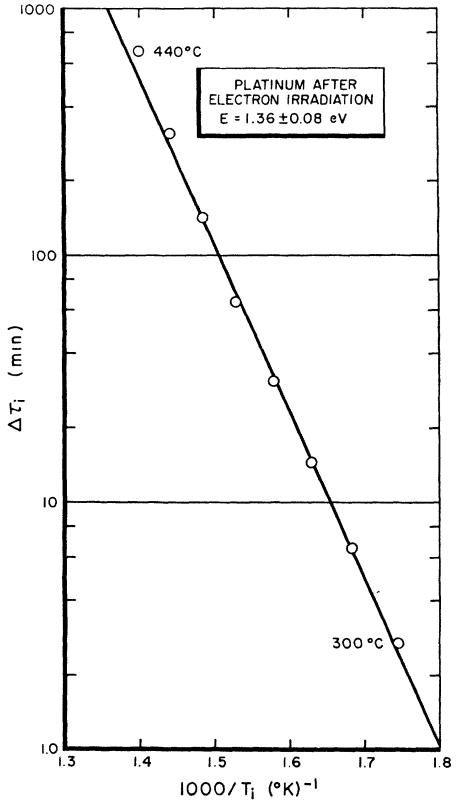

FIG. 2. MB analysis applied to the stage IV recovery after electron irradiation. $\Delta\tau_i$ is the equivalent time at 380°C and T_i is the temperature of the ith isochronal pulse. The slope of the line gives the value of the activation energy.

[9] C. J. Meechan and J. A. Brinkman, Phys. Rev. **103**, 1193 (1956).

[10] F. Bell, Acta Met. **13**, 363 (1965).

[11] It should be noted that the value of the activation energy reported by different investigators may depend on the technique used in deducing these values. The conditions which give rise to such discrepancies do not appear to apply here. For a discussion of these effects see J. W. Kauffman and G. J. Dienes, Acta Met. **13**, 1049 (1965).

TABLE I. Defects mobile in platinum above 0°C.

Source of defects	Temperature range of recovery (°C)	Activation energy (eV)	Defect
Electron irrad. at 80°K[a]	250–450	1.36±0.08	Vacancy
Quench from 1000°C[b]	370–480	1.38	Vacancy
Quench from below 1400°C[c]	450–580	1.42	Vacancy
Quench from below 1400°C[d]	370–490	1.48±0.08	Vacancy
Quench from above 1600°C[e]	300–500	1.13±0.12	Divacancy
Neutron irrad. at 50°C[e]	150–400	1.46±0.05	Vacancy
Deformation at 80°K[e]	200–400	1.43±0.09	Vacancy

[a] This work.
[b] See Ref. 2.
[c] See Ref. 3.
[d] See Ref. 4.
[e] See Ref. 5.

If one uses the activation energy as the "signature" of a defect, one can identify our value of the activation energy with the 1.38-eV and even with the 1.42- and 1.48-eV activation energies reported after quenching, due to overlapping uncertainties. This energy—about 1.38 eV—can be attributed to single vacancy migration with confidence. To demonstrate this, we observe that no recovery is observed below stage IV following low-temperature quenching (below 1400°C). Since 2-MeV electron irradiation results almost exclusively in single vacancies and interstitials, we attribute the 1.36-eV activation energy measured here to the motion of single vacancies as well. Note that the possibility of appreciable divacancy formation after irradiation is small, since it would require that single vacancies be more mobile than divacancies—contrary to the quenching results.

B. Annealing Kinetics

During electron irradiation near threshold nearly equal concentrations of interstitials and vacancies are produced. Upon subsequent warmup to a temperature below the stage IV recovery region, interstitials become mobile and annihilate mostly at vacancies. In order to observe a stage IV recovery, if due to the migration of vacancies, some of the interstitials must be either trapped and immobilized prior to stage IV (probably at impurities) or migrate to sinks other than vacancies. Then the vacancies can either migrate to the impurity-trapped interstitials and annihilate, or diffuse to sinks such as dislocations. The modulus measurements of Keefer *et al.*[12] indicate quite conclusively that some of the interstitials in stage III and vacancies in stage IV migrate to dislocations in copper and gold. Since the recovery is complete in stage IV we suggest that the resistivity contributions of both interstitials and vacancies effectively vanish when they reach dislocations. The alternative possibility, that vacancies migrate along the dislocations until they annihilate at the previously trapped interstitials on the dislocations, we feel, is a less likely mechanism.

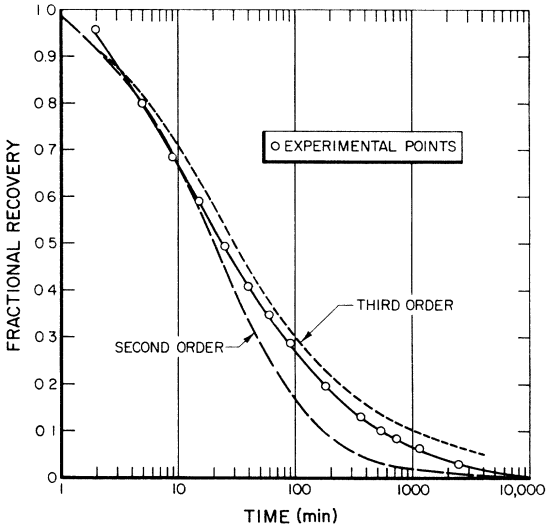

FIG. 3. Isothermal fractional recovery at 380°C after electron irradiation. Broken line is the recovery expected from second- and third-order kinetics of the chemical rate theory.

In contrast, during deformation unequal concentrations of interstitials and vacancies may be produced. Thus the diffusion of vacancies to sinks is a very natural recovery mechanism for stage IV recovery after deformation. In fact, stage IV recovery of deformed copper is considerably more prominent than the stage IV recovery after electron irradiation.

If the vacancy annihilation after electron irradiation in stage IV takes place at interstitials trapped at impurities, we would expect second-order recovery kinetics. This is due to the fact that the trapped interstitial concentration is nearly equal to the concentration of vacancies. In Fig. 3 we show the results of the isothermal recovery at 380°C after electron irradiation. The two data points for times longer than 1000 min. were measured at 460 and 480°C. The equivalent time at 380°C was then calculated with the 1.36-eV activation energy. The curves labeled second and third order were calculated from the chemical rate equation,

$$dn/dt = -Kn^{\gamma}, \qquad (1)$$

where n is the number of defects present in the lattice, K is a constant for any fixed temperature, and γ is the order of the reaction. One notes from Fig. 3 that the experimental points lie between the second- and third-order curves. This suggests that the data might be fitted to a nonintegral value of the order of kinetics—between two and three. In Fig. 4 we show the results of the MB analysis for the kinetics determination applied to our isothermal data. We have included the parallel results for the recovery of deformed nickel from the data of Sosin and Brinkman[6] (their Fig. 13), which we will discuss below. In all cases the data fit the straight line

[12] D. Keefer, J. C. Robinson, and A. Sosin, Acta Met. 13, 1135 (1965).

only moderately well. The recovery measurements reported by Piercy[5] after neutron irradiation of platinum, yielded a value of 2.8 for the order of kinetics. He suggested that the 2.8 value may be due to a nonrandom initial distribution of defects which is possible after neutron irradiation. Since electron irradiation results in a homogeneous distribution of defects, Piercy's explanation does not apply here. In any case the interpretation of annealing kinetics of order greater than two is quite ambiguous.

IV. APPLICABILITY OF DIFFUSION

If one compares the two curves in Fig. 4, one notes a small but systematic deviation from the straight-line behavior. It was this deviation, in part, that led Sosin and Brinkman[6] to investigate whether the recovery in nickel is better described by a diffusion equation. As emphasized by Reiss,[13] solid-state recovery processes are generally diffusion-controlled reactions rather than simple chemical rate processes.

Sosin and Brinkman[6] used a model based on volume diffusion of an initially uniform concentration of defects (vacancies in this case) out of regions with spherical boundaries—representing inexhaustible sinks, such as formed by grain boundaries. They found that the

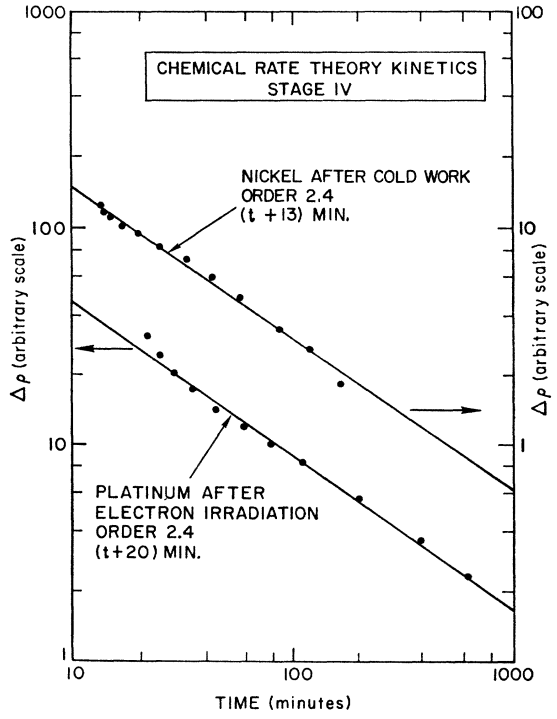

FIG. 4. MB analysis for kinetics applied to the recovery of platinum after electron irradiation and nickel after deformation. $\Delta\rho$ is the resistivity remaining in the stage IV recovery after annealing for the indicated time. See Ref. 9 for an explanation of the time correction.

[13] H. Reiss, J. Appl. Phys. 30, 1141 (1959).

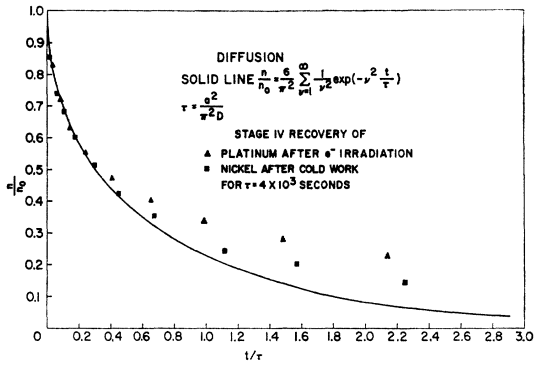

FIG. 5. Fractional recovery as a function of reduced time at constant temperature. The solid line is the recovery expected on the basis of a diffusion-controlled reaction discussed in text.

amount of recovery at early times is proportional to $t^{1/2}$ as is generally true in diffusion processes. This time dependence was observed experimentally by Sosin and Brinkman. We have re-examined their data at longer times. Our isothermal measurements on platinum and the re-examined nickel data are shown in Fig. 5. The solid line is the recovery to be expected on the basis of diffusion to spherical boundaries (discussed below). One notes that the data can be fitted to the diffusion theory up to a fractional recovery of 50%. The rest of the recovery is considerably slower than predicted by the theory.

There are a number of mechanisms which may account for this delay in the recovery. These include: clustering of the vacancies, exhaustible sinks, and concurrent trapping of vacancies by impurities during the diffusion process. The clustering of vacancies can be ruled out, because divacancies are more mobile than single vacancies making formation of higher order clusters unlikely. The possibility of exhaustible sinks playing a major role in the delay of the annealed platinum sample cannot be dismissed. However, we feel that it is unlikely, since a similar delay occurs in the recovery of deformed nickel (albeit somewhat reduced), where the dislocation network is sufficiently dense to be an inexhaustible sink.

The problem of concurrent trapping and release of vacancies by impurities during the diffusion of vacancies to sinks has been treated in the previous paper.[14] We now apply this theory to the stage IV recovery of platinum. The concentration of vacancies present at time t as measured by the resistivity decrease is

$$n(t)=M_v(t)+fM_c(t)\,, \qquad (2)$$

where f is the specific resistivity contribution of a trapped vacancy (presumably $0<f<1$) and $M_v(t)$ and $M_c(t)$ the concentration of free and trapped vacancies, respectively, given by Eq. (19) of Ref. 14. In Fig. 6 we

[14] A. Sosin and W. Bauer, preceding paper, Phys. Rev. 147, 478 (1966).

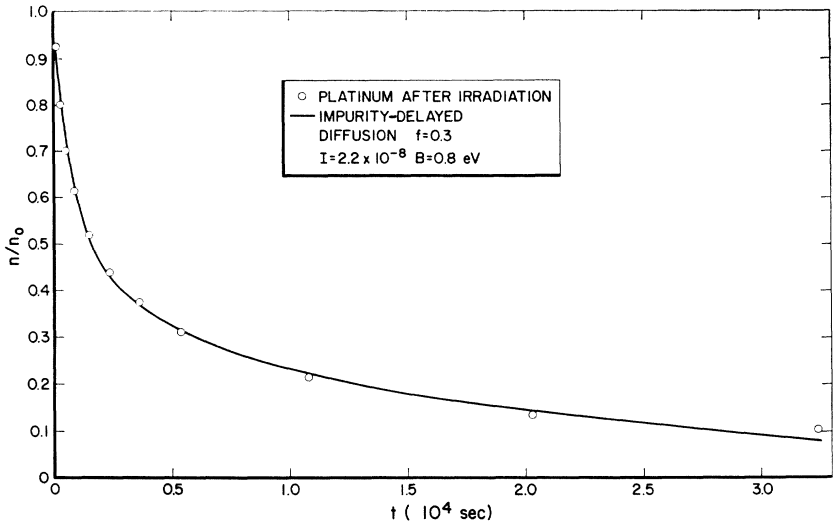

FIG. 6. Fractional recovery as a function of reduced time at constant temperature. The solid line is the recovery expected on the basis of an impurity-modified diffusion theory discussed in text.

show the experimental results for platinum and the results of Eq. (2) which were calculated for the following values of the parameters.

$$\lambda = 2.66\times10^{-4} = 84 I \nu e^{-E/kT}, \tag{3}$$

$$\mu = 5\times10^{-4} = 7\nu e^{-(E+B)/kT}, \tag{4}$$

$$K_n = -n^2 10^{-4} = -n^2(\pi^2 a^2/R^2)\nu e^{-E/kT}, \tag{5}$$

$$f = 0.3. \tag{6}$$

We refer the reader to the previous paper for an explanation of the symbols. From the experimental results ($E=1.36$ eV, $T=653$°K), and choosing a value of $\nu=4.4\times10^{12}$ sec^{-1}, we have

$I=2.2\times10^{-8}$, impurity concentration,

$B=0.8$ eV, binding energy,

$R=1.5\times10^{-4}$ cm, sink radius.

A number of observations can be made:

1. The agreement between theory and experiment is considerably improved, but at long times is still not complete. A possible explanation might be that instead of only one type of trapping center, or more precisely one binding energy, a variety of binding energies might be appropriate to the problem. It can be readily seen, from the previous paper, that the introduction of a higher binding energy species of small concentration would delay the recovery at longer times. Also part of the explanation may be inherent in the assumption of spherical sinks with equal radii.

2. The indicated values of the parameters in Fig. 6 are not unique. However, the values of I, R, ν, and f are physically reasonable. Recently Takamura[15] deduced a value of $f=0.36\pm0.11$ for an aluminum vacancy bound to a zinc impurity and $f=0.30+0.09$ for an aluminum vacancy bound to a silicon impurity. The value of B, while somewhat large, cannot be dismissed as unreasonable on the basis of our present knowledge of binding energies of vacancy-impurity complexes. In fact the value of B is well beneath the upper bound given by the vacancy formation energy (1.5 eV).

3. In a previous section we suggested that the migration energy for vacancies in platinum reported in this work, 1.36 ± 0.08 eV, may be indistinguishable from other determinations, ranging as high as 1.48 ± 0.08 eV, because of experimental uncertainties. It is now evident that these small variations of the measured activation energy might alternatively be due to the trapping effects of the residual impurities. The degree to which the impurities affect the measured value of the migration energy is a function of the value of B and I and has been evaluated by Damask and Dienes.[16] They found that in aluminum for a value of $B=0.2$ eV the correct value of the vacancy migration energy is achieved only for $I\leq10^{-7}$.

We now refer to the stage IV recovery studies of copper after deformation by Bowen *et al.*,[17] as reexamined by Brinkman *et al.*[18] They were able to fit the experimental data to the diffusion theory, *without* impurities, to a relative concentration of $n/n_0=0.15$. At longer times the experimental curve fell *below* the theoretical curve, i.e., the recovery is faster than predicted by the theory. Since recrystallization occurs in copper near the stage IV recovery region, with the sample purity used by these investigators, the additional re-

[15] Jin-Ichi Takamura, in *Lattice Defects in Quenched Metals* (Academic Press Inc., New York, 1965), p. 558.

[16] A. C. Damask and G. J. Dienes, Phys. Rev. **120**, 99 (1960).

[17] D. B. Bowen, R. R. Eggleston, and R. H. Kropschot, J. Appl. Phys. **23**, 630 (1952).

[18] J. A. Brinkman, C. E. Dixon, and C. J. Meechan, Acta Met. **2**, 38 (1954).

sistivity decrease is probably due to the rearrangement of the dislocation network. Recrystallization occurs well above the stage IV recovery region in platinum and nickel.

V. CONCLUSIONS

1. Stage IV recovery in platinum is due to the migration of single vacancies.
2. The natures of the recoveries after electron irradiation in platinum and after deformation of nickel in stage IV region are very similar.
3. We suggest that the recovery mechanism is predominantly the diffusion of vacancies to inexhaustible sinks with concurrent trapping and releasing of vacancies by impurities.
4. Small concentrations of impurities with binding energies of the order of 0.8 eV are effective in delaying the recovery.
5. This suggests that the stage IV recovery in platinum and nickel, and possibly also in other metals, might be substantially affected by the introduction of selective impurities of low concentration.

ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of W. Goeppinger in the experimental part of this work.

PHYSICAL REVIEW VOLUME 147, NUMBER 2 15 JULY 1966

Magnetic Properties of Solid Solutions of the Heavy Rare Earths with Each Other

R. M. BOZORTH AND R. J. GAMBINO
IBM Watson Research Center, Yorktown Heights, New York
(Received 28 February 1966)

The Curie and Néel points, and other critical points, of alloys of heavy rare earth elements with each other have been determined for 14 binary alloy systems. To a good approximation the Néel points of all of the alloys vary linearly with the $\frac{2}{3}$ power of the average de Gennes factor, $J(J+1)(g-1)^2$, as previously known. The Curie points, however, are definitely characteristic of the alloy system, each system showing a different dependence on concentration. The properties of each system are discussed, and related when possible to the transformations found in the elements and to atomic processes. Special effects are noted when the average $4f$ electron concentration lies between 10 (Ho) and 11 (Er), where the Stevens factor changes sign. Magnetization processes in several alloys are interpreted according to the model of Kitano and Nagamiya.

INTRODUCTION

PREVIOUS work[1–3] has shown that the Néel points T_N of the heavy rare earths and their alloys with each other can now be predicted; that is, T_N is closely proportional to the $\frac{2}{3}$ power of the average de Gennes factor[4] of the material; this is amply confirmed in the present work though some systematic deviations can be detected. The Curie points, however, are distinctly characteristic of each alloy system. We have examined the binary systems in the range of elements Gd to Lu, omitting those with Yb, which do not form continuous solid solutions, and those with Tb, which have been studied by Child *et al.*[5,6] A partial understanding is acquired of the diverse behaviors of the Curie points and other transformations of the individual systems, as discussed below under each system.

PREPARATION

The rare earth elements were obtained as 99.9% purity grade ingot or sponge, and all had been distilled except thulium. Alloys were prepared by argon arc melting using a nonconsumable tungsten electrode and a water-cooled copper hearth. The button ingots were turned over and remelted a minumum of five times to insure mixing. In all of the alloys except those containing Tm the weight loss on melting was less than 3%. The weight loss of the Tm alloys was much higher, some to 20%; these compositions were corrected assuming the loss to be all Tm. The samples were annealed in tantalum envelopes in quartz tubes at 1050°C (except those containing Tm which were annealed at 850°C) for 16 to 20 hr and furnace cooled. X ray, microhardness, and metallographic examination showed all used alloys to be homogeneous solid solutions.

Single crystals of selected alloy compositions were

[1] S. Weinstein, R. S. Craig, and W. E. Wallace, J. Appl. Phys. **34**, 1354 (1963).
[2] W. C. Koehler, E. O. Wollan, H. R. Child, and J. W. Cable, *Third Rare Earth Conference* (Gordon and Breach, Science Publishers, Inc., New York, 1964), p. 199.
[3] Reviewed by W. C. Koehler, J. Appl. Phys. **36**, 1079 (1965).
[4] P. G. de Gennes, Compt. Rend. **247**, 1836 (1958).
[5] W. C. Koehler, H. R. Child, E. O. Wollan, and J. W. Cable, J. Appl. Phys. **34**, 1335 (1963).
[6] H. R. Child, thesis, University of Tennessee, 1965 (unpublished).