likely in view of the form of (26) that $\chi(v)$ would prove to be algebraic.

Another method of mimicking the high-temperature expansion is that employed by Domb and Sykes[8] for the corresponding ferromagnetic problem. They write

$$\chi(v)=A(1-t)^{-7/4}+\psi(t), \quad 1/t=v_c/v, \tag{31}$$

the polynomial $\chi(t)$ being chosen to reproduce the known terms correctly. The values they quote for the triangular lattice give $\chi(-v_f)=0.3385$ which is correct to 0.23%, but the number of significant figures quoted is inadequate for the antiferromagnetic problem and only 8 terms were at their disposal. With the 12 terms now available, the representation (31) could be improved and the method is again adequate for summation in the high-temperature region. As $T\rightarrow 0$, $t\rightarrow -\infty$ and the form of $\psi(t)$ makes an estimation of $\chi(-1)$ by this method impracticable.

6. CONCLUSIONS

A formula has been given that enables the antiferromagnetic susceptibility of the plane triangular lattice to be evaluated over the entire temperature range with a maximum error of 5 parts in 10 000 at $T=0$. That this has proved possible results from three facts. First, the magnetic moment transformation yields an expansion that converges up to $T=0$. Second, the asymptotic behavior of the coefficients is well established and this makes a reliable summation possible. Third, a counting theorem enables an adequate number of terms of the series to be derived.

We have found that, while adequate for estimating $\chi(v)$ in the range $0>v>-v_f$, none of the approximate methods previously proposed for extrapolating the high-temperature susceptibility series enables the susceptibility to be evaluated at low temperatures. In the range $\frac{1}{2}T_f<T<\infty$, the energetic approximation is the most satisfactory. Unfortunately, although this is probably still true for three-dimensional lattices, the energy is not known exactly in these cases.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the constant advice and encouragement of Professor C. Domb and Dr. M. E. Fisher. The calculations for this paper were made on the Pegasus computer at the Northampton College of Advanced Technology and we are indebted to the computing staff for much advice and assistance.

PHYSICAL REVIEW VOLUME 124, NUMBER 2 OCTOBER 15, 1961

Influence of Silver Impurities on the Annealing Kinetics of Quenched Gold Specimens

F. CATTANEO AND E. GERMAGNOLI*
Laboratori Centro Informazioni Studi Esperienze, Milano, Italy

(Received June 14, 1961)

The recovery of quenched-in extra resistivity has been studied in thin gold wires, to which atomic concentrations of silver equal to 1.2×10^{-3} or 1.4×10^{-4} have been added. Recovery occurs at higher temperatures than for pure specimens, the effective activation energy being larger than 1 ev. The interpretation is that vacancy-impurity complexes are formed, whose binding energy is about 0.3 ev. Evidence of motion of defects at low temperature is also obtained in the case of impure specimens.

I. INTRODUCTION

A GREAT deal of attention has been devoted in the last few years to the kinetics of lattice vacancies in face-centered cubic metals. After the first results by Koehler *et al.*[1] for gold, the quenching method has been widely used to inject vacancies into the specimens; the features of recovery of quenched-in extra resistivity during annealing at suitable temperatures have been assumed to be directly related to the behavior of lattice vacancies.

Experimental evidence has been accumulated, however, to show that recovery is very seldom a simple process. Actually, if the equilibrium concentration of vacancies at the quench temperature is large, divacancies are very likely to be formed during quench, which influence the annealing kinetics.[2,3] Moreover, electron microscope observations by Silcox and Hirsch[4] and investigation of changes in mechanical properties during annealing by Mori, Meshii, and Kauffman[5] provided clear experimental evidence that the formation of vacancy clusters is also important in quenched gold.

Annealing kinetics seem to be simple and reflect essentially the behavior of pure vacancies only if the

---

[*] Laboratori Centro Informazioni Studi Esperienze and Istituto di Fisica del Politecnico, Milano, Italy.

[1] J. W. Kauffman and J. S. Koehler, Phys. Rev. **97**, 555 (1955).

[2] J. S. Koehler, E. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

[3] G. J. Dienes and A. C. Damask, Trans. Faraday Soc. (to be published).

[4] J. Silcox and P. B. Hirsch, Phil. Mag. **4**, 72 (1959).

[5] T. Mori, M. Meshii, and J. W. Kauffman, Acta Met. **9**, 71 (1961).

initial concentration of vacancies is very low, corresponding to a quench temperature lower than 700°C in the case of gold.

Recent calculations by Damask and Dienes[6] have taken into account the possible influence of impurity atoms on the kinetics of vacancy annealing. Even if formation of extended clusters of defects around impurity atoms is neglected, which effect has been considered in principle by Kimura *et al.*,[7] vacancy-impurity complexes may be responsible for a noticeable deviation of the value of the activation energy for recovery from the value of the migration energy of pure vacancies. Nevertheless, simple exponential annealing kinetics is predicted theoretically,[6] and therefore it is advisable to repeat the annealing experiments with the use of specimens which contain impurity atoms of a well-defined type and in controlled concentrations.

In the case of gold the basic parameters describing the behavior of lattice vacancies and of their simplest aggregates have been fairly well established. The activation energy for formation of lattice vacancies E_F is 0.98 ev,[8,9] the migration energy of vacancies E_M is found equal to 0.83 ev,[8,10] within very narrow limits.

The self-diffusion energy E_D is 1.81 ev,[11] which value is consistent with the sum E_F+E_M. The activation energy for migration of divacancies has been estimated as equal to about 0.6 ev.[10,12]

Gold is commercially available with an impurity content of about 5×10^{-6} in the most favorable cases. Further purification by the zone-refining method appears very difficult although some increase of purity in zone-refined gold has been reported in literature.[13] The present writers have succeeded so far in reducing the content of silver and of some other impurities by about 50%, but it was felt convenient to defer to a subsequent research the investigation of the behavior of gold of such or possibly greater purity.

The results to be described concern mainly gold specimens whose initial purity is somewhat better than 10^{-5} and to which silver has been added in known amounts. Data on the behavior of lattice vacancies when impurities are present can be derived from our results, though they have to be considered as preliminary to some extent.

2. EXPERIMENTAL METHOD AND PRELIMINARY RESULTS

The specimens were thin wires, 0.07 and 0.04 mm in diameter and about 20 cm long. Quenches were performed at temperatures which in most cases were lower than 700°C, so that concentrations of frozen-in vacancies were smaller than 10^{-5}. In order to vary the quenching rates within a wide range, water and helium at 10 atm were used as cooling agents, and moreover, many quenches were performed in air, letting the wires cool down naturally. At low quenching temperatures the changes in resistivity were practically independent of the cooling rate.

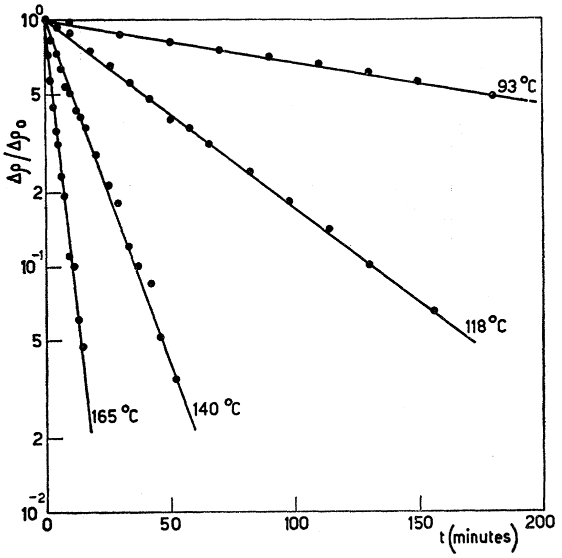

FIG. 1. Isothermal annealing curves obtained with 0.04 mm pure gold wires. Quenching temperature 700°C.

Isothermal annealing measurements which were performed with wires of the above indicated purity showed that the kinetics of recovery is exponential with all the quenching procedures, and that the induced resistivity changes recover completely within a few percent. The activation energy for vacancy migration turned out to be 0.84±0.03 ev according to these measurements, in close agreement with the results of the above quoted authors. The orders of magnitude of times which are required for recovery at various temperatures are shown in Fig. 1.

Silver was introduced in atomic concentrations equal to 1.4×10^{-4} and 1.2×10^{-3} by means of electroplating followed by a diffusion annealing for several hours at 850°C. The concentration of silver was checked both by weighing and by adding a small amount of Ag^{110} of known specific activity to the electrolytic bath.

Most of the results described in the following sections were obtained with $\text{Au}+10^{-3}$ Ag wires. The changes in resistivity were measured according to an already described method,[14] in which the resistance of the actual wire is compared with that of a dummy, pure gold specimen.

---

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

[7] H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, Acta Met. **7**, 154 (1959).

[8] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

[9] W. DeSorbo, Phys. Rev. **117**, 444 (1960).

[10] W. Schüle, A. Seeger, F. Ramsteiner, D. Schumacher, and K. King, Z. Naturforsch. (to be published).

[11] S. M. Makin, A. H. Rowe, and A. D. LeClaire, Proc. Phys. Soc. (London) **70**, 545 (1957).

[12] S. Yoshida and J. S. Koehler, Acta Met. **8**, 878 (1960).

[13] J. H. Wermick, D. Dorsi, and J. J. Byrnes, J. Electrochem. Soc. **106**, 245 (1959).

[14] A. Ascoli, M. Asdente, E. Germagnoli, and A. Manara, J. Phys. Chem. Solids **6**, 59 (1958).

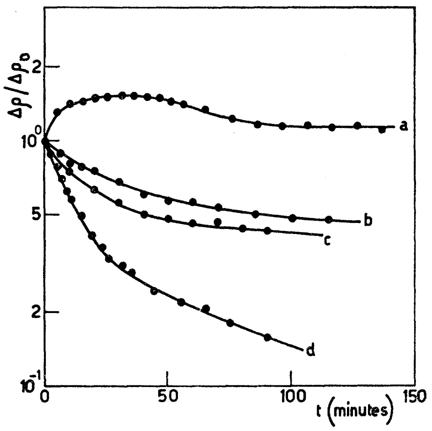

FIG. 2. Isothermal annealing curves obtained with 0.04-mm Au+1.2×10^{-3} Ag wires. Quenching temperature 660°C, annealing temperature 126°C. a. After quench subsequent to a 10-min 800°C annealing. b. After quench subsequent to one quench and 350°C annealing. c. After quench subsequent to four quenches and 350°C annealings. d. After quench subsequent to seven quenches and 350°C annealings.

3. EXPERIMENTAL RESULTS: Au+1.2×10^{-3} Ag

(a) The values of the quenched-in resistivity for impure specimens are identical to the ones found in the case of pure gold. A preliminary investigation of the annealing behavior of impure specimens showed that their characteristic recovery times are longer than the typical ones for pure specimens, but the results were very poorly reproducible. In this respect the outstanding feature was that, if a specimen underwent several isothermal annealing curves at the same temperature after quenches at a fixed temperature, the recovery rate increased gradually. This behavior is shown in Fig. 2. The interpretation of curve a in this figure will be discussed later.

It is apparent that this behavior has to be attributed to disorder being accumulated within the specimen due to repetitive quenches. Additional sinks for lattice defects are presumably supplied by clusters, which are also responsible for some additional extra resistivity that does not recover even at 350°C. The influence of impurities is the enhancement of this effect which was noticed already for pure specimens by Bauerle and Koehler[8] for quenching temperatures of about 900°C or higher.

Figure 3 shows that the percentage of $\Delta\rho$, left after a 155°C annealing, decreases if the quenching temperature is decreased, but is still not negligible if the quenching temperature is as low as 650°C. The effect is peculiar to impure specimens.

(b) Much more reproducible results are achievable whenever the specimens have been annealed for 10–30 min at 800°C before each quench. It is likely that with this procedure the situation existing before quench and annealing has been recovered, a substantial portion of clusters formed during the previous quench having been annihilated.

Figure 4 shows a few isothermal annealing curves obtained immediately after quenches with the procedure discussed in the above paragraph. They are different from those obtained with pure specimens in two main respects: A resistivity maximum is apparent for annealing temperatures between 20° and 150°C or thereabout, and no subsequent recovery can be noticed even at temperatures at which lattice vacancies appear to be mobile in pure specimens. These facts suggest that the defects responsible for the observed changes in resistivity are no longer single vacancies, but defects which are mobile even at room temperature, namely divacancies. Moreover, more complicated defects, which are practically immobile and stable even around 150°C, must be present.

(c) Some isothermal annealing curves are shown in Fig. 5. In this case specimens containing silver (1.2×10^{-3} atomic concentration) were quenched at 660°C and subsequently annealed at 120°C for one hour. With this preliminary treatment the existence of a second stage of recovery was demonstrated. Apart from a fast initial transient, first-order kinetics are obeyed, the characteristic activation energy being equal to 1.05 ±0.10 ev. The residual $\Delta\rho$, after such recovery, corresponds to about 10% of the $\Delta\rho$ which is left after the preliminary treatment, and disappears only after a very high temperature annealing.

Figure 6 gives the characteristic times for this annealing stage and also, for comparison, the characteristic times which were observed with pure specimens quenched at the same temperature. It is apparent that a different activation energy is obtained and that recovery is much slower in impure specimens. The

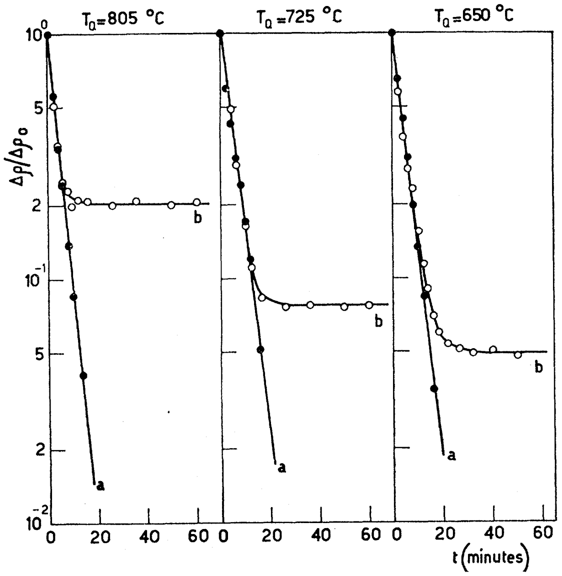

FIG. 3. The influence of quenching temperature on the residual extra-resistivity which does not recover at 155°C. Curves a: pure Au wire. Curves b: Au+1.2×10^{-3} Ag wires.

pre-exponential factor τ_0 in the Arrhenius equation,

$$\tau = \tau_0 \exp(Q/kT),$$

is, however, about 10^{-8} sec in both cases.

4. EXPERIMENTAL RESULTS: $Au+1.4\times10^{-4}$ Ag

Similar, though less extended, measurements were carried out with gold wires to which silver had been added with an atomic concentration of 1.4×10^{-4}. Such specimens behaved in some way intermediately between pure wires and 10^{-3} Ag wires. This statement is illustrated in Fig. 7, where three isothermal annealing curves at 126°C are compared: They refer to three specimens whose impurity content is different. It is apparent that if the silver content is about 10^{-4}, recovery obeys a first-order equation over a wide interval, the characteristic time being, however, noticeably longer than for a pure specimen. A resistivity maximum is also noticed, similar to the case of 10^{-3} Ag wires. The maximum occurs at an earlier time and is not as high as for the more impure wire, though it is still fairly evident at lower annealing temperature.

5. DISCUSSION

The two reactions in the annealing of vacancies to sinks in the presence of impurities which have been taken into account by Damask and Dienes[6] are

$$V_1 + I \underset{K_2}{\overset{K_1}{\rightleftarrows}} C,$$

$$V_1 \overset{K_3}{\longrightarrow} \text{sinks},$$

where V_1, I, and C are the concentrations of vacancies, unbound impurities, and vacancy-impurity complexes, and K_1, K_2, K_3 are appropriate rate constants. The integration of the corresponding differential equations showed that after a fast transient C and V decay steadily, the effective rate constant being

$$K_e = K_3 \bigg/ \left(1 + \frac{K_1}{K_2} I_0\right), \qquad (1)$$

where I_0 is the total impurity concentration. If the K's used by the above quoted authors are introduced into (1), one gets

$$K_3/K_e = 1 + 6 I_0 \exp(B/kT),$$

and the binding energy B of the silver atom plus vacancy complex can be deduced from the measured K_3/K_e ratio, as long as K_e and K_3 are obtained at the same annealing temperature T.

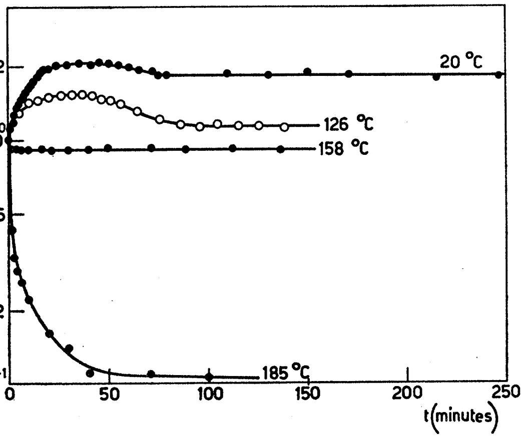

FIG. 4. Isothermal annealing curves obtained with 0.04-mm $Au+1.2\times10^{-3}$ Ag wires. Quenching temperature 660°C.

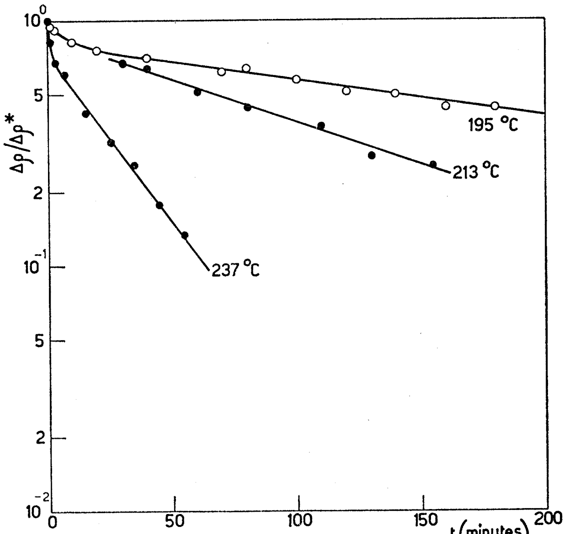

FIG. 5. Isothermal annealing curves obtained with 0.04-mm $Au+1.2\times10^{-3}$ Ag wires. Quenching temperature 660°C. One hour preliminary annealing at 120°C.

Unfortunately it is very hard to obtain accurate values of B with the help of this procedure, the main reason being that the characteristic times for recovery at one fixed temperature are different for different wires as the density of sinks for defects are seriously affected by the previous history of each wire, in particular by the diffusion annealing which is necessary to introduce impurities. When this method was used on data like those from Fig. 5 and Fig. 7, the resulting values of B were

$$B = 0.26 \pm 0.06 \text{ ev}, \quad (Au+10^{-4}\text{ Ag wires}),$$

$$B = 0.41 \pm 0.08 \text{ ev}, \quad (Au+10^{-3}\text{ Ag wires}).$$

It is not understood at present if this difference between specimens containing different concentrations of silver can be explained simply by the rather poor reproducibility of the measurements of characteristic times for recovery.

A lower limit for B can be obtained by comparing

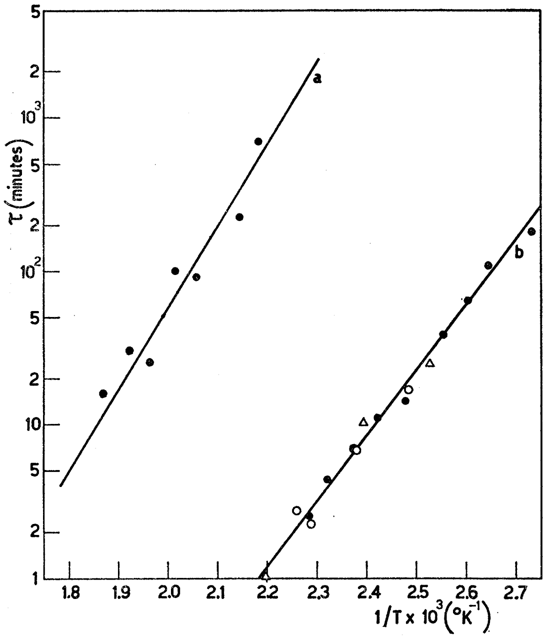

FIG. 6. Characteristic times for recovery of quenched-in extra-resistivity. Curve a: Au+1.2×10^{-3} Ag wires. Curve b: pure Au wires. ● 0.04-mm wires, air quenching. ○ 0.07-mm wires, air quenching. △ 0.07-mm wires, water quenching.

the effective activation energies for recovery which are found from Fig. 6 in the cases of pure and impure specimens:

1.05 ± 0.10 ev, (Au+10^{-3} Ag),
0.83 ± 0.02 ev, (Au, average value according to several authors).

In this way the binding energy B proves to be $\gtrsim 0.2$ ev.

The equality would be valid provided that gold specimens with an impurity concentration near 10^{-5} can be considered as infinitely pure and if specimens containing a 10^{-3} Ag concentration are such as will fit the extreme conditions considered by Damask and Dienes. In this last case

$$K_3/K_e = 6I_0 \exp(B/kT),$$

and the effective migration energy of defects is actually E_M+B.

This conclusion does not seem warranted on the basis of the above results with the Au+10^{-3} Ag specimens. In fact, an inspection of Fig. 5 of the quoted paper by Damask and Dienes shows that a simply exponential relationship between K_e and $1/T$ is not necessarily valid in our experimental conditions: This fact could suggest that the above reported effective activation energy for recovery could be somewhat larger than 1.05 ev in the case of Au+10^{-3} Ag wires.

Not enough data were obtained with the Au+10^{-4} Ag specimens to derive a reliable value of the effective activation energy for recovery.

It is felt that the binding energy of the silver atom-vacancy complex is about 0.3 ev, and it can be safely concluded that the annealing stage at 150–250°C and the results which are summarized in Fig. 5 and Fig. 6 suggest that the ideas put forward by Damask and Dienes are correct.

An attempt should be made to explain the maximum followed by a plateau observed during short time isothermal annealings of impure specimens. The proposal of Sosin[15] of a change in resistivity as single vacancies become bound to impurities was considered. If Sosin had allowed β's greater than one (see Fig. 8 of the quoted paper), it is evident that a rise to a saturation, or a maximum followed by a decrease to zero, could result, but not the observed maximum followed by a plateau reported here. Therefore the following scheme is proposed. Since impure specimens anneal at temperatures as low as 20°C, it is likely that the most mobile observed defects are divacancies. The hypothesis which is put forward here is that clusters of defects are formed during the quench of impure specimens. Clusters, whose contribution to the extra-resistivity is presumably small, are essentially stable and immobile at low temperature, as shown by the general features of the recovery curves, apart from the fact that they evaporate divacancies at low temperature, thereby increasing the resistivity; divacancies in turn either disappear to sinks or get bound in impurity-divacancy complexes.

If notations similar to the ones used by Damask and Dienes are used, the additional reactions between defects which have to be considered in the low-temperture situation are the following:

$$\text{Clusters} \xrightarrow{\lambda} V_2,$$

$$V_2+I \underset{\lambda_2}{\overset{\lambda_1}{\rightleftarrows}} C',$$

$$V_2 \xrightarrow{\lambda_3} \text{sinks}.$$

Here V_2 means divacancy, I means impurity atom, and C' indicates a V_2+I complex, similar to the one considered by Damask and Dienes: $C=V_1+I$. λ, λ_1, λ_2, λ_3 are appropriate rate constants.

An attempt at solving the corresponding set of differential equations has been made, clusters having been assumed for the sake of simplicity to act like an inexhaustible source of divacancies, I held constant, and the concentration of divacancies immediately after quench having been assumed to be very small. A $V_2(t)$ curve was obtained which shows a trend which is in qualitative agreement with the experimental ones, but no serious attempt was made to determine the characteristic parameters such as the rate constants.

---

[15] A. Sosin, Phys. Rev. **122**, 1112 (1961).

From an experimental point of view, the facts that the higher the annealing temperature, the faster the maximum in resistivity is reached, and the higher the annealing temperature the less marked is the maximum, seem to confirm that the initial increase in resistivity is related to the boiling off of the divacancies.

The fast initial annealing stage of recovery which is noticed in curves like those given in Fig. 5 is likely to be attributed to the disappearance of divacancies which are left in transient equilibrium conditions at 120°C, either free or bound in C' complexes.

6. CONCLUSIONS

The results reported in the previous sections are believed to give a picture, though far from complete, of the behavior of quenched-in lattice defects in gold specimens containing silver as impurity. Generally speaking, the theory developed by Damask and Dienes appears to be confirmed, though the pattern seems more complicated than expected, due to the non-negligible probability that large complexes are formed in quenched impure specimens.

The general ideas which are suggested by these results have been confirmed from further measurements carried out with gold specimens to which a 5×10^{-4} atomic percent of nickel has been added. Detailed investigations are in progress and show similar kinetics, though less prominent maxima were obtained during annealing at low temperature and the characteristic recovery times between 90° and 150°C are much more similar to the ones obtained for pure gold than in the case of the silver-doped specimens.

Much purer specimens and more accurate and reproducible measurements are needed in order to obtain precise values of the binding energies of vacancy-impurity complexes and to confirm the fact that a silver content of 10^{-5} or slightly less does not affect appreciably the kinetics of lattice vacancies in gold when the initial concentrations of vacancies are sufficiently low. This fact seems to have been reasonably well established here, but investigations with extremely pure specimens, to which impurity atoms have been added in controlled amounts, are highly desirable.

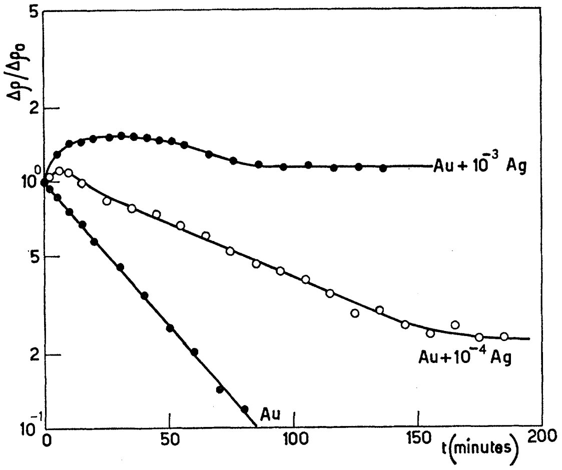

FIG. 7. Influence of the impurity content on isothermal annealing curves at 126°C.

ACKNOWLEDGMENTS

The help of B. Rossi in taking the experimental data is gratefully acknowledged. The authors are indebted to Dr. G. J. Dienes and Dr. A. C. Damask for stimulating discussions, helpful comments, and criticism of the manuscript.