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Atomic Mobility in a Cu-Al Alloy after Quenching and Neutron Irradiation*†

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A study of atomic mobility in a Cu−Al (17 atomic percent Al) solid solution is carried out by anelastic relaxation methods. Measurements are made under equilibrium conditions, after quenching, and after neutron irradiation. The results differ significantly in two ways from the quenching experiments of Kauffman and Koehler on pure gold. First, the ratio J/Q (where J is the activation energy for migration of the appropriate lattice defect, and Q the activation energy for equilibrium atomic diffusion) is 0.6 in the present experiments and only 0.36 for the quenched gold. This difference in ratio corresponds to a difference of about two orders of magnitude in the vacancy concentration at the melting point. Second, in contrast to the behavior of the pure metal, the irradiated Cu−Al alloy shows no evidence for the annealing of point defects in the range of temperature in which quenching effects anneal out. It is therefore difficult to reconcile the present results with those on pure gold if one assumes that the same lattice defect is responsible for both. A survey of other quenching experiments and of measurements on the annealing of cold worked metals provides additional evidence for a defect for which $J/Q=0.5-0.6$ in various metals. A tentative interpretation of existing data may be given in terms of the assumption that the low-mobility (high J/Q) defect is the single vacancy while the high-mobility defect is the divacancy.

I. INTRODUCTION

ANELASTIC measurements provide a valuable method in the study of atomic mobility in substitutional solid solutions. The method is based on a relaxation phenomenon in these alloys first discovered by Zener[1] and known variously as "the pair-reorientation effect," "stress-induced ordering," or simply "the Zener relaxation." The phenomenon manifests itself as a nearly exponential relaxation of stress under constant strain, a recoverable creep at constant stress, and a sharp peak in internal friction as a function of temperature. Zener[2] first suggested a mechanism for this relaxation phenomenon, whereby pairs of solute atoms undergo preferential reorientation under an applied stress. A more refined treatment by Le Claire and Lomer[3] regards the effect as a change in short-range order induced by an applied stress. This change in short-range order will in general be different for each of the nearest-neighbor directions when the stress is not hydrostatic.

Regardless of the correctness of this mechanism, there is no doubt that anelastic relaxation in solid solutions is due to atomic rearrangement under an applied stress. Thus, the reciprocal of the relaxation time, τ, may be taken as a measure of atomic mobility. Since both species of atoms which comprise a binary solid solution do not have the same mobility, it has been proposed[4] that the slower moving constituent controls the relaxation rate. The exact relation of the relaxation time, τ, to the separate mean atomic jump times of the two types of atoms has not yet been established, although a relation has been suggested[4] based on simplifying assumptions.

For a mechanism of diffusion which involves lattice defects (in particular, for a vacancy mechanism) the relaxation rate should be given by[5]

$$\tau^{-1}=Ace^{-J/kT}, \tag{1}$$

where A is a frequency factor which includes the entropy of activation, c is the mole fraction of lattice defects, and J is the rate controlling activation energy for migration (jump) of a defect. Equation (1) is valid whether or not defects are present in equilibrium quantities. In the special case of thermal equilibrium, the concentration of defects is given by

$$\bar{c}=Be^{-H/kT}, \tag{2}$$

where H is the heat of formation of a defect and B is an entropy factor ($B=\exp\Delta S_f/k$, where ΔS_f is the entropy of formation). Thus the equilibrium relaxation rate may be written

$$\bar{\tau}^{-1}=ABe^{-Q/kT}, \tag{3}$$

with

$$Q=J+H. \tag{4}$$

Equation (1) may be applied more generally, for example under such nonequilibrium conditions as after quenching or after irradiation with high-energy nuclear particles. Both of the latter procedures introduce an excess of lattice defects. Thus c would be initially equal to the equilibrium concentration $\bar{c}$ at some elevated temperature. In the case of quenching, for example, the concentration of trapped defects equals the equilibrium

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[1] C. Zener, Trans. Am. Inst. Mining Met. Engrs. 152, 122 (1943).

[2] C. Zener, Phys. Rev. 71, 34 (1947).

[3] A. D. Le Claire and W. M. Lomer, Acta Metallurgica 2, 731 (1954).

[4] A. S. Nowick, Phys. Rev. 88, 925 (1952).

[5] A. S. Nowick and R. J. Sladek, Acta Metallurgica 1, 131 (1953).

concentration at the quenching temperature, provided none were lost during the quench; more generally, the concentration of trapped defects is equal to the equilibrium concentration at some lower temperature, T_F, the "freezing-in temperature." Thus

$$c(0)=\bar{c}(T_F), \qquad (5)$$

where $c(0)$ represents the initial concentration of defects after quenching. This initial value is not stable, so that at any temperature the defect concentration decays with time, i.e., $c=c(t)$. Correspondingly τ^{-1}, which begins at an abnormally high value, will change with time in proportion to $c(t)$, in accordance with Eq. (1). It is therefore possible to detect and observe the rate of disappearance of defects introduced by quenching or by irradiation simply by observing the anelastic relaxation time in a solid solution as a function of time at constant temperature.

Such experiments have already been carried out in quenched silver-zinc solid solutions.[5,6] This alloy was selected because of the large Zener relaxation obtainable in the composition range 30–33 atomic percent zinc. The principal results of these quenching experiments are that excess vacancies may be retained by quenching and that these defects decay out of the lattice in two stages. The evidence and interpretations concerning these stages will be discussed later in this paper. It was also possible to obtain separate measurements of J and of Q [Eq. (4)], from which it is found that the ratio J/Q is very nearly equal to 0.6, i.e., that 60% of the activation energy for atomic mobility was in the defect jump energy and 40% in the defect formation energy.

The value of J/Q obtained in the experiments on the quenching of Ag$-$Zn alloys is quite different from the value of 0.36 obtained by Kauffman and Koehler[7] for J/Q in quenching experiments on pure gold.[8] In the latter work, which utilized resistivity measurements, H was determined from the variation of the extra resistivity with quenching temperature, and J from the rate of annealing out of the extra resistivity. It was found that $J+H$ was very nearly equal to the value of Q determined independently in experiments on self-diffusion in gold, thus strongly suggesting that these quenching experiments were observing the effects of vacancies responsible for diffusion at elevated temperatures.

In view of the fact that the energies J and H appear in exponentials, the difference between $J/Q=0.6$ obtained for Ag$-$Zn and $J/Q=0.36$ obtained for gold seems very significant. Three illustrations will be given to show the importance of this difference in the ratio J/Q.

(1) From Eq. (2), the equilibrium concentration of vacancies at the melting point depends on B and on the ratio of H to the melting temperature, T_m. Inasmuch as the entropy factor B lies in the range[5,9] from 1 to 10, and the ratio Q/kT_m is very nearly a constant (equal to 18 ± 2) for a large number of metals and alloys[10,11] it follows that the equilibrium concentration of vacancies at the melting point, $\bar{c}(T_m)$, is for the most part determined by the ratio H/Q for vacancies. For a value $H/Q=0.4$ (consistent with the results on Ag$-$Zn) we find $\bar{c}(T_m)\cong3\times10^{-3}$. On the other hand, for $H/Q=0.65$ (consistent with the results on gold), $\bar{c}(T_m)\cong3\times10^{-5}$. The difference between a concentration of vacancies at the melting point of 0.3% and a concentration two orders of magnitude lower than this value is certainly significant with regard to the extent to which vacancies may contribute to the high-temperature properties of metals and alloys.

(2) A low ratio of J/Q of about 0.35 means that vacancies have significant mobility in the vicinity of room temperature for such metals as Cu, Ag, and Au and their alloys. On the other hand, $J/Q=0.6$ means that there is no appreciable rate of migration of vacancies is such metals until somewhat more elevated temperatures. Thus, for example, Kauffman and Koehler[7] found appreciable decay rates for the excess resistivity introduced by quenching starting below room temperature, while for Ag$-$Zn, decay of quenching effects began at about 50°C. Yet Q of the Ag$-$Zn alloy is only 0.7 times that for gold. If the alloy had a value of Q equal to that for gold, the corresponding migration range (for defects for which $J/Q=0.6$) would be about 170°C.

(3) Copper irradiated at liquid nitrogen temperature shows what appears to be a unique recovery process,[12,13] which obeys nearly second-order kinetics, in the vicinity of -20°C. The activation energy for this recovery is about 0.7 ev. Since this activation energy is about 0.35 of Q for self-diffusion in copper, this 0.7-ev recovery process could be ascribed to vacancies if one accepts the ratio $J/Q=0.35$ for vacancies. On the other hand, if $J/Q\cong0.6$ for vacancies in copper, this unique recovery process in irradiated copper would have to be ascribed to some other type of defect.

It is hardly likely that the ratio J/Q for vacancies will differ greatly for different metals which are similar in nature, such as Cu, Ag, and Au; however, a large difference in this ratio between an alloy and a pure metal is not necessarily unreasonable. To justify such a difference, it may first be assumed that the formation

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[6] A. E. Roswell and A. S. Nowick, J. Metals **5**, 1259 (1953).

[7] J. W. Kauffman and J. S. Koehler, Phys. Rev. **88**, 149 (1952); **97**, 555 (1955).

[8] There are other evidences concerning J/Q in pure metals which will be discussed in Sec. IV of this paper. These other evidences, however, do not seem to be capable of as direct and clear-cut an interpretation as the experiments of Kauffman and Koehler.

[9] H. Brooks, *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955), p. 1.

[10] A. D. Le Claire, Acta Metallurgica **1**, 438 (1953).

[11] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[12] A. W. Overhauser, Phys. Rev. **90**, 393 (1953).

[13] R. R. Eggleston, Acta Metallurgica **1**, 679 (1953).

energy H, for a vacancy in an alloy is much smaller than the same quantity in the corresponding pure metal. An assumption of this sort may be justified in terms of the local distortions in a solid solution, which might make it easier to introduce a vacancy. In view of the fact that Q for an alloy is roughly the same as for a pure metal of the same melting point, it must also be assumed that J is larger for an alloy than for a pure metal, and in fact, enough larger to compensate for the decrease in H. This second assumption may be more difficult to justify, but nevertheless does not appear to be ruled out completely on theoretical grounds. These assumptions, that J is unusually high and H unusually low for vacancies in alloys as compared to pure metals, seem to provide the most direct interpretation of the observed differences in the ratio J/Q. In terms of this interpretation, it must be assumed that J/Q for a vacancy in copper is about 0.35; therefore, in accordance with item (3) above, the defect which is annealed out of irradiated copper with an activation energy of 0.7 ev is the simple vacancy. It is further anticipated that the same annealing effect which takes place in irradiated copper below room temperature should occur at higher temperatures in irradiated alloys, in fact, in the same temperature range as the annealing which takes place after quenching.

The purpose of the present experiments was primarily to check this prediction by a comparison of relaxation rates following neutron irradiation with those following quenching. The use of Ag—Zn alloys, which show the largest Zener relaxation and for which the quenching experiments have already been carried out, was ruled out by practical considerations, i.e., the strong activity and long half life of the radioactive isotope Ag^{110}, produced by neutron irradiation of Ag. Thus, another alloy had to be found which would show a Zener relaxation and yet which could be handled not too long after irradiation. For this purpose, the solid solution alpha Cu—Al (17 atomic percent Al) was chosen. It shows a smaller Zener relaxation (by an order of magnitude) than Ag—Zn, which somewhat limits the precision of the determination of τ by static methods; however it is quite suitable for the proposed irradiation experiments. Since neither equilibrium measurements of relaxation time nor quenching experiments had been done on this alloy previously, it was necessary to start with such measurements.[14,15]

II. EXPERIMENTAL METHODS

The Cu—Al alloy was a commercial aluminum bronze furnished in the form of 0.125-inch diameter rod by the American Brass Company. This rod was then drawn down to 0.029- and 0.016-inch diameter wires. Analysis showed 7.90 weight percent (16.8 atomic percent) aluminum. Other impurities were: 0.015 Si, 0.001 Pb, 0.020 Fe, 0.035 Zn, 0.01 Ni, 0.01 As, 0.01 P (all in weight percent).

The drawn wires were sealed under vacuum in quartz tubes and annealed at 900°C for two days in order to obtain a large grain size and thereby to minimize the importance of grain-boundary relaxation[16] in these specimens.

All measurements were made in a torsion pendulum similar to that of Kê.[16] The length of the specimen wires between the upper and lower pin vises in the pendulum was usually 10 inches, except for some of the irradiated specimens which had a 4.5-inch gauge length. The temperature variation over the 10-inch specimen length was within 2°C at 300°C. Temperature was controlled to within 0.5°C by means of an electronic temperature controller.

Internal friction was measured in the conventional way by attaching an inertia member to the vertical extension of the lower pin vise. All measurements of relaxation time after quenching and irradiation were by means of static (*viz.*, elastic after-effect) techniques. These measurements were carried out in the same way as reported previously.[4,5] The wires were twisted for the desired length of time and, upon release, strain was observed as a function of time. The time to reach the inflection point in a plot of strain *vs* log time is the most convenient measure of the relaxation time, τ. The finer wires (0.016-inch diameter) were used for elastic after-effect measurements to permit a relatively large twist without the onset of plastic flow. The use of large angles of twist, relative to the earlier work, was necessary in view of the small relaxation strength for the Zener relaxation in Cu—Al. The use of the finer wire for irradiation experiments also served to keep down the level of radioactivity. Experiments were carried out to show that there was no effect of wire diameter on the measured value of τ.

A separate vertical furnace was used for quenching. Dry nitrogen was passed through the furnace to prevent oxidation. Specimens were suspended freely by means of a thin copper wire and quenching was effected by setting this suspension wire free and allowing the specimen to drop into a long tube containing water at 0°C. The quenching temperature was 570°C for all experiments reported herein. Following the quench, the specimen was mounted in the torsion pendulum and successively twisted and released at a desired temperature to determine the variation of relaxation time with time of annealing at that temperature.

Neutron irradiation was carried out by placing specimens in the reactor of the Brookhaven National Laboratory for a period of 3 to 4 weeks. The integrated neutron flux for this irradiation is about 10^{19} nvt. One group of specimens was subjected to irradiation at

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[14] Equilibrium measurements have been reported for a 15 atomic percent Cu—Al alloy,[15] but due to the difference in composition and the limited range over which τ was measured, these previous measurements are of no help for present purposes.

[15] B. G. Childs and A. D. Le Claire, Acta Metallurgica 2, 718 (1954).

[16] T. S. Kê, Phys. Rev. 71, 533 (1947).

50°C, a second at 35°C, and the final group was irradiated at liquid nitrogen temperature using the low temperature facility described by McReynolds *et al.*[17] Following irradiation, all specimens were stored at 80°K for about one month, to allow for a decay of radioactivity to a safe level. They were then brought to room temperature, mounted in the torsion pendulum and measured in the same manner as the quenched specimens.

III. RESULTS AND DISCUSSION

A. Equilibrium Experiments

Internal friction measured as a function of temperature at a frequency $f=0.655$ cps showed the existence of a Zener peak in the present Cu—Al alloy. The height of this peak corresponds to a relaxation strength of 0.015. This peak is an order of magnitude lower than the corresponding internal friction peak in Ag-30% Zn, but is still well resolved from the grain boundary peak in coarse grained specimens. From the condition[4] that $\omega\tau=1$ at the peak (where $\omega=2\pi f$) we obtain $\bar{\tau}(360°\text{C})=0.243$ sec. By means of static (elastic after-effect) measurements, the range of measured values of $\bar{\tau}$ can be extended to lower temperatures. The temperature range actually covered by combining low-frequency internal friction and elastic after-effect measurements is from 367°C to 216.5°C. Values of $\log\bar{\tau}$ obtained are plotted on a straight line *vs* T^{-1}, in accordance with Eq. (3), to give

$$Q=1.81\pm0.08 \text{ ev},$$
$$AB=9.1\times10^{14} \text{ sec}^{-1}.$$

For comparison with diffusion data it is convenient to define the *relaxation diffusion coefficient*, D_r, by

$$D_r=a^2/12\bar{\tau}, \tag{6}$$

where a is the lattice parameter of the alloy. This definition is analogous to the relation obeyed by the individual diffusion coefficients of the two atomic species of the alloy, e.g., $D_A=a^2/12\tau_A$, where D_A is the diffusion coefficient of A atoms as measured by radioactive tracers in the chemically homogeneous solid solution, τ_A is the mean atomic jump time of A atoms, and the factor of 1/12 is a geometrical factor which has this value for all face-centered cubic structures.[10] Figure 1 shows a plot of $\log D_r$ against T^{-1} (solid circles) and a comparison of these data with chemical diffusion coefficients, D_c, obtained at high temperatures for the same alloy composition by Matano analysis.[18] Although attempts have been made to relate theoretically D_c to D_r,[15,19] the results of such efforts are not too reliable since it is necessary to make some drastic simplifying assumptions. For example, in the application of the Darken equation[20] (which relates D_c to D_A and D_B) it must be assumed that there is no porosity in the chemical diffusion experiment. Furthermore, a "thermodynamic factor" must be known experimentally as a function of temperature. In the case of Cu—Al, data required to compute this factor have not been measured. It therefore seems as if the most useful information will come from a comparison of D_r with the quantities D_A and D_B measured by means of radioactive tracer diffusion. Such measurements have recently been made[21] for the alloy alpha brass.

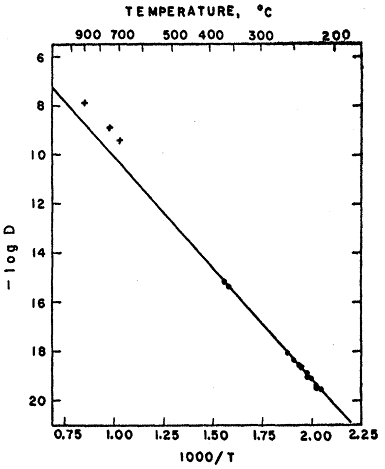

FIG. 1. Comparison of the relaxation diffusion coefficient, D_r, (solid circles) with chemical diffusion coefficients, D_c, (crosses) at various temperatures, for the Cu—Al alloy.

In spite of all the complexities in relating D_r to D_c there is good reason to expect that the value of Q for chemical diffusion and for relaxation will be nearly alike (i.e., within about 20%). Figure 1 shows that Rhines and Mehl's data agree very well with the relaxation data in this respect.

B. Quenching Experiments

As shown in the Introduction, quenching-in a nonequilibrium concentration of defects should result in abnormally low values of relaxation time (high relaxation rates) at a given temperature of measurement. Furthermore, it is possible to study the manner in which the defect concentration varies with time by observing the variation of τ with time at constant temperature. Experiments of this type, similar to those already carried out for the Ag—Zn alloys, were performed on the Cu—Al alloy. In view of the higher melting temperature and Q value for the present alloy as compared to Ag—Zn, a higher quenching temperature was used. It was decided to standardize the procedure by always quenching from 570°C into water at 0°C. Results of the elastic after effect measurements, by means of which τ was determined as a function of time at various annealing temperatures following the quench, are given

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[17] McReynolds, Augustyniak, McKeown, and Rosenblatt, Phys. Rev. **98**, 418 (1955).

[18] F. N. Rhines and R. F. Mehl, Trans. Am. Inst. Mining Met. Engrs. **128**, 185 (1938).

[19] A. D. Le Claire, Phil. Mag. **42**, 673 (1951).

[20] L. S. Darken, Trans. Am. Inst. Mining Met. Engrs. **175**, 184 (1948).

[21] Hino, Tomizuka, and Wert (private communication).

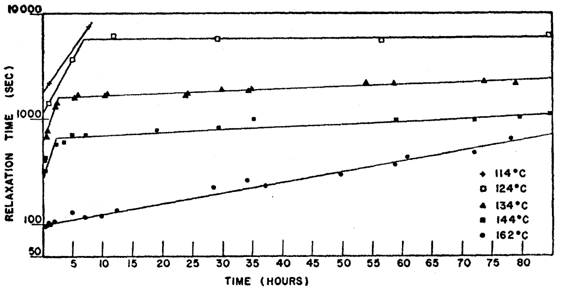

FIG. 2. Variation of the time of relaxation with annealing time at five different annealing temperatures, after quenching the Cu—Al alloy from 570°C. Data from two independent runs are shown both at 134°C and at 144°C.

in Fig. 2. As in the case of the Ag—Zn alloys, sharp breaks appear in the plots of $\log\tau$ *vs* time where the rate of approach to equilibrium slows down abruptly. This result indicates that the decay of lattice defects takes place in two stages. The early and later stages will be referred to respectively as stage I and stage II. At the lowest temperature of measurement reported in Fig. 2, τ became too large to be measured conveniently (i.e., greater than 10^4 sec) before the onset of stage II. On the other hand, at the highest of the annealing temperatures used, stage I was over in such a short time that data were obtained corresponding only to stage II. At each temperature, the equilibrium relaxation time, $\bar{\tau}$, is several powers of ten higher than the initial τ value after quenching (e.g., at 124°C the initial τ is 1200 sec while $\bar{\tau}$ is 1.01×10^8 sec). Although qualitatively the present results are in good agreement with the previous work on Ag—Zn, the precision of the measurement of τ is not as good, due to the smaller relaxation strength in the present alloy. For two of the annealing temperatures, the data points shown in Fig. 2 include runs on two different quenched samples in order to determine the decay curve with greater precision.

Since the quenching temperature and quenching procedure are always the same, the same concentration of defects, $c(0)$, is always obtained initially. Then, from Eq. (1), the initial relaxation time $\tau(0)$ for various temperatures should be proportional to $\exp(J/kT)$. Curve A in Fig. 3 shows a plot of $\log\tau(0)$ against T^{-1}. The straight line is drawn so as to place the least reliability on the point obtained from the 114°C run (since only two measurements were made at this temperature), and to take into account the fact that a value $\tau(0)\sim60-70$ sec at 162°C seems reasonable from Fig. 2. From the slope of this straight line the best value for J and its estimated reliability are as follows:

$$J=1.08\pm0.08 \text{ ev}.$$

From Eq. (4), it then follows that $H=Q-J=0.73$ ev. The ratio $J/Q=0.60$ is then very nearly equal to that previously obtained for the Ag—Zn alloys. From the intercept of the straight line of curve A in Fig. 3, we obtain [Eq. (1)]

$$Ac(0)=3\times10^{10} \text{ sec}^{-1}.$$

Since the value of the product AB has already been obtained from the equilibrium measurements, it requires only a separate estimate of B in order that $c(0)$, the quenched-in defect concentration, may be calculated. Using the value $B=3$, which should be valid to within half an order of magnitude,[5,9] the following values are obtained for the frozen in vacancy concentration and for the equilibrium concentration at the melting point:

$$c(0)=1\times10^{-4},\quad \bar{c}(T_m)=5\times10^{-3}.$$

The calculation of the freezing-in temperature, T_F [see Eq. (5)], is not dependent on the assumed value of B, since combining Eqs. (1) and (2) gives

$$Ac(0)/AB=\exp(-H/kT_F), \tag{7}$$

in which all quantities other than T_F have been obtained from experimental measurements. The value obtained is $T_F=538$°C, which is consistent with the requirement that T_F is less than the quenching temperature.[22]

When the straight line of stage II in the decay curves of Fig. 2 are extrapolated to zero time, we obtain a quantity $\tau_{\text{II}}(0)$, which also varies exponentially with the reciprocal of the absolute temperature (see Fig. 3*B*). From the slope of this plot, an activation energy and and intercept

$$J_{\text{II}}=1.60\pm0.08 \text{ ev},\quad [\tau_{\text{II}}(0)]_0=3\times10^{-17} \text{ sec}$$

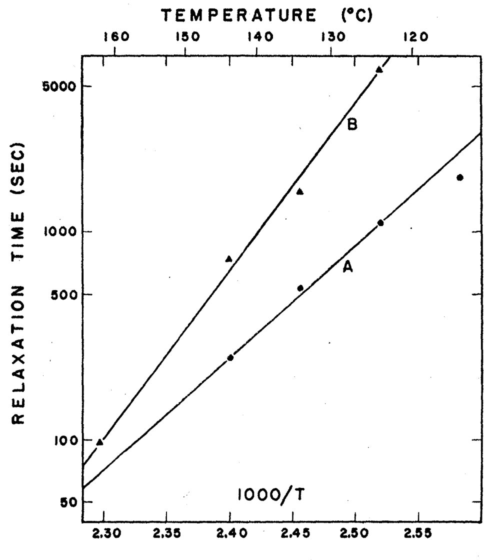

FIG. 3. Curve A: Variation of initial relaxation time immediately after quenching with temperature. Curve B: Initial relaxation time for stage II as a function of temperature.

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[22] Another approach is to obtain an independent estimate for H from Eq. (7), by substituting the quenching temperature, T_Q, for T_F and solving for H. Since $T_Q\geqq T_F$, the value of H obtained is an upper limit. In this way a value $H\leqq0.75$ ev is obtained, which is quite consistent with the value $Q-J=0.73$ ev.

are obtained. These values can be helpful in distinguishing between possible mechanisms to explain the existence of two stages in the decay curves. In a previous paper,[6] two possible mechanisms were suggested to explain the two-stage nature of the decay process. These two possibilities will now be reviewed in the light of the present data on the Cu-Al alloy.

(1) One possible interpretation for the two-stage decay curves is the operation of two different types of defect, which have different mobilities, in producing atom movements. In accordance with this hypothesis, the quantity J obtained from curve A and J_{II} from curve B in Fig. 3 represent respectively the activation energies for migration of these two defects. The intercept of stage II then has the interpretation that $[\tau_{\text{II}}(0)]_0^{-1} = A_{\text{II}}c_{\text{II}}(0)$, where A_{II} is the frequency factor, and $c_{\text{II}}(0)$ the initial concentration of the stage II defect. From the present results, the quantity $A_{\text{II}}c_{\text{II}}(0)$ must be 10^6 times larger than the corresponding product $Ac(0)$ for stage I. Since the frequency factors cannot reasonably be expected to differ by more than one order of magnitude, this would mean that $c_{\text{II}}(0) \gg c(0)$. In view of the relatively large value of $c(0)$ (about 10^{-4}) estimated above, it is impossible that $c_{\text{II}}(0)$ be much larger. Thus, the present results seem to eliminate the hypothesis that two different types of defects are responsible for the two stages in the decay curves.

(2) The second interpretation advanced to explain the two stages of the decay curves is the existence of trapping centers in which the mobility of quenched-in defects is considerably less than in the bulk of the lattice. It was suggested that such regions may be either positions where solute concentration fluctuates considerably from the average for the alloy, or regions near dislocations. In terms of this hypothesis, stage I involves the migration of defects to trapping centers while stage II is controlled by the release of defects from traps. Thus the quantity J, obtained from the slope of Fig. 3A represents the normal activation energy for defect migration. Lomer and Cottrell[23] show that J_{II} is not simply a migration energy but that it also includes the binding energy of the defects in the traps. They also suggest that the trapping centers may be impurity atoms.

A more thorough analysis of the mechanism of the two stages in the light of new experimental data will be presented in another paper.[24]

C. Irradiation Experiments

Wire specimens neutron irradiated at 50°C were first examined. On the basis of the quenching experiments, it is to be expected that if the same defects can be created by irradiation as were frozen in by quenching, abnormally low τ values should be observed. Furthermore, these defects should not decay out at an appreciable rate below 100°C. The following procedure was used in an attempt to detect the presence of nonequilibrium defects. The wire was first twisted at room temperature for abut 5000 sec; it was then released and observed for any after-effect. Following this measurement, the wire was again twisted for about the same length of time while the temperature of the torsion pendulum was raised 25°C. Again the wire was released and any change from the initial position resulting from the twist as well as any after-effect were recorded. This procedure was then repeated again and again as the temperature was raised in 25°C steps up to 200°C. It was found that in all these experiments there was no measurable relaxation effect in times of the order of 3000 seconds. The absence of any nonequilibrium relaxation behavior was further verified by using four new irradiated specimens and making separate runs at 70°, 100°, 150°, and 180°C (one specimen being used for each temperature). Within experimental error, the results showed no observable anelastic behavior at these four temperatures. Additional static measurements were made with an irradiated specimen within the temperature range 230°-250°C, where equilibrium values of τ had been measured previously (see Fig. 1). The values of $\bar{\tau}$ for this irradiated specimen were identical to those obtained previously for unirradiated wires.

It was then felt that in view of the phenomenon of irradiation annealing,[25] enough recovery might have taken place during the irradiation at 50°C to eliminate a large fraction of the excess defects created by irradiation. Accordingly two new groups of specimens were irradiated, the first at 35°C and the final group at liquid nitrogen temperature. Each group was carried through a series of experiments similar to that already described for the set irradiated at 50°C. Again it was found that there was no detectable deviation from equilibrium behavior in the irradiated specimens.

A possible explanation for these negative results is that an insufficient number of lattice defects was created by the irradiation. This suggestion may be eliminated by noting that for pure copper, the resistivity change produced by a low temperature neutron irradiation very similar to the one given the present alloy, is about 0.037 micro-ohm cm.[26] About half of this amount anneals below room temperature in the range attributed to defect migration. According to theoretical calculations[27] one percent of vacancies should produce a resistivity change of about 1.3 micro-ohm cm in copper. Thus, neutron irradiation introduces a defect concentration of at least 1.4×10^{-4}. It seems hardly likely that the defect concentration produced by a similar neutron irradiation for Cu-Al should be much less than this

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[23] W. M. Lomer and A. H. Cottrell, Phil. Mag. **46**, 711 (1955).

[24] A. E. Roswell and A. S. Nowick (to be published).

[25] J. S. Koehler and F. Seitz, *Report of the Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 222.

[26] Reference 17 and D. B. Rosenblatt (private communication)

[27] P. Jongenburger, Phys. Rev. **90**, 710 (1953).

value.[28,29] The concentration of defects produced by irradiation is then of the same order of magnitude as the number obtained by quenching (see Sec. III.B). Therefore, there is good reason to believe that a sufficient number of defects is introduced in a low-temperature irradiation to be detectable in terms of abnormally high relaxation rates. The fact that no such enhancement of the relaxation rate has been observed above room temperature means that these defects have annealed out by the time the specimens have been warmed up to room temperature.

It is most reasonable to explain the negative results of these irradiation experiments by assuming that interstitials, which are created by the irradiation in equal numbers with vacancies, are the more mobile defect (in accord with theory[30]); the interstitials therefore move below room temperature, predominantly to vacancies, thus producing annihilation in pairs. Although the number of vacancies originally created by the low-temperature irradiation may have been large enough to produce abnormally rapid relaxation rates, such annihilations reduce this number by orders of magnitude. Thus, by the time the range of temperatures of rapid vacancy mobility (above 100°C) is reached, there are not enough vacancies left to produce a detectable enhancement of relaxation rates. This interpretation is completely consistent with the results of recent irradiation and annealing experiments on alpha brass,[29] which show that practically all of the excess resistivity induced by neutron irradiation at liquid nitrogen temperature is annealed out in the vicinity of -30°C (similarly to pure copper). These results of Rosenblatt *et al.* suggest the desirability of carrying out low-temperature relaxation experiments on specimens irradiated at liquid nitrogen temperature. No such measurements have been carried out to date, principally because of experimental difficulties.

The negative results of the present irradiation experiments and the above interpretation of these results are not consistent, however, with the interpretation by Kauffman and Koehler of their experiments on quenched gold. As discussed in the Introduction, the quenching results on pure gold and on alloys could best be reconciled on the assumption that the ratio J/Q is abnormally large for the alloys ($\sim$0.60), as compared to pure metals ($\sim$0.35). On this basis the principal annealing effects after irradiation of an alloy should have appeared in the same temperature range as the annealing of the quenching effects, i.e., above 100°C for the Cu—Al alloy. If we wish to maintain the assumption that in both the gold and the alloys the defect annealing out is the simple vacancy, it is necessary to hypothesize for alloys, not only that J/Q is higher than for pure metals, but also that at low temperatures interstitials annihilate vacancies much more effectively than in pure metals. This assumption seems hardly tenable, especially in view of the similarity between annealing of resistivity in low-temperature irradiated copper and brass.[29]

It may be concluded that an attempt to interpret both the resistivity experiments of Kauffman and Koehler and the present experiments on alloys as due to the quenching-in of the same lattice defect (i.e., single vacancies) leads to unreasonable assumptions. It therefore appears that two different kinds of defects are involved in the two sets of experiments. The desirability of determining what these defects may be, and in particular which set of experiments deals with single vacancies, is without question. In this connection, a survey of other evidences concerning the ratio J/Q for lattice defects in metals and alloys will be helpful, even if some of the evidences are fairly indirect. The next section deals with this survey.

IV. FURTHER EVIDENCE CONCERNING J/Q

The most unambiguous evidence concerning lattice vacancies may be expected to come from quenching experiments, since it may be assumed that in such experiments defects which have high formation energies, such as interstitials, do not appear. Data for pure metals and for alloys are presented, respectively, in Tables I and II. All values of Q, J, and H reported in these tables are those deduced from independent experiments; thus, when all three of these quantities have been determined (as in the case of Table I), the values of the quantities J/Q and H/Q need not be expected to add up precisely to unity. In the case of pure gold (Table I) there is the work of Kauffman and Koehler, already quoted, and also the experiments of Lazarev and Ovcharenko.[31] In both cases the extra resistivity was measured after quenching. The principal differences seem to relate to the manner of quenching. Kauffman and Koehler quenched to room temperature by means of a jet of helium gas, while allowing the heating current to continue to flow. They held the specimen at room temperature for less than one second

TABLE I. Results of quenching experiments on pure gold.

Authors	Q(ev)	J(ev)	H(ev)	J/Q	H/Q	$\mathcal{C}(T_m)$
Kauffman and Koehler[a]	1.90[c]	0.68	1.28	0.36	0.67	6×10^{-5}
Lazarev and Ovcharenko[b]	1.90[c]	0.52 (0.96)[d]	0.79	0.27 (0.51)[d]	0.42	4×10^{-3}

[a] See reference 7.
[b] See reference 31.
[c] This Q-value, from the self-diffusion experiments of H. W. Mead and C. E. Birchenall (to be published), seems to be the most reliable one thus far.
[d] Estimated value.

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[28] In fact it may be higher, since the increase in residual resistivity due to irradiation is considerably higher in alloys such as alpha brass than it is in copper.[29]

[29] Rosenblatt, Smoluchowski, and Dienes, J. Appl. Phys. **26**, 1044 (1955).

[30] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

[31] B. G. Lazarev and O. N. Ovcharenko, Doklady Akad. Nauk U.S.S.R. **100**, 875 (1955). This paper also includes data for platinum, which do not seem to be as reliable as those for gold. Also Q for Pt is not known.

before dropping it into liquid nitrogen. The Soviet workers, on the other hand, quenched by shutting off the heating current. Also, they appear to have allowed their specimens to stand at room temperature for longer periods of time following the quench. As a result, they miss the resistivity change that anneals out easily at room temperature; however, the effect they did study, which is annealed out near 150°C, was ignored by the American workers as caused by an "impurity effect." Since the decision that this latter effect is due to impurities was made on the basis of resistivity measurements, this conclusion does not seem to be justified at present.

It is striking that the work of Lazarev and Ovcharenko shows values of H/Q and J/Q which add up only to 0.7. The value of H was determined from the extra resistivity quenched in from various temperatures, and should be reasonably reliable. The value of J was determined from the rates at which the extra resistivity annealed out at three different temperatures; these data are apparently not too precise, since they do not give a good straight line on a plot of log(annealing time) *vs* T^{-1}. In fact, the value of J reported (0.52 ev) for this annealing which occurs near 150°C is lower than that for the defect which anneals at room temperature in Kauffman's work. The writer has estimated what appears to be a better value for J, from the fact that the extra resistivity quenched in by Lazarev and Ovcharenko anneals out at 400°K in about 10^3 seconds and under the assumption that the defects make 10^5 jumps before they are annihilated. This value, and the corresponding ratio J/Q are given in parentheses in Table I. Although the value of J obtained in this way is more reasonable than the originally reported value, it is not clear that the correct number of jumps is as low as 10^5, unless the defects annealing out combine in pairs. If a larger number of jumps were taken, it would result in a decrease in the writer's estimate of J. Nevertheless, this discussion shows that the equation $H+J=Q$ (where Q is the self-diffusion activation energy) is roughly obeyed for both sets of data in Table I, although the two obviously relate to different lattice imperfections. The last column of Table I is an estimate of the equilibrium mole fraction of vacancies at the melting point, $\bar{c}(T_m)$, based on the experimental values of H and an entropy factor $B=3$ [see Eq. (2)]. As discussed in the Introduction, the predictions concerning $\bar{c}(T_m)$ for the different H/Q ratios are strikingly different.

TABLE II. Results of quenching experiments on alloys.

Authors	Alloy	Method	Q(ev)	J(ev)	H(ev)	J/Q
Present work	Cu-17% Al	Anelasticity	1.81	1.08	···	0.60
Roswell and Nowick[a]	Ag-33% Zn	Anelasticity	1.41[c]	0.81	···	0.57
Wechsler[b]	AuCd	Resistivity	···	0.6	0.38	0.61

[a] See reference 6.
[b] See reference 32.
[c] This value supercedes that given in reference 6 (i.e., 1.33 ev), based on additional data.

TABLE III. Results of annealing experiments on cold-worked metals.

Authors	Metal	Q(ev)	J(ev)	J/Q
Brinkman *et al.*[a]	Cu	2.05[d]	1.19	0.58
Boas *et al.*[b]	Ni	2.90[e]	(1.45)[g]	0.50
Semmel and Machlin[c]	Ag	1.98[f]	1.23	0.62

[a] See reference 34.
[b] See references 38 and 39.
[c] See reference 41.
[d] Kuper, Letaw, Slifkin, Sonder, and Tomizuka, Phys. Rev. **96**, 1224 (1954).
[e] R. E. Hoffman (to be published).
[f] Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. **23**, 1032 (1952).
[g] Estimated value.

Table II gives similar data for quenching of alloys. The results of the previous anelastic relaxation measurements on Ag–Zn and of the present work on Cu–Al are supported by recent work of Wechsler[32] on the alloy AuCd, using resistivity measurements. In these three cases, the J/Q ratios are in remarkably good agreement. In the AuCd work, Q has not been determined independently. However, the low value of $J+H=0.98$ ev is not inconsistent with the open (CsCl type) structure of this alloy.

Finally some results of the annealing of cold worked metals are given in Table III. Such data involve the most indirect kind of evidence concerning lattice vacancies, due to the presence of dislocations in high concentrations, and to the possibility for a wide variety of point defects including interstitials and complex clusters of vacancies and interstitials. Nevertheless, several authors claim to have found evidence for the presence of vacancies[33] (or another simple type of point defect) in cold-worked metals. Brinkman *et al.*[34] analyze annealing data on deformed copper[35] and conclude that the early part of this annealing is controlled by defect diffusion, with $J=1.19$ ev. This value gives a ratio J/Q of 0.58, in excellent agreement with the results of quenching experiments on alloys (Table II). The same group of workers[36] obtained an independent estimate of H from measurements of resistivity of copper near the melting point which, together with the value $J=1.19$ ev, obeyed the relation $J+H=Q$ remarkably well; however, the interpretation of these resistivity measurements has been seriously questioned.[37] Clare-

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[32] M. S. Wechsler, Bull. Am. Phys. Soc. Ser. II, **1**, 114 (1956).

[33] Deformed metals (in contrast to irradiated samples) may have an excess of vacancies over interstitials, due to the difference in formation energy of these defects. Annealing effects due to vacancies might therefore be anticipated owing to the fact that interstitials will not completely annihilate the vacancies at low temperatures. Also the high density of dislocations may serve to remove a large number of interstitials which might otherwise annihilate vacancies.

[34] Brinkman, Dixon, and Meechan, Acta Metallurgica **2**, 38 (1954).

[35] Bowen, Eggleston, and Kropschot, J. Appl. Phys. **23**, 630 (1952).

[36] C. J. Meechan and R. R. Eggleston, Acta Metallurgica **2**, 680 (1954).

[37] J. F. Nicholas, Acta Metallurgica **3**, 411 (1955).

brough[38] and Boas[39] report a group of annealing effects in cold-worked nickel which are very strongly suggestive of the annealing out of a simple point defect. The experiments show a peak in the release of stored energy, a drop in resistivity, and an increase in density, all very close to 250°C. They report a rough value of 1 ev for J. A better estimate seems to be obtainable as follows: A recent analysis[40] of low-temperature recovery effects in cold-worked metals shows that J/kT_1 is very close to 32 for a large number of metals at the temperature T_1 at which the recovery time is about 10^3 sec. Using this ratio, an estimate of $J=1.45$ ev is obtained for the defect that anneals out at 250°C in Ni. As shown in Table III, this corresponds to $J/Q=0.50$. Finally, Semmel and Machlin[41] report that the driving force for recrystallization in bent single crystals of silver is the presence of a point defect for which $J/Q=0.62$.

From the negative results of the irradiation experiments reported earlier in this paper, it had been concluded that the observations of Kauffman and Koehler and the present work on alloys could not be dealing with the same lattice defect. The material in Tables I to III now supports this contention by showing that both in pure metals and in alloys there is a variety of evidence for a defect which has a high J/Q ratio (of the order 0.5–0.6), which contrasts sharply with the value $J/Q=0.36$ of Kauffman. If none of the measurements are to be discounted, we must consider that two different defects are being observed. For convenience, the two species of defects involved in these experiments will be referred to as the "low mobility" (high J/Q) and "high mobility" types.

Presumably one of these defect types is the simple vacancy. It might be expected that theoretical calculations might determine the correct J/Q ratio for single vacancies. A recent critical review of such calculations has been given by Brooks[9] who concludes that the best values for vacancies in copper are $J\sim 1$ ev and $H\sim 1$ ev with uncertainties in such a direction as to favor a greater formation than migration energy. Thus the best theoretical values give $J/Q=0.5$ or slightly less, which falls just between the value of this ratio for the low-mobility and the high-mobility defect. In view of uncertainties in this type of calculation, it appears that the theoretical values are inconclusive in establishing which type of defect is the simple vacancy.

In view of our inability to arrive at the J/Q ratio for vacancies by purely theoretical means, it seems best to examine various reasonable assumptions to see which best fits the facts. Let it be first assumed that the high-mobility defect is the single vacancy. The strongest argument for this assumption lies in the fact that J and H have been determined independently, for the high-mobility defect in gold, and found to add up very nearly to Q for self-diffusion.[7] Since it is generally believed that the single vacancy is predominantly responsible for high-temperature diffusion, this argument favors the assignment of the lower J/Q ratio to the single vacancy. However, recent measurements by Roswell[24] have independently determined H for the Ag–Zn alloy and it is also found that Eq. (4) is obeyed within experimental error. (Also, see reference 22 for an independently estimated upper limit for H, based on the present experiments.) Since the low-mobility defect is observed in these alloys, the above argument appears to be neutralized. There are other difficulties in designating the high-mobility defect as the single vacancy. For example, it would then be necessary to determine the nature of the low-mobility defect. The latter could not be the divacancy (bound pair of vacancies) since the divacancy has a higher mobility than the single vacancy.[42] Another possibility in the case of alloys (Table II) is that the quenching effects are due to the freezing in of abnormally low degrees of short-range order. It would then be necessary to conclude that J represents the atomic mobility in the more highly disordered state and Q the atomic mobility for equilibrium order. There is no evidence that would permit one to believe that a decrease in short-range order in a solid solution can produce a 40% decrease in activation energy for atomic mobility. Furthermore, the numerical value of the intercept of the straight line of Fig. 3*A* could not be explained, [since there would no longer be a factor $c(0)$, of the order 10^{-4}]. One would also anticipate that low-temperature irradiation should have produced disorder and thereby shortened τ, in contradiction to the present experiments. Finally, there would be no explanation for the evidence (Tables I and III) pointing to a low-mobility defect in pure metals. It therefore appears that the principal difficulty in designating the high-mobility defect as the single vacancy is in determining what the low-mobility defect might be.

The second alternative is to designate the low-mobility defect as the vacancy. It might then appear reasonable that the other defect is the divacancy.[43] This assignment would mean that the ratio of the activation energy for migration of a divacancy, J_d, to that for a vacancy, J_v, is in the range $J_d/J_v=0.6-0.7$ (depending on whether J_v/Q is taken as 0.6 or 0.5). This result is quite consistent with Bartlett and Dienes' estimate[42] that this ratio should lie between 0.35 and 0.70. A further consequence of this assignment is that the formation energy H_d for a divacancy in gold is 1.28 ev (Table I). It is readily apparent that H_d is given by

$$H_d=2H_v-H_b,$$

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[38] Clarebrough, Hargreaves, and West, Phil. Mag. **44**, 913 (1953).

[39] W. Boas, *Report of the Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 212.

[40] A. S. Nowick, Acta Metallurgica **3**, 312 (1955).

[41] J. W. Semmel and E. S. Machlin (to be published).

[42] J. H. Bartlett and G. J. Dienes, Phys. Rev. **89**, 848 (1953).

[43] The possibility that Kauffman and Koehler's observations were related to divacancies was first suggested by Bartlett and Dienes, reference 42.

where H_v is the single vacancy formation energy and H_b the binding energy of two vacancies. If it is assumed that $H_v/Q=0.40$, then the above value for H_d gives, for the case of gold, $H_b=0.24$ ev. For $H_v/Q=0.50$, the value $H_b=0.62$ ev is obtained. Theoretically, a value of 0.59 ev is obtained.[42] The agreement is quite satisfactory in view of the fact that the methods used in the calculation of Bartlett and Dienes are very crude. There are some difficulties which remain, however, in the assignment which regards the high mobility defect as the divacancy. Firstly, if one takes the ratio of the quenched in resistivity increment to the estimated number of quenched in defects from the work of Lazarev and Ovcharenko (where presumably single vacancies are being observed) as well as from that of Kauffman and Koehler, one is led to conclude that the resistivity contribution per defect is about four times greater for the divacancy than for the single vacancy. This ratio appears to be unreasonably large. Secondly, the identity of the defect which anneals out of irradiated copper with a unique activation energy of 0.7 ev is left open. There is no reason why this defect should necessarily be the divacancy. On the contrary, Brinkman, Dixon, and Meechan,[34] as a result of a comparison of annealing data for irradiated copper with that for irradiated Cu_3Au, have concluded that the 0.7-ev defect must be one that cannot produce ordering, such as the interstitial.

In spite of these difficulties, the assumption that the high-mobility defect is the divacancy and the low-mobility defect the single vacancy seems to be the most nearly consistent with present experimental evidence and with theoretical calculations. It is very desirable, however, that measurements similar to those of Kauffman and Koehler be repeated, since theirs is the only work which now serves as evidence for the existence of a "high mobility" defect in quenched metals.

Note Added in Proof.—Recently, self-diffusion measurements in gold have been made with great care by B. Okkerse [Bull Am. Phys. Soc. Ser. II, **1**, 149 (1956)], who obtained a value of $Q=1.71$ ev. If this result is taken as more nearly correct than the 1.90-ev value quoted in Table I, then $J+H$, as measured by Kauffman and Koehler, is now distinctly greater than Q. Such a discrepancy further supports the contention that the high-mobility defect is not the single vacancy.

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