Concentration Dependence of Zener Relaxation in Silver-Gold Solid Solutions*

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Zener relaxation studies were performed with an inverted torsion pendulum on silver-gold solid solutions with concentrations ranging from 25 to 80 atomic percent gold. Arrhenius plots obtained from curves of $\ln \tau_r vs.$ concentration yield activation energies ranging from 42 to 39.5 kcal/mole extrapolated across the composition range from pure silver to pure gold. The intercepts, $\log_{10} \tau_{r_0}$, range from -14.2 to -14.7 indicating that the entropy changes by approximately +2 units of R in contradistinc-

• tion to results from diffusion studies in which the entropy by -2 units of R. Within the accuracy of the activation energy determinations the peak widths agree with those of a single relaxation process.

§1. Introduction

The advantage which may be gained from using internal friction effects to study smallscale atomic movements has been summarized elsewhere.^{1),2),3)} Conventional diffusion techniques are usually limited to high temperatures because of the long diffusion times required and inaccuracies inherent in low temperature measurements. In the case of substitutional solid solutions the internal friction effect, termed Zener Relaxation, cannot be used with the greatest benefit because of a lack of detailed knowledge of the atomic movements involved.

The first detailed study of the concentration dependence of Zener relaxation was performed by Nowick²⁾ working with solutions ranging from 15 to 32 atomic percent zinc silver. At the lower concentrations the measurement was limited by the magnitude of the effect and at the higher concentrations by the phase boundary. Since the atomic jump rate in the relaxation process is expected to depend on the jump rates of each type of atom, Nowick points out that the Arrhenius equation

$$\tau_r = \tau_{r_0} \,\mathrm{e}^{-H_r/RT} \tag{1}$$

should be only approximately valid. In fact, upon measuring a relaxation time over eight cycles of ten he showed a slight curvature in the Arrhenius plot, log τ_r vs. inverse temperatures. However, the mean values of H_r that he obtained from these plots indicate

that the activation energy for the process, H_r , varies linearly with concentration, decreasing with increasing concentration of zinc. The values of the intercepts, τ_{r_0} , obtained from the plots were the same to within one-tenth of a logarithmic cycle, thus Nowick concludes that the variation of relaxation time (and, therefore of atomic mobility) with concentration is attributable almost entirely to the quantity H_r and not to τ_{r_0} .

Following the notation of Nowick we write

$$\frac{1}{\tau_r} = \alpha \Gamma_r \tag{2}$$

where α is a dimensionless constant relating the relaxation time τ_r and Γ_r the appropriate jump frequency. From statistical mechanical considerations we may write

$$\Gamma_r = 12\nu e^{-\Delta G/RT} = 12\nu e^{\Delta S/R} e^{-H/RT}$$
 (3)

where ΔG is the appropriate thermodynamic potential, ν is the lattice vibrational frequency and 12 is the coordination number for a facecentered-cubic lattice. Combining Eqs. (2) and (3) we get Eq. (1) with

$$\frac{1}{\tau_{r_0}} = 12\alpha\nu \,\mathrm{e}^{\,\mathrm{d}S/R} \,\,. \tag{4}$$

Nowick assumed that the entropy change in the relaxation process is the same as that in the diffusion process (the diffusion of the slower component). Thus a knowledge of the entropy change coupled with the experimentally determined τ_{r_0} makes it possible to calculate α . Unfortunately diffusion data was not available, but an entropy change was calculated from the change in the shear modulus and activa-

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tion energy of the process. Thus values of α were obtained ranging from .26 to .42.

Furthermore, the question of whether the slow diffusor, or the faster moving component, operates to control the relaxation process has been unresolved. This question was briefly reviewed in a previous work⁴⁾ in which data based on only two concentrations of AuAg led to the conclusion that one is measuring the diffusion of the faster moving component, since H_r and τ_r were very nearly equal to H_{Ag} and τ respectively. Here τ is the mean time of stay of the diffusing silver atom extrapolated to the temperature region common to Zener relaxation phemomena.

Since the AuAg system forms a single facecentered-cubic solid solution over the entire range of composition, and since extensive diffusion data are presently available, it is not subject to the disadvantages inherent in the AgZn system. Thus it was felt that a study of the Zener relaxation process over an extended concentration range would contribute to a better understanding of the process involved.

§2. Experimental

Internal friction measurements have been made on a series of gold-silver alloys by using a specimen in the form of a wire as the torsion member of an inverted torsion pendulum.

The AgAu wire specimens were drawn from boules prepared from 99.999% pure pellets placed in graphite crucibles which were sealed in vycor capsules at pressures less than $3 \times$ 10^{-5} mm of Hg. Homogeneity of the boule was achieved by throughly agitating the melt by rocking the furnace, followed by quick cooling.

The boule was reduced to 50 mil wire after several passes through a rolling mill. Further reduction to the final 28 mil diameter was effected by the use of dies. A 10" length of the specimen was sealed in a quartz capillary at a pressure of 3×10^{-5} mm of Hg and pulled through a zone furnace at 1 cm per hour. The construction of the furnace was such as to maintain a molten zone 0.5 cm in length. One inch was cut from each end of the single crystal, or large grain, wire specimen so obtained. To facilitate handling and mounting in the apparatus the ends of the 8" long specimen were silver soldered into 1" long copper chucks made of 1/4" diameter rod. The composition of the AgAu alloys was calculated by assuming a linear relationship between density and concentration. The density was determined by the immersion method prior to rolling and drawing the wire, and again at the conclusion of all internal friction measurements. These concentrations are accurate to ± 0.5 atomic percent. Laue X-ray shots were also made along the length of the specimen to determine the degree to which the specimen was single crystal.

The construction and operation of the torsion pendulum has been previously described.⁴⁾ However the background logarithmic decrement has been reduced to less than 2×10^{-4} by replacing the nylon string support with a bronze ribbon. The torsion pendulum is operated in a vacuum chamber at a pressure of 5×10^{-5} mm of Hg. Temperatures are controlled to ± 0.5 °C and are monitored over the 8" length of the specimen by three chromel-alumel thermocouples calibrated against a Bureau of Standards PT. vs. Pt-Rh. couple.

§3. Results

Zener relaxation studies were performed in silver-gold solid solutions of nominal composition 25, 32, 46, 49, 61, 71, and 80 atomic percent gold. Typical plots of the logarithmic decrement vs. reciprocal temperature are shown in Fig. 1. Runs such as these were



Fig. 1. Logarithmic decrement $vs. 1000/T[^{\circ}K]$ for five alloys of AuAg at a frequency of approximately 1 cps. The peak occurs at the Centigrade temperature indicated.

obtained for each specimen with the frequency varying from approximately 0.2 to 4 cycles/sec. and the temperature from ambient to 800°K. The quantities which are of particular interest in these relaxation studies are (a) the relaxation strength, (b) the activation energy and (c) τ_{r_0} defined by Eqs. (1) and (4).

(a) Relaxation Strength: The height of the peak is an indication of the relaxation strength. At each concentration the peaks are well defined and sufficient background data was obtained so that one could subtract the exponential high-temperature background to obtain the peak height and width. It has been reported earlier⁴) that the peak height and hence relaxation strength is greater on the gold rich side, but it is surprising to note how much larger the relaxation strength appears to be at 80% compared to that at 25%. These "subtracted" peak heights for 25 and 33 atomic % plotted vs. concentration yield a line that passes through the origin. Hence one is tempted to conclude that at least for these concentrations the relaxation strength varies linearly with concentration. However, because of orientation dependence any conclusions derived from these peak heights must be quite tentative. Although the wires were prepared in precisely the same way and a preferred orientation should predominate some are oriented differently and the anisotropy of the relaxation strength is unknown in the gold-silver system at present, but is being studied.

(b) Activation Energies: Fig. 2 is an Arrhenius plot of the relaxation time vs. reciprocal temperature for the various concentrations. The temperatures were obtained from the subtracted peak posititions. These subtracted peak widths agreed, within the experimental accuracy of the activation energy. with the theoretical width obtained from a single relaxation process. Thus it was not necessary to apply the correction of Nowick and Berry⁵⁾ for a distribution of relaxation times. To obtain the slope of the lines and hence the activation energy a least squares analysis was performed for each concentration, assuming the temperature to be correct. The accuracy of this data is of course limited by the frequency range of the torsion pendulum. *i.e.*, approximately one and one-half cycles of ten. However, by plotting data from a number of concentrations the accuracy can be improved. For example, Fig. 3 is a plot of $\ln \tau_r vs.$ concentration.

Those points distinguished by the solid



Fig. 2. Arrhenius plots ($\tau_r vs. 1000/T[^{\circ}K]$) for five AuAg alloys.



Fig. 3. Ln τ_{τ} vs. concentration. Solid circles are obtained form 1000/T intercepts of the least-squares lines in Fig. 2.

circles, are obtained from the intercepts at various values of inverse temperature from Fig. 2. Relaxation times obtained from these smoothed curves are then used to obtain activation energies with an increased accuracy. Fig. 4 is a plot of the activation energies obtained by these two methods.



Fig. 4. Activation energy vs. concentration. The open circles are given by the least-squares slopes in Fig. 2. The solid circles are averaged activation energies obtained from the lines in Fig. 3.

The open circles show the values obtained from the least squares analysis of the experimental data. The solid circles are the activation energies obtained from the "smoothed" curves at composition intervals of 10 atomic %. The remaining curves are for comparison purposes and are the activation energies for diffusion of each tracer into the various solid solutions.

The accuracy of these energy determinations was increased by extending the range of the Arrhenius plot over two more cycles of ten using elastic-after-effect data. Even though the apparatus described in an earlier publication4) can detect an angular motion of less than .02°, the magnitude of the effect in the 25 and 33 percent concentrations was too small to be measured. Hence, rather than distort the data by including elastic-aftereffect results for only a few compositions, the torsion pendulum data alone is analyzed The activation energies so obtained are here. approximately 2 or 3 Kcal/mole less than those obtained employing combined torsion pendulum and elastic-after-effect results. The corrections for the analysis of elastic-after-effect data described by Nowick and Berry,⁵⁾ though small, nevertheless would lead to a larger discrepancy between these two types of data.

Though this represents a very small change in slope the effect can be seen in the Arrhenius plots published earlier.⁴⁾ The data shown in Fig. 4 are consistent with these torsion pendulum data alone. They are also consistent with the findings of Nowick²⁾ and Hino, *et al.*³⁾ in that the activation energy obtained in the process is less than that of either tracer diffusing into the solid solution.

 τ_{r_0} : The linear dependence of $\ln \tau_r$ upon concentration shown in Fig. 3 indicates that its change with concentration occurs primarily in the exponential terms. Thus from Eq. (4) we can see that the change in τ_{r_0} with concentration must occur primarily in the entropy term. Values of the intercept Γ_{r_0} are provided from the least squares analysis of the data shown in Fig. 2. However, more accurate values can be obtained from Eq. (1) in the form

$$\ln \tau_{r_0} = -\frac{H_r}{RT_1}$$

where T_1 is the temperature for a relaxation time of one second as obtained from "smoothed" curves. Similarly H_r is obtained from the line drawn in Fig. 4. These are the curve averaged values shown in Table I along with the values of τ_{r_0} and H_r obtained from the least squares analysis.

Table I. Least squares analysis of experimental data

Conc.	25	32	46	49	61	71
H_r	41.74	40.7	41.19	41.45	40.83	40.81
$\log_{10} \tau_{r_0}$	14.45	14.21	14.52	14.58	14.60	14.76

Averages obtained from curves

Conc.	20	30	40	50	60	70	80
H_r	41.5	41.4	41.2	40.8	40.8	40.3	40.2
T_1	634	629	623	619	613	607	600
$\log_{10} \ au_{r_0}$	14.33	14.37	14.45	14.45	14.50	14.55	41.62

Fig. 5 is a plot of the $\log_{10}\tau_{r_0}$ values vs. concentration shown in Table I which yields a straight line and from Eq. (4) indicates the entropy change associated with the process increases by a approximately 2 units of R as the composition changes from pure Ag to pure Au.

This agrees with the value obtained from a direct calculation from the equation:



Fig. 5. $\log_{10} \tau_{r_0}$ vs. concentration for data in Table I.

$$\Delta S_a - \Delta S_b = \frac{H_a}{T_a} - \frac{H_b}{T_b}$$

where the temperature are those at which $\tau_r=1 \sec$ for the concentrations involved. However, if H_a and H_b vary by 0.5 Kcal/mole in opposite directions this entropy difference changes from 2 to .5 units of R so the figure has limited reliability.

Mallard, *et al.*⁶⁾ conclude from their diffusion studies that the activation entropy for each tracer decreases linearly with increasing gold fraction by a total of 2R from pure silver to pure gold.

Simmons and Balluffi⁷⁾ have measured this formation entropy in pure gold to be 1.0 Rwhile Doyama and Koehler⁸⁾ have measured the formation entropy in pure silver to be 1.5 R. Mallard, *et al.*⁶⁾ combined this data with theirs to deduce that the entropy of migration decreases linearly by 1.5 R from pure silver to pure gold.

This is contrary to the result expressed above for the Zener relaxation process in which the entropy increases as one increases gold concentration, indicating an opposite trend from that observed in diffusion. From Fig. 1 and Fig. 2 it can be seen that the peak moves to a lower temperature as the concentration of gold is increased, thus the intercept in Fig. 2 must be lower or the Arrhenius plots of the various concentrations would cross before arriving at the origin. This would be true regardless of any slight variation in their slopes. From Eq. (4) it is clear that as τ_{r_0} decreases exponentially then the entropy change must increase.

If one assumes that the entropy changes in the relaxation process must be approximately equal to those in self-diffusion then from the data and equations given by Mallard, *et al.*⁶) one can calculate the product $\nu e^{dS/R}$ for each tracer diffusing into each concentration. If these values are substituted into Eq. (4) to obtain α one finds that α increases exponentially with increasing gold concentration. From 20 to 80 atomic percent gold employing entropy changes from the silver tracer α changes from 1.4 to 3.1. Using data from the gold tracer α changes from 1.1 to 2.7.

Secondary Peak: In Fig. 6(a) one can see that at approximately 0.59 on the abscissa a point is above the curve. It might appear to be ordinary scatter in the data, but such a deviation occurred at a number of frequencies and at a number of concentrations. In other runs it has appeared as a slight peak. When an additional one hundred grams was added to the counter weight the peak shown in Fig. 6(b) appeared. When the additional counterweight was removed the secondary peak was not affected. The consistent appearance of this effect near the primary Zener peak, and its enhancement with load suggests that it might be a Zener peak influenced by the dislocation content of the specimen.



Fig. 6. Logarithmic decrement vs. 1000/T[°K](a) Pre-anneal (b) Post-anneal with additional counterweight.

Another interesting feature is apparent from an examination of the primary peaks in Fig. 6(a) and (b). The (a) peak is the first run on a single crystal, unstrained specimen, with no annealing history after its growth. The narrower (b) peak is the second run which demonstrates the annealing effects of the first run. There is no suggestion here of a grain boundary peak annealing out as was demonstrated earlier.⁹⁾ This also accounts for the difference in widths of the peaks for the 49 and 61 percent specimens illustrated in Fig. 1 because the 49% plot is of an initial run whereas the 61% is not. The precise way in which such an anneal promotes a single time of relaxation at the expense of a distribution of relaxation times is not clear. More conclusive explanations of these phenomena must await further investigation.

§4. Conclusions

These results are consistent with earlier results⁴⁾ in that the relaxation time is equal to the extrapolated mean time of stay of the faster diffusor at concentrations above 40 percent gold. Below this concentration there is a constant deviation from the silver time of stay toward that of gold. However this is quite small. At 25% the approximate times are $\tau_{Ag} = .3 \text{ sec}$, $\tau_r = .45 \text{ sec}$, and $\tau_{Au} = 2.5 \text{ sec}$. From Fig. 3 one can see that at the lower concentrations there is a more appreciable difference between H_r and H_{Ag} . The width of the peaks and the variation of H_r with concentration are consistent with the prediction of Nowick and Berry¹⁰⁾ that the Zener peaks should be quite narrow when the change in activation energy with concentration is small.

The change in H_r with concentration of 2 Kcal/mole is surprising in view of the fact that the formation energies of vacancies for the pure metals differ by 3 Kcal/mole, 25.4 Kcal/mole for Ag⁸⁾ and 22.4 Kcal/mole for Au.¹¹⁾

The results of entropy calculations are also surprising, the change with concentration going in the opposite direction from that of diffusion. The comparison with mean times of stay and activation energies from diffusion studies suggest that basically the process is a simple one involving primarily the motion of silver atoms. However the entropy values indicate that the mechanism is more involved. The final solution of the problem may require a knowledge of the concentration dependence of the relaxation strength.

References

- 1 A. D. Le Claire: Phil. Mag. 42 (1961) 673.
- 2 A. S. Nowick: Phys. Rev. 88 (1952) 925.
- J. Hino, C. Tomizuka and C. Wert: Acta Met.
 5 (1957) 41.
- 4 T. J. Turner and G. P. Williams: Acta Met. 10 (1962) 305.
- 5 A. S. Nowick and B. S. Berry: IBM Journ. of Res. 5 (1961) 297.
- 6 W. C. Mallard, A. B. Gardner, R. A. Bass, and L. M. Slifkin: To be published.
- 7 R. O. Simmons and R. W. Balluffi: Phys. Rev. 119 (1960) 600.
- 8 M. Doyama and J. S. Koehler: Phys. Rev. 127 (1962) 21.
- 9 T. J. Turner and G. P. Williams: Acta Met. 8 (1961) 891.
- 10 A. S. Nowick and B. S. Berry: Acta Met. 10 (1962) 312.
- R. O. Simmons and R. W. Balluffi: Phys. Rev. 125 (1962) 862.