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THE POSSIBILITY OF "FREEZING-IN"
RADIATION DAMAGE EFFECTS IN SIMPLE
METALS

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June 20, 1950

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2

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ATOMIC ENERGY RESEARCH DEPARTMENT

THE POSSIBILITY OF "FREEZING-IN" RADIATION DAMAGE EFFECTS IN SIMPLE METALS

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ABSTRACT

The desirability of observing radiation damage effects in simple metals has led to the suggestion that damage could be "frozen-in" by conducting experiments at low temperature. Vand's data has been utilized to estimate the necessary low temperature for a number of metals, with the result that exposures at solid CO₂ temperatures will probably be adequate in many cases and experiments conducted at liquid air temperatures will almost certainly be successful. This conclusion is supported by experimental data for copper, for which damage effects have been retained at ~ 110° K.

This report is based on studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

I. INTRODUCTION

Simple metals, metals which consist of only one type of atom and which are good conductors, have exhibited only relatively minor radiation damage effects in experiments which have been carried out in the past. From the standpoint of fundamental insight into radiation damage phenomena, it is very desirable to have available for experimental study substantial radiation damage effects in simple metals and in insulators which may be compared with the damage effects which have been found in semi-conductors. Damage effects in alloy systems have been reported,¹ but these effects may be partly attributable to a process analogous to heat treatment and are not entirely satisfactory for a fundamental comparison of damage in different solid types.

It has been suggested that in order to obtain substantial damage effects in simple metals, experiments should be conducted at low temperature in order to inhibit possible thermal annealing effects which remove the damage effects at room temperature. There also may be another annealing which occurs during bombardment due to the bombarding particles themselves, the so-called radiation annealing.

The following considerations are to apply only to thermal annealing. The estimates that can be made on thermal annealing are so crude that the omission of the radiation annealing effect from consideration is academic.

II. VARIATION OF TIME SCALE WITH TEMPERATURE

The time scale for thermal annealing may be expected to vary with temperature as:

$$\frac{1}{t} = f \exp(-A/T) \quad \dots (1)$$

Here: t is the time scale, the time for an effect to diminish by a factor e ; f is a frequency, presumable of the order of the Debye frequency; A is an activation temperature, the activation energy divided by Boltzmann's constant; and T is the absolute temperature of the sample.

In general, the activation temperature, A , cannot be identified with the activation temperature for self diffusion.³ A widely accepted diffusion model assumes that diffusion consists of two steps; creation of a special diffusing disturbance (activation temperature A_1), and diffusion of this disturbance (activation temperature A_2). The observed activation energy, A_D , for self diffusion is then composite, given by:

$$A_D = A_1 + A_2 \quad \dots (2)$$

It may be possible to identify the thermal annealing activation temperature with A_1 or A_2 , but probably not with A_D . Experimental values of A_D are therefore not directly useful, and special annealing studies of cold work or other effects will be needed to determine by direct experimental means the thermal annealing activation temperature, A . Theory³ indicates that A_2 may be less than A_1 in many metals. If a comparison is made utilizing Eq. (1) with $A = A_D$ and $A = A_2 \sim \frac{1}{3} A_D$, the result indicates that room temperature annealing is slow if $A = A_D$ and low temperature experiments are needed to get a reasonably long time scale if $A \sim A_2$.

The experimental data compiled by Vand⁴ on the annealing of the electrical resistivity of disordered metal films deposited from the vapor at low temperature seems to offer appropriate information for the estimation of the activation temperature for annealing of radiation damage effects. A plausible argument can be made that these data are somewhat more appropriate than data on the annealing of cold work.⁵ The argument points out that cold work probably has its major effect by affecting the size of crystallites and the character of the crystallite boundaries, while radiation damage is spread uniformly throughout the volumes of the crystallites and does not affect their size. The annealing of radiation damage should be more "local" than the annealing of cold work. Vand⁴ has indicated that this type of local annealing is the most probable mechanism in the healing of imperfections in disordered metal films which he has studied.

III. NUMERICAL ESTIMATES

In Table I are listed some data taken from Vand's paper. The values of the Debye frequencies listed in Column 2 are used, for given activation energy, to compute the temperature-time scale relationship according to Eq. (1). We do not actually know that this is the appropriate frequency for making this estimate except in order of magnitude. Fortunately, however, for the activation energies which evidently exist, f could be changed by a factor of ten without appreciably altering the temperature corresponding to a given time scale. The binding temperatures shown in Column 3 are listed mainly to show that the activation temperatures listed are not inconsistent with what is evidently an upper limit. The diffusion activation temperatures in Column 4 were, of course, determined from relatively high temperature self-diffusion data. However, there does not seem to be any reason to believe that these would not also characterize self-diffusion at low temperatures. As has been pointed out above (Eq. (2)) these activation temperatures, though lower than the binding temperature, should also be greater than those characterizing annealing of radiation damage. Column 5 of the table contains the most important information; namely, the activation temperatures for the re-ordering of metallic films as determined by Vand and which, we claim, should also characterize radiation damage healing. In his paper, Vand indicates that a single activation temperature may not be sufficient to characterize the metallic film re-ordering process but that a continuous distribution of activation temperatures can be employed to explain the details of his data. The spread in his curves is also partly due to his analytic approximations, a fact which he points out. However, he has shown that if a single activation state is adequate, the maximum of his curve corresponds to the true activation energy. The values of activation temperature in Column 5 are those for the maxima in Vand's residual resistance vs activation temperature curves. In the experiments, the nature of the backing for the metallic film, the temperature of deposition, and the film thickness all affect the final result. Thus, for each metal, Vand reports many values of A_M . The ranges of these values are indicated in Column 5 along with the "best" value obtained by a suitable weighted average. From these activation temperatures and the frequencies of Column 2, estimated temperatures of bombardment are computed from Eq. (1) and listed in

Column 6. The criterion used was that the characteristic time be one hour. Again, because of the nature of the equation, this is taken to be equivalent to the criterion that the time is of the order of magnitude of one hour. It is to be noted that, for most of the metals, the indication is that liquid air temperature would certainly be sufficiently low for radiation damage effects to become manifest.

Although, as was pointed out above, cold work data are probably not so pertinent, we wish to point out that, for one of the metals of Vand's work (i.e., Cu) the activation temperature for the healing by annealing of one of the effects of cold work has been shown to be fairly close to Vand's value of A_M . G. W. Brindley⁶ measured the thermo-electric effect for cold rolled, heat treated Cu strips. He was able to correlate his experimental data sufficiently well on the basis of a single activation energy or temperature, but his results differed depending on whether the heating in the experiment was isothermal or tempering (heated for time Δt at each of several successively higher temperatures). The results were 21.6 K cal/mol or 10,900° K for the isothermal experiments and 11.5 K cal/mol or 5800° K for the isochronal experiments. In Table II a comparison of annealing activation temperatures from Vand and Brindley are given. The corresponding temperatures for a one hour time scale are also listed. It is interesting to note that if the activation temperature for self-diffusion is assumed, experiments above room temperature should be possible.

There is still another means of estimating the appropriate activation temperature for radiation damage healing which is to identify it with the quantity A_2 of Eq. (2) which may be computed from the experimental value of A_D and a theoretical value of A_1 . For Cu the activation energy for diffusion is 2.6 electron volts. Seitz and Huntington⁷ have shown theoretically that self-diffusion in Cu should occur predominately by the vacancy mechanism and, for this, they compute, after much labor, a value of 1.4 ev for the vacancy creation activation energy, A_1 . Thus, we obtain $A_2 = 2.6 - 1.4 = 1.2$ ev. This corresponds to an activation temperature of 13,900 K. This is seen to be not greatly different from Vand's A_M for Cu. However, in the self-diffusion theory, the characteristic frequency corresponding to f of Eq. (1) differs quite appreciably from the Debye frequency (smaller by a factor of order 200) so that the "estimated bombardment temperature" will be less than would be suggested by this activation energy alone.

When this is taken into account, the bombardment temperatures as estimated from the three independent methods are in fairly good agreement but have a range of from about 150° K to room temperature. Now it is known that little radiation damage is done in Cu at room temperature, but recent, unpublished results obtained by the experimental group at NAA⁸ indicate "permanent" damage (change in electrical resistance) can be obtained, utilizing cyclotron particles, at a temperature of $-161 \pm 12^{\circ}$ C ($\sim 110^{\circ}$ K). This temperature is of the order of the above estimates.

IV. CONCLUSION

Although the above considerations are not conclusive, they provide combined experimental-theoretical indication that radiation damage may be "frozen-in" at low temperatures in simple metals. The evidence is definite for Cu since actual "freezing-in" has in fact been observed, but one may expect that damage would be observable for other metals as well when bombardments are at temperatures of the order of that of solid CO_2 and be quite confident of such observation for bombardments at liquid air temperature.

9

TABLE I

Column (1) METAL	(2) DEBYE FREQUENCY f, 1/sec	(3) BINDING TEMP. deg. K*	(4) DIFFUSION ACTIVATION TEMP., deg. K	(5) ESTIMATED ACTIVATION TEMPER- ATURES, A _M , FOR ANNEALING RADIATION DAMAGE, deg. K			(6) ESTIMATED BOMBARDMENT TEMPER- ATURES, T,** FOR OBSERVING RADIATION DAMAGE, deg. K		
				BEST	MAX.	MIN.	BEST	MAX.	MIN.
Mg	6.00 x 10 ¹²	20,800	—	6,420	7,440	6,420	171	198	171
Zn	5.25	16,400	10,030 $\parallel$ -c 15,600 $\perp$ -c	6,200	8,970	5,830	165	263	156
CD	3.60	14,200	—	6,270	8,540	4,730	169	230	127
Cu	7.00	38,200	30,900	10,800	10,800	10,800	286	286	286
Ag	4.50	32,400	23,100	15,000	15,000	7,300	402	402	196
Au	3.55	41,800	26,700	6,930	16,580	6,930	187	447	187
Tl	2.09	22,200	—	7,010	7,010	7,010	192	192	192
Pb	1.84	25,700	14,050	5,620	7,600	4,730	154	209	130
Hg	1.40	9,350	—	2,040	2,620	2,040	56	72	56

*Binding energy divided by Boltzmann's constant.

**T is computed from: $T = A/(\ln f t)$ for $t = 3600$ sec, see Eq. (1).

TABLE IICOMPARISON OF ANNEALING OF DISORDER EFFECTS
IN COPPER

EXPERIMENTAL ACTIVATION TEMPERATURES		CORRESPONDING TEMPERATURE FOR ONE HOUR TIME SCALE
Self Diffusion	30,900° K	817° K
Metal Film Annealing (Vand)	10,800	290
Cold Work Annealing (Brindley)		
Isothermal aging	10,900	290
Tempering (pulse annealing)	5,800	155

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