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THE RADIATION ORDER-DISORDER TRANSFORMATION - INITIAL TRANSIENT[+]

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Abstract

A refined model for ordered alloys is presented to describe the combined effect of radiation disordering and radiation enhanced reordering when the sink density varies with time due to radiation induced loop formation. Point defect concentrations which are directly dependent on sink density are responsible for the reordering process. The efficiency of reordering by vacancies is higher at early times in the case of thermal neutron irradiation due to focused replacement sequence events being the dominating disordering mechanism.

This sink density increase is necessary to fit the low dose irradiation results in fast and thermal neutron irradiated Cu_3Au.

1. Introduction

Ordered alloys may undergo order-disorder transformations under particle irradiation and extensive reviews [1,2] have been devoted to this area in recent years. The theory of this radiation induced order-disorder transformation must include both radiation induced disordering and enhanced thermal ordering. In an earlier paper by the authors [3] (ZW), a model for order-disorder transformation under irradiation was presented which included both processes for the case of constant sink density for point defects, the diffusion of which is responsible for reordering.

Experimental data for neutron irradiated Cu_3Au by Kirk and Blewitt [4,5] exhibit an initial transient before approaching a steady state value of the order parameter. (In fact, much of the data was for insufficient time to reach such steady state.) This previous model (ZW) is able to fit satisfactorily the results for large doses but does not include the initial transient.

We demonstrate in this paper that the initial transients for fast neutron irradiated Cu_3Au can be fitted by using a varying sink density in our theory. A similar transient for thermal neutron irradiation can also be explained by including varying sink density and an enhanced efficiency for vacancy reordering at small doses.

2. The Order-Disorder Transformation Model

The radiation effect on order-disorder transformation can be divided into two independent effects. One is radiation disordering and the other is radiation enhanced thermal reordering.

The radiation disordering process is quite simple. It is reasonable to assume that the disordering process involves random exchange of atoms. Using the common radiation damage unit of displacement per atom (dpa), we can write

the disordering rate as,

$$\left(\frac{dS}{dt}\right)_{irr} = -\varepsilon K S \tag{1}$$

where S is the instantaneous long range order parameter of Bragg and Williams [6], K is the displacement rate (dpa/sec) and ε is the number of replacements per displacement.

The radiation enhanced thermal reordering process is more complicated. Dienes [7] used chemical rate theory for a pair reaction. The rate constants for the ordering reaction and the disordering reaction can be written as,

$$\begin{aligned} k_1 &= \nu_1 \exp(-U/k_B T) \\ k_2 &= \nu_2 \exp - [(U + V)/k_B T] \end{aligned} \tag{2}$$

where U is the energy barrier for the ordering jump and V is the order energy. ν_1 and ν_2 are frequency factors which can be taken to be equal. To be consistent with Bragg and Williams theory [6], the ordering energy is assumed to be,

$$V = V_0 S \tag{3}$$

where V_0 is the ordering energy when the alloy is completely ordered.

In this model, the reordering process is assumed to be accomplished by vacancy migration. In Cu_3Au, interstitial motion does not change the degree of order due to the large size difference between copper and gold atoms. The

energy barrier U then simply becomes the vacancy reordering jump energy (E_m^0). The number of available vacancy sites around a disordered pair is $(Z_\alpha + Z_\beta - 2)$, Z_α being the number of α sites around a β site and Z_β the number of β sites around an α site. The probability of having a vacancy in any nearest neighbor position to make the necessary exchange is $(Z_\alpha + Z_\beta - 2)C_v$ where C_v is the vacancy concentration. The two opposing rate constants of Eq. 2 are then,

$$k_1 = (\nu_v/2)(Z_\beta/X_B)\, C_v\, (Z_\alpha + Z_\beta - 2)\, \exp(-E_m^0/k_BT)$$

$$k_2 = (\nu_v/2)(Z_\beta/X_B)\, C_v\, (Z_\alpha + Z_\beta - 2)\, \exp -[(E_m^0 + V_0S)/k_BT] \tag{4}$$

with ν_v as the vacancy attempt frequency. The factor of 2 comes from the double vacancy jump required for pair exchange. Using chemical rate theory, the net reaction rate can be written as,

$$\left(\frac{dS}{dt}\right)_{thermal} = (\nu_v/2)\, C_v\, (Z_\beta/X_B)(Z_\alpha + Z_\beta - 2)\, \exp(-E_m^0/k_BT)$$
$$\{X_AX_B(1 - S)^2 - \exp(-V_0S/k_BT)[S + X_AX_B(1 - S)^2]\} \tag{5}$$

where X_A and X_B are the atomic fractions of the two components in the alloy.

To obtain the vacancy concentration C_v under irradiation, we assume that point defects are at steady state concentation at all times. By using the approach of Brailsford and Bullough [8], we can obtain these concentrations.

The overall change in degree of order is a balance between the disordering and reordering rates obtained by combining Eqs. 1 and 5,

$$\frac{dS}{dt} = \left(\frac{dS}{dt}\right)_{irr} + \left(\frac{dS}{dt}\right)_{thermal} \cdot \tag{6}$$

3. Varying the Sink Density

In our earlier paper (ZW), a constant dislocation density (ρ_d) was used which is quite reasonable for long irradiation times when the sink density has reached a steady state value. However, at earlier times of irradiation, defect sinks formed by cascade collapse and loop nucleation are still evolving which implies that ρ_d increases with dose. The sink density rise can generally be expressed as,

$$\rho_d(t) = \rho_d^0 + \int_0^t (\dot{\rho}_d)_{t'}\, dt'$$
$$(\dot{\rho}_d)_{t'} = \left(\frac{d\rho_d}{dt}\right)_{t=t'} \quad . \tag{7}$$

ρ_d^0 is the initial sink density and $(\dot{\rho}_d)_{t'}$ is the growth rate of sink at time t'. To first order, we assume that ρ_d rises linearly with time and so

$$\rho_d(t) = \rho_d^0 + \dot{\rho}_d t \quad . \tag{8}$$

ρ_d of course depends on the irradiation conditions. The vacancy concentration when the sink density is varying is,

$$C_v(t) = C_{ve}/2 - Z_i D_i \rho_d(t)/2\alpha + \{[C_{ve}/2 + Z_i D_i \rho_d(t)/2\alpha]^2 + K_v D_i Z_i / Z_v D_v \alpha\}^{1/2} \quad . \tag{9}$$

D_v is the vacancy diffusion coefficient and is governed by $D_v = D_{ov}\exp(-E_m/k_B T)$. ($E_m$, the vacancy migration energy is not necessarily the same as the ordering jump barrier E_m^0.) D_i is the interstitial migration energy, Z_i and Z_v are the bias factors for the two defects, α is the recom-

bination constant, C_{ve} is the thermal equilibrium vacancy concentration and K_v is the free vacancy production rate. This vacancy concentration can now be inserted into Eq. 5 to obtain the enhanced thermal reordering rate.

The rate equation (Eq. 6) can only be solved by numerical methods for long range order as a function of time using $S = S_0$ at $t = 0$ as a boundary conditions where S_0 is the initial order. Many numerical integration packages are available. In this work, the Episode [9] package was used.

4. Fitting of Experimental Data

Kirk and Blewitt [4,5] irradiated Cu_3Au with both fast and thermal neutrons. The fitting of these data at large doses together with data from other authors was completed earlier (ZW) using the same set of thermodynamic parameters throughout. This set of parameters is listed in Table 1. For justification of the parameters used, the readers are referred to ZW. Here we demonstrate that by using varying sink density models, even the initial transient of the fast neutron data of Kirk and Blewitt can be fitted.

The degree of long range order is generally measured in terms of resistivity. The Muto [10] theory seems to provide good agreement with experiment as discussed in ZW. The following expression to convert resistivity to order parameter will be used:

$$\rho_s = \rho_{s=0} - S^2 (\rho_{s=0} - \rho_{s=1}) \qquad (10)$$

where ρ_s is the resistivity of order S and $\rho_{s=1}$ and $\rho_{s=0}$ are resistivities at complete order and complete disorder respectively.

The lower curve of Fig. 1 shows the fitting of Kirk and Blewitt's data for the partially ordered Cu_3Au irradiated with fast neutrons at an irradi-

ation temperature of 150°C. The replacement to displacement ratio used is 80 which is typical for fast neutrons. The sink density is approximated to increase linearly with time at a rate of 5400/cm^2/sec after an incubation period with constant sink density of 10^7/cm^2 as shown in Fig. 2. The sink then saturates at a density of 2.17 x 10^9/cm^2.

The fitting of the model to the initially highly ordered Cu_3Au is shown in the upper curve of Fig. 1. The irradiation temperature is again at 150°C. The rate of sink density increase used was 2700/cm^2/sec after an incubation period with constant sink density of 10^7/cm^2 as shown in Fig. 3. Again it is obvious that an excellent fit to the data is obtained at all doses. The lower sink density increase rate required for the ordered sample compared to the partially ordered one arises because the ordering energy ($V = V_0S$) is higher at higher order and this makes the structure more resistant to defect sink formation. The sink density will of course eventually saturate but at a dose well beyond that used in this work.

The incubation period at constant sink density was required to produce the good fit shown in each case. A sink density displaying an incubation period is characteristic of dislocation loop formation. Theoretical estimates of nucleation dose for this process are available [11,12,13] but at much higher dose rates and temperatures than those used in Fig. 1. Nevertheless, the incubation doses obtained in these studies agree very well with those shown which are needed to fit the ordering data.

Transmission electron microscopy studies by Jenkins and Wilkens [14] of Cu_3Au irradiated with energetic copper ions have shown that both vacancy loops and disorder cascade patches were formed in the cascades. The formation of such defects would suggest that the sink density should rise from the very

beginning without any incubation. However, this experiment was performed at room temperature while Kirk and Blewitt's neutron irradiation was done at 150°C. At these high temperatures, the cascade debris anneals out quickly leaving nucleated interstitial loops as the dominant sinks.

The model described was designed for the three dimensional ordering diffusion of point defects appropriate to the fast neutron case. Thermal neutrons, however, predominantly disorder by replacement collision sequences. A replacement collision sequence consists of a row of atoms all displaced one atomic jump from their original positions causing a previously ordered row to become disordered.

In Fig. 4, the thermal neutron irradiation data is fitted with the same model used for fast neutrons (dash line). The irradiation temperature is at 135°C and the displacement rate is 2.5×10^{-10} dpa/sec. Replacement to displacement ratio used is 20. The dashed line shows the best fit possible using a linear rise of sink density of $500/cm^2/sec$. As expected, it is found that the entire curve cannot be fitted successfully by using any reasonable linearly increase of sink density.

Since each faulted row of the replacement collision sequences can be easily ordered by one vacancy moving along it, it is probable that the ordering rate is much higher than in the case of fast neutrons where the cascades cause disordering of three dimensional regions. In the fast neutron case, only wrong atoms on the surface of the cascade are adjacent to the ordered matrix which defines the proper sublattice. Only vacancies moving along this layer have the high efficiency of reordering characteristic of the replacement collision sequences. Therefore it is obvious that the reordering rate in the case of thermal neutron irradiation needs to be modified such that

it is higher at early times and approaches the normal value when overlapping of replacement sequences begins.

To model this effect, the reordering rate was multiplied by a factor of [2.3 exp(-t/60000) + 1] where t is the irradiation time in seconds. This means that the vacancy is more than three times as effective in reordering at the start. Each vacancy then has to reorder on the average about three disordered pairs in each sequence. This implies that the average replacement sequence length is around six pairs (or 12 atoms). Since an ε value of 20 is used, this means each displacement induces one to two such sequences, which is quite reasonable.

With this modification, the initial transient in the thermal neutron case can also be fitted successfully as the solid line of Fig. 4 shows. The sink density increase is taken as $500/cm^2/sec$ with initial sink density of $10^7/cm^2$.

5. Conclusions

The refined model for radiation induced order-disorder transformation has been successfully applied to fit the data of Cu_3Au irradiated with fast and thermal neutrons by Kirk and Blewitt at all doses.

This model takes time varying point defects sink density into account. It has been shown to successfully fit the fast neutron irradiation data with a linear rise in sink density after an incubation period. This is characteristic of the loop nucleation process. The sink density rise rate is strongly dependent on the state of order of the material. Material with a higher degree of order is more resistant to defect sink formation.

For the thermal neutron irradiation case, the vacancy reordering efficiency is higher at earlier times due to replacement collision sequences. Using the modified reordering rate with a multiplier factor of

[2.3 exp(-t/60000) + 1], the thermal neutron irradiation data can also be fitted at all times.

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Table 1

Parameters Used in Fitting Cu_3Au Data

Vacancy motion energy	E_m = 0.8 eV
Vacancy ordering motion energy	E_m^0 = 0.84 eV
Vacancy pre-exponential diffusion coefficient	D_{ov} = 0.78 cm^2/s
Vacancy formation energy	E_{fv} = 1.28 eV
Vibrational frequency	$\nu_v = \nu_i = 10^{13}$ Hz
Interstitial motion energy	E_{im} = 0.12 eV
Interstitial pre-exponential diffusion coefficient	D_{oi} = 7.8 x 10^{-3} cm^2/s
For fast neutrons	
Vacancy loss fraction	f_v = 0.95
Replacement to displacement ratio	ε = 80
For thermal neutrons	
Vacancy loss fraction	f_v = 0.0
Replacement to displacement ratio	ε = 20
Dislocation bias for interstitials	Z_i = 1.02
for vacancies	Z_v = 1.0
Recombination coefficient	$\alpha = 10^{17}/cm^2 \times D_i$
Copper concentration	X_A = 3/4
Ordering energy	V_o = 0.35 eV

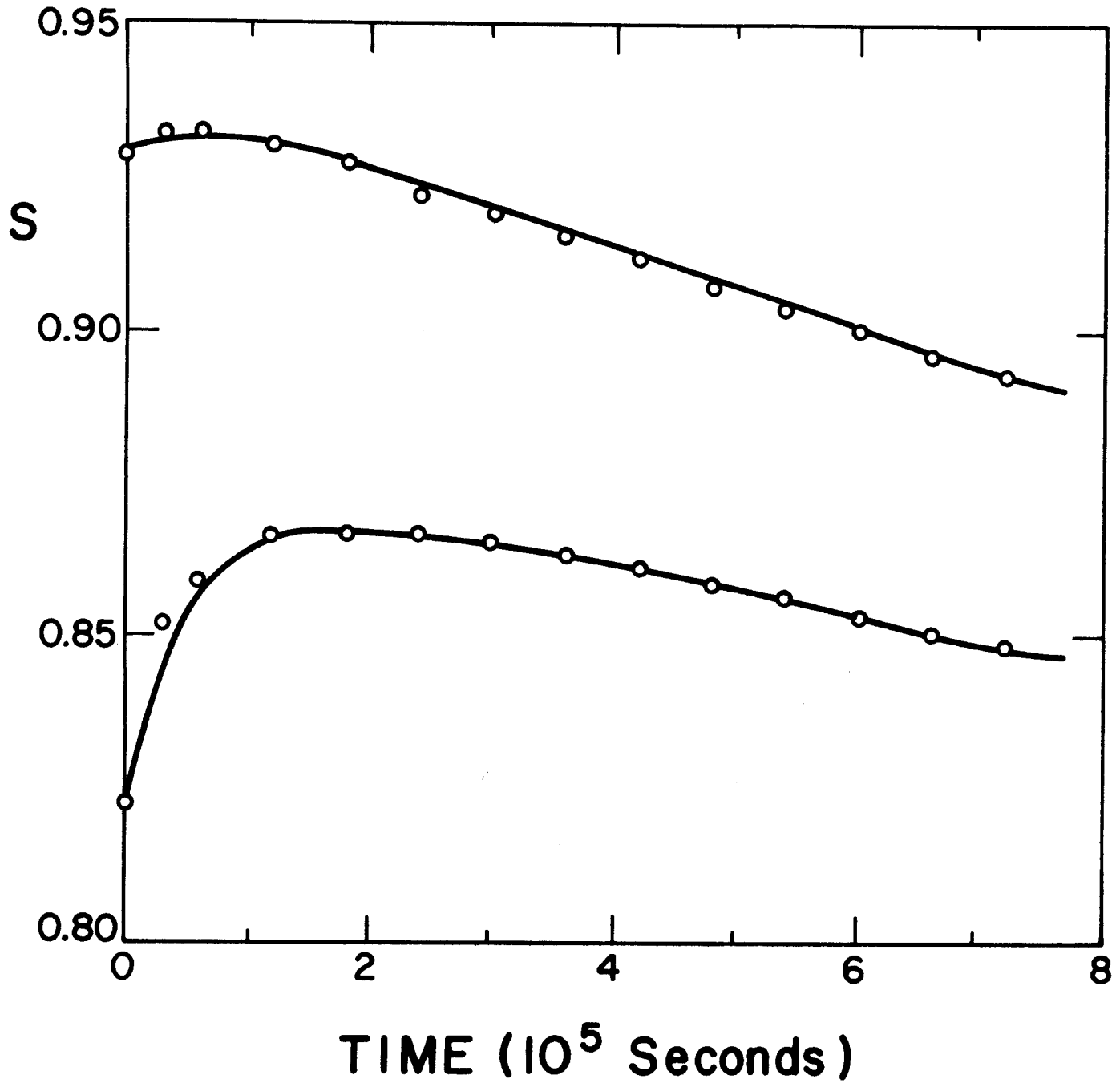

Fig. 1: The change of order during fast neutron irradiation of Cu_3Au at 150 °C from Kirk and Blewitt [4,5]. The circles represent datum points. The two curves represent different starting values of the order parameter. The lines show a data fit using parameter values in Table 1 with K = 1.4 x 10^{-9} dpa/sec and ε = 80. The lower curve (initially partially ordered sample) uses a sink density rise as shown in Fig. 2 while the upper curve (initially highly ordered sample) uses that shown in Fig. 3.

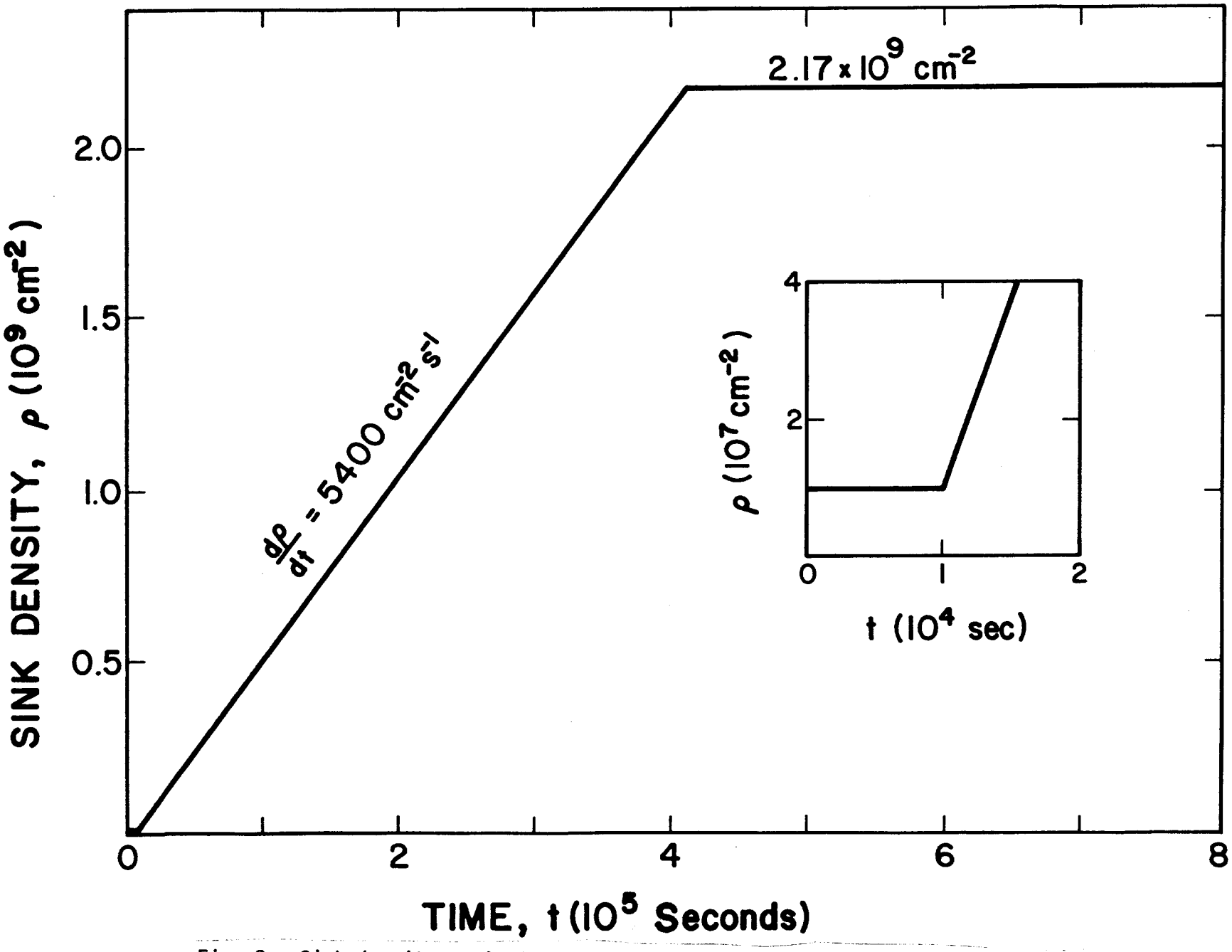

Fig. 2: Sink density variation under fast neutron irradiated Cu_3Au for the initially partially ordered case (lower curve of Fig. 1).

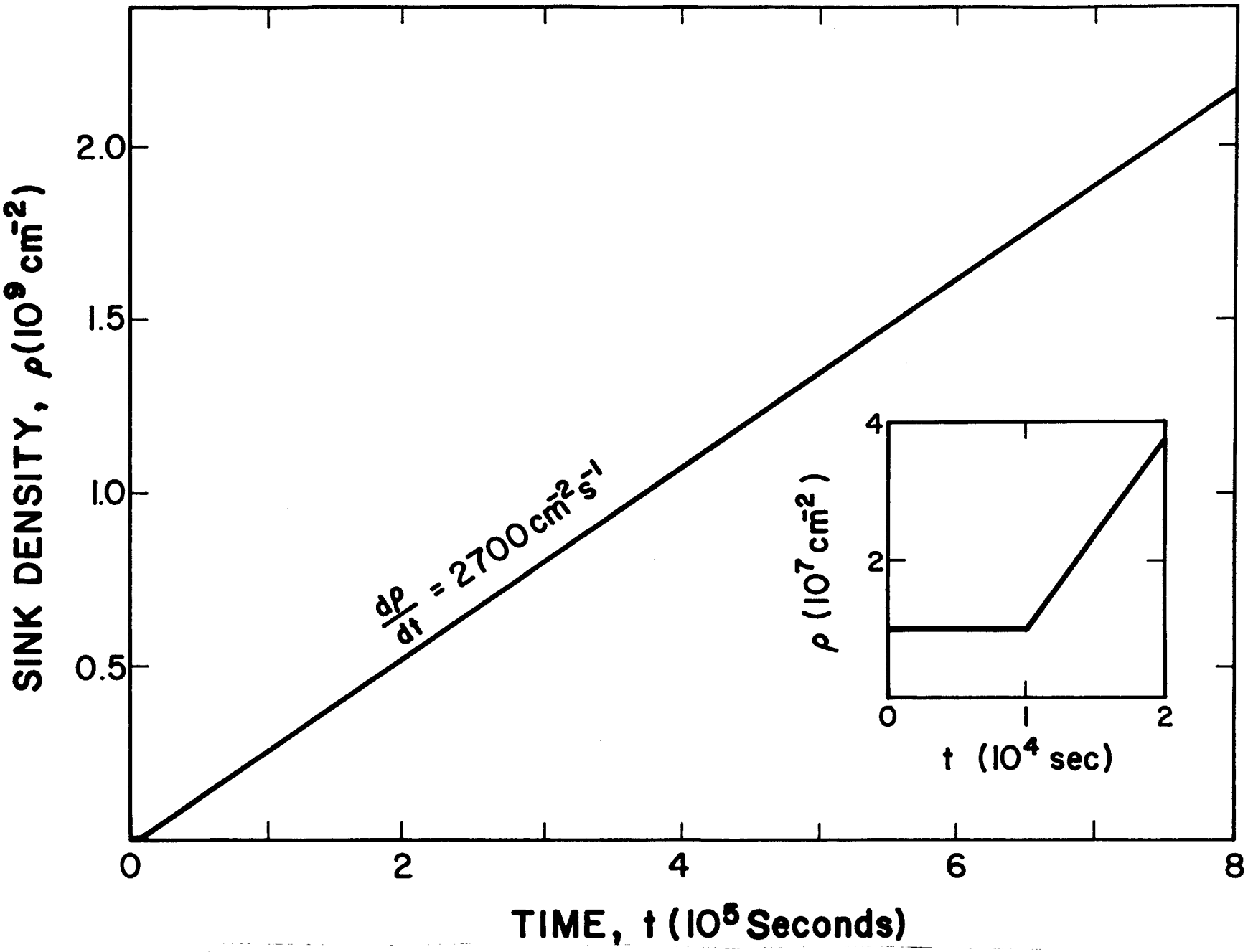

Fig. 3: As for Fig. 2 but for the initially highly ordered case (upper curve of Fig. 1).

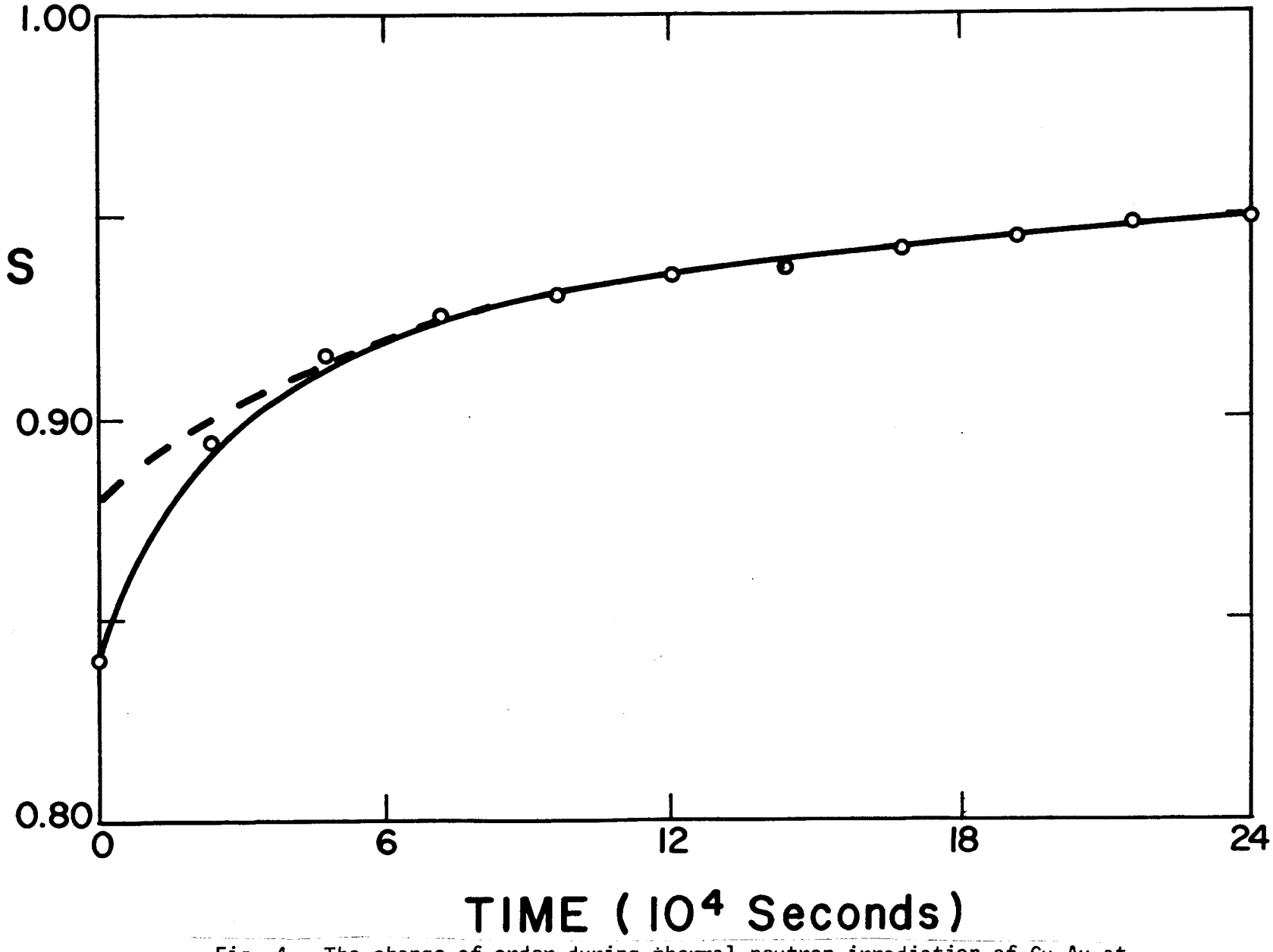

Fig. 4: The change of order during thermal neutron irradiation of Cu_3Au at 135 ^{o}C from Kirk and Blewitt [4,5] using ϵ = 20, K = 2.5 x 10^{-10} dpa/sec and sink density increase of 500/cm^2/sec.