

Some Simple Situations Described by the Equations Governing the Kinetics of Point Defects*

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The differential equations which govern the kinetics of single-, di-, tri-, and one configuration of tetra-vacancies are presented. The equations are very complex and cannot be integrated in a simple way. Three examples are discussed where matters are deliberately arranged so that only a few processes occur simultaneously, and that the equations become relatively simple: (1) the production of divacancies during quenching; (2) the condition for the formation of vacancy clusters; (3) the achievement of the equilibrium ratio of singles and divacancies during annealing.

§ 1. Introduction

During the past two years an appreciable amount of information concerning point defects has been gained both from equilibrium¹⁾ and from non-equilibrium²⁾ observations. In the present note we would like to describe a general point of view which we believe is useful both when one is interested in designing simple experiments and also when one attempts to interpret various kinetic measurements.

More specifically the procedure is as follows: One first writes out the general kinetic equations describing the time rate of change of the local point defect concentrations. In addition for any given problem it is necessary to write out initial and boundary conditions. For any very general situation these equations are very complex. Moreover the solution even if one could obtain it easily would not be very illuminating. We therefore, in conducting experi-

ments, seek to deliberately arrange matters so that only a few processes occur simultaneously.

In attempting to arrange matters so that an experiment is simple it is often necessary to guess some of the parameters which enter. The kinetic equations allow us to calculate the consequences of such estimates. These consequences are then compared with the observations as a check.

In what follows we shall write out the phenomenological equations which describe the changes in vacancy and the various cluster concentrations. For simplicity we shall assume a pure material³⁾. We shall then use the equations in several simple cases to illustrate the procedure.

§ 2. The Phenomenological Kinetic Equations

The kinetic equations for pure metals assuming short range defect interactions are:⁴⁾

$$\begin{aligned} \frac{dc_1}{dt} = & -2\alpha_1 c_1^2 + 2\alpha_2 c_2 - \beta_1 c_1 c_2 + \beta_2 c_3^{60} - \gamma_1 c_1 c_2 + \gamma_2 c_3^{90} - \delta_1 c_1 c_2 + \delta_2 c_3^{90} - 3\varepsilon_1 c_1^3 \\ & + 3\varepsilon_2 c_3^{90} - \zeta_1 c_1 c_2 + \zeta_2 c_3^{120} - \eta_1 c_1 c_2 + \eta_2 c_3^{120} - 3\theta_1 c_1^3 + 3\theta_2 c_3^{120} - \kappa_1 c_1 c_2 + \kappa_2 c_3^{180} \\ & - \lambda_1 c_1 c_2 + \lambda_2 c_3^{180} - 3\mu_1 c_1^3 + 3\mu_2 c_3^{180} - \chi_1 c_1 c_3^{60} + D_1 \nabla^2 c_1 \end{aligned} \quad (1a)$$

$$\begin{aligned} \frac{dc_2}{dt} = & +\alpha_1 c_1^2 - \alpha_2 c_2 - \beta_1 c_1 c_2 + \beta_2 c_3^{60} - \gamma_1 c_1 c_2 + \gamma_2 c_3^{90} - \delta_1 c_1 c_2 + \delta_2 c_3^{90} - \zeta_1 c_1 c_2 + \zeta_2 c_3^{120} \\ & - \eta_1 c_1 c_2 + \eta_2 c_3^{120} - \kappa_1 c_1 c_2 + \kappa_2 c_3^{180} - \lambda_1 c_1 c_2 + \lambda_2 c_3^{180} - 2\varepsilon_1 c_1^2 + D_2 \nabla^2 c_2 \end{aligned} \quad (1b)$$

$$\frac{dc_3^{60}}{dt} = +\beta_1 c_1 c_2 - \beta_2 c_3^{60} + \pi_1 c_3^{90} - \pi_2 c_3^{60} + \sigma_1 c_3^{120} - \sigma_2 c_3^{60} - \chi_1 c_1 c_3^{60} \quad (1c)$$

$$\begin{aligned} \frac{dc_3^{90}}{dt} = & \gamma_1 c_1 c_2 - \gamma_2 c_3^{90} + \delta_1 c_1 c_2 - \delta_2 c_3^{90} + \varepsilon_1 c_1^3 - \varepsilon_2 c_3^{90} + \pi_2 c_3^{60} - \pi_1 c_3^{90} \\ & + \varphi_1 c_3^{120} - \varphi_2 c_3^{90} + D_3 \nabla^2 c_3^{90} \end{aligned} \quad (1d)$$

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$$\frac{dc_3^{120}}{dt} = \zeta_1 c_1 c_2 - \zeta_2 c_3^{120} + \eta_1 c_1 c_2 - \eta_2 c_3^{120} + \theta_1 c_1^3 - \theta_2 c_3^{120} - \sigma_1 c_3^{120} + \sigma_2 c_3^{60} - \varphi_1 c_3^{120} + \varphi_2 c_3^{90} + \phi_1 c_3^{180} - \phi_2 c_3^{120} + D_3^{120} \nabla^2 c_3^{120} \quad (1e)$$

$$\frac{dc_3^{180}}{dt} = \kappa_1 c_1 c_2 - \kappa_2 c_3^{180} + \lambda_1 c_1 c_2 - \lambda_2 c_3^{180} + \mu_1 c_1^3 - \mu_2 c_3^{180} + \phi_2 c_3^{120} - \phi_1 c_3^{180} \quad (1f)$$

$$\frac{dc_4}{dt} = \chi_1 c_1 c_3^{60} + \xi_1 c_2^2 \quad (1g)$$

Table I. The rate constants for the formation and the dissociation of single-, di-, tri-, and tetra-vacancies.

Description	Reaction	Migrating Defect
$\alpha_1 = 84\nu_1 \exp(-E_m^1/kT)$	$s + s \rightleftharpoons d$	s
$\alpha_2 = 14\nu_1 \exp[-(E_m^1 + B_2)/kT]$	$s + d \rightleftharpoons t^{60}$	s
$\beta_1 = 20\nu_1 \exp(-E_m^1/kT)$	$s + d \rightleftharpoons t^{90}$	d
$\beta_2 = 15\nu_1 \exp[-(E_m^1 + B_3^{60})/kT]$	$s + d \rightleftharpoons t^{90}$	s
$\gamma_1 = 8\nu_2 \exp(-E_m^2/kT)$	$s + s + s \rightleftharpoons t^{90}$	s
$\nu_2 = 4\nu_2 \exp[-(E_m^2 + B_3^{90})/kT]$	$s + d \rightleftharpoons t^{120}$	d
$\delta_1 = 24\nu_1 \exp(-E_m^1/kT)$	$s + d \rightleftharpoons t^{120}$	s
$\delta_2 = 12\nu_1 \exp[-(E_m^1 + B_3^{90})/kT]$	$s + d \rightleftharpoons t^{180}$	d
$\varepsilon_1 = 48\nu_1 \exp(-E_m^1/kT)$	$s + s + s \rightleftharpoons t^{180}$	s
$\varepsilon_2 = 4\nu_1 \exp[-(E_m^1 + B_3^{90} + B_2)/kT]$	$s + d \rightleftharpoons t^{180}$	d
$\zeta_1 = 24\nu_2 \exp(-E_m^2/kT)$	$s + s + s \rightleftharpoons t^{180}$	s
$\zeta_2 = 6\nu_2 \exp[-(E_m^2 + B_3^{120})/kT]$	$d + d \rightleftharpoons \text{tetravac.}$	
$\eta_1 = 56\nu_1 \exp(-E_m^1/kT)$	$t^{60} \rightleftharpoons t^{90}$	t
$\eta_2 = 14\nu_1 \exp[-(E_m^1 + B_3^{120})/kT]$	$t^{60} \rightleftharpoons t^{120}$	t
$\theta_1 = 72\nu_1 \exp(-E_m^1/kT)$	$s + t^{60} \rightarrow \text{tetrav.}$	
$\theta_2 = 3\nu_1 \exp[-(E_m^1 + B_3^{120} + B_2)/kT]$	$t^{90} \rightleftharpoons t^{120}$	t
$\kappa_1 = 14\nu_1 \exp(-E_m^1/kT)$	$t^{120} \rightleftharpoons t^{180}$	t
$\kappa_2 = 14\nu_1 \exp[-(E_m^1 + B_3^{180})/kT]$		
$\lambda_1 = 8\nu_2 \exp(-E_m^2/kT)$		
$\lambda_2 = 8\nu_2 \exp[-(E_m^2 + B_3^{180})/kT]$		
$\mu_1 = 12\nu_1 \exp(-E_m^1/kT)$		
$\mu_2 = 2\nu_1 \exp[-(E_m^1 + B_3^{180} + B_2)/kT]$		
$\xi_1 = \xi_{10\nu_2} \exp(-E_m^2/kT)$		
$\pi_1 = 4\nu_2' \exp(-E_m^{2'}/kT)$		
$\pi_2 = 6\nu_2' \exp[-(E_m^{2'} + B_3^{60} - B_3^{90})/kT]$		
$\sigma_1 = 2\nu_2' \exp(-E_m^{2'}/kT)$		
$\sigma_2 = 6\nu_2' \exp[-(E_m^{2'} + B_3^{60} - B_3^{120})/kT]$		
$\chi_1 = 12\nu_1 \exp(-E_m^1/kT)$		
$\varphi_1 = 2\nu_2' \exp(-E_m^{2'}/kT)$		
$\varphi_2 = 4\nu_2' \exp[-(E_m^{2'} + B_3^{90} - B_3^{120})/kT]$		
$\phi_1 = 2\nu_2' \exp(-E_m^{2'}/kT)$		
$\phi_2 = 8\nu_2' \exp[-(E_m^{2'} + B_3^{120} - B_3^{180})/kT]$		
$D_1 = a^2\nu_1 \exp(-E_m^1/kT)$		
$D_2 = \frac{1}{8}a^2\nu_2 \exp(-E_m^2/kT)$		
$D_3^{90} = D_3^{120} = d_{30}a^2\nu_3 \exp(-E_m^3/kT)$		

s=single vacancy

d=divacancy

t=trivacancy

In these equations c_1 is the fractional concentration of single vacancies, c_2 is the fractional concentration of divacancies, c_3^{90} is the concentration of trivacancies, c_3^{120} is the concentration of three vacancy clusters having nearest neighbor bonds at 90° , c_3^{180} is the concentration of three vacancy clusters having connecting bonds at 120° , c_3^{180} is the concentration of three vacancy clusters having connecting nearest neighbor bonds at 180° ⁵⁾. For simplicity we have included only one kind of tetravacancy. No larger vacancy clusters are included. ν_1 is the frequency of vibration of the atoms which are nearest neighbors of a lattice vacancy. ν_2 is the frequency of vibration of the four atoms which are nearest neighbors to both of the vacancies in a divacancy. The frequency of vibration of the other fourteen nearest neighbors of a divacancy has been selected to be ν_1 . D_1 is the diffusion constant associated with the motion of single vacancies; D_2 is the diffusion constant associated with divacancy migration; D_3 is that associated with trivacancies. Table I defines the coefficients which appear in the differential equations and gives the "chemical" reaction associated with that particular term in the differential equations. E_m^1 and E_m^2 are the energies of migration of single vacancies and of divacancies respectively. B_2 , B_3^{90} , B_3^{120} and B_3^{180} are the binding energies of divacancies and of the various species of trivacancies respectively. It has been assumed that no long range interactions exist between the various defects.

A. The production of divacancies during a quench

In general one succeeds in quenching in an appreciable concentration of vacancies because the specimen starts from an equilibrium condition. In equilibrium the time rates of change of all the defect concentrations are zero. Moreover during the initial stages of quenching, at high temperature, although the defects are very mobile the supersaturations are low so that the tendency to get rid of defects, say, at dislocations is small.

Let us, however, suppose that the dislocation density in our specimen is so low that during a quench from a temperature near the melting point only a very small fraction

of the vacancies is lost. We would like to determine how many divacancies are formed during the quench. Assume for the moment that very few larger vacancy clusters are formed. This point will be considered later. Then the first kinetic equation becomes:

$$\frac{dc_1}{dt} = -84\nu_1 c_1^2 \exp[-E_m^1/kT] + 14\nu_1 c_2 \exp[-(E_m^1 + B_2)/kT]. \quad (2)$$

Since no vacancies disappear one has:

$$c_{10} = \text{constant} = c_1 + 2c_2. \quad (3)$$

In addition there is a given relation, *i.e.* the measured quenching curve, between the specimen temperature and the time. For example, for a quench into a liquid medium:

$$T = T_0 - bt. \quad (4)$$

For a gas quench one finds:

$$T = T_0 e^{-at}. \quad (5)$$

At high temperatures both divacancy formation and breakup occur so rapidly that the divacancies are maintained at the equilibrium value appropriate for the instantaneous temperature. Fujiwara⁶⁾ has carried out numerical solutions of the above problem in the case of a linear quench which show that a critical temperature T^* exists. Below T^* divacancy formation is too slow to maintain the equilibrium divacancy concentration appropriate for the instantaneous temperature. Fujiwara shows that the freezing out of divacancy formation occurs rather abruptly at T^* . Eq. (2) shows that the rate at which vacancies disappear (giving divacancies) is always less than the first term on the right. However, the rate of change of the vacancy concentration required if singles and divacancies maintain their instantaneous equilibrium ratio is obtained by differentiating the equilibrium equation:

$$c_2 = 6c_1^2 \exp[B_2/kT] \quad (6)$$

and using Eq. (4) above. One finds for a linear quench:

$$\left(\frac{dc_1}{dt}\right)_e = -\frac{6c_1^2 B_2 b \exp[B_2/kT]}{kT^2(1 + 12 \exp[B_2/kT])}. \quad (7)$$

The critical temperature is reached when the rate required by equilibrium just equals the rate given by the first term of Eq. (2). Thus T^* can be found from:

$$\frac{\nu_1}{kbB_2} = \frac{\exp[(E_m^1 + B_2)/kT^*]}{k^2 T^{*2}(1 + 12c_1 \exp[B_2/kT^*])}. \quad (8)$$

Table II.
Critical temperatures and divacancy concentrations from quenching in gold

	$T_0=700^\circ\text{C}$ $c_{10}=2.278 \times 10^{-5}$ ($\nu_1=10^{13}$ cycles/sec)		
	$B_2=0.10$ eV	$B_2=0.20$ eV	$B_2=0.30$ eV
	$b=3 \times 10^4$ K/sec $b=6 \times 10^4$ K/sec $a=4.1 \times 10^1$ /sec $T^*=447.7^\circ\text{K}$ $c_2=4.16 \times 10^{-8}$ $T^*=461.1^\circ\text{K}$ $c_2=3.86 \times 10^{-8}$ $T^*=440.1^\circ\text{K}$ $c_2=4.35 \times 10^{-8}$	$T^*=511.2^\circ\text{K}$ $c_2=2.92 \times 10^{-7}$ $T^*=524.8^\circ\text{K}$ $c_2=2.60 \times 10^{-7}$ $T^*=500.4^\circ\text{K}$ $c_2=3.22 \times 10^{-7}$	$T^*=553.8^\circ\text{K}$ $c_2=1.67 \times 10^{-6}$ $T^*=570.6^\circ\text{K}$ $c_2=1.39 \times 10^{-6}$ $T^*=544.3^\circ\text{K}$ $c_2=1.87 \times 10^{-6}$
	$T_0=800^\circ\text{C}$ $c_{10}=6.771 \times 10^{-5}$		
	$B_2=0.10$ eV	$B_2=0.20$ eV	$B_2=0.30$ eV
	$b=3 \times 10^4$ K/sec $b=6 \times 10^4$ K/sec $T^*=443.5^\circ\text{K}$ $c_2=3.77 \times 10^{-7}$ $T^*=456.7^\circ\text{K}$ $c_2=3.49 \times 10^{-7}$	$T^*=503.2^\circ\text{K}$ $c_2=2.77 \times 10^{-6}$ $T^*=518.5^\circ\text{K}$ $c_2=2.42 \times 10^{-6}$	$T^*=543.1^\circ\text{K}$ $c_2=1.67 \times 10^{-5}$ $T^*=559.9^\circ\text{K}$ $c_2=1.38 \times 10^{-5}$
Equilibrium divacancy concentrations in quenched gold at 40°C			
$T_0=700^\circ\text{C}$	$c_{10}=2.278 \times 10^{-5}$		
	$B_2=0.1$ eV $c_{2e}=1.27 \times 10^{-7}$	$B_2=0.20$ eV $c_{2e}=2.89 \times 10^{-6}$	$B_2=0.30$ eV $c_{2e}=8.74 \times 10^{-6}$
$T_0=800^\circ\text{C}$	$c_{10}=6.771 \times 10^{-5}$		
	$B_2=0.10$ eV $c_{2e}=1.12 \times 10^{-6}$	$B_2=0.20$ eV $c_{2e}=4.73 \times 10^{-6}$	$B_2=0.30$ eV $c_{2e}=2.93 \times 10^{-5}$

For an exponential gas quench one replaces b in Eq. (8) by aT^* . Once T^* is known the resulting divacancy concentration can be found using the equilibrium ratio at T^* given by Eq. (6) and the initial total void concentration c_{10} . Some results are given in Table II.

It is clear from the results of this calculation that if B_2 is greater than 0.10 eV an appreciable fraction of the voids will form divacancies especially during quenches from the highest temperatures. The value of a used is appropriate for a helium gas quench (The current heating a 2 mil diameter wire suspended in gaseous helium at about one atmosphere pressure is suddenly turned off. The glass container is immersed in liquid nitrogen⁷¹). In the case of silver Doyama⁷¹ obtains a binding energy of 0.38 eV so that an appreciable fraction of the voids are divacancies even after a 700°C quench which gives an initial void concentration of about 3×10^{-6} . In section C below we will consider the way singles and divacancies come into equilibrium during the initial states of annealing after a quench.

B. Avoiding large-sized clusters during annealing

After a quench one anneals at some temperature which is selected to give simple results. Palmer⁸¹ annealed gold specimens

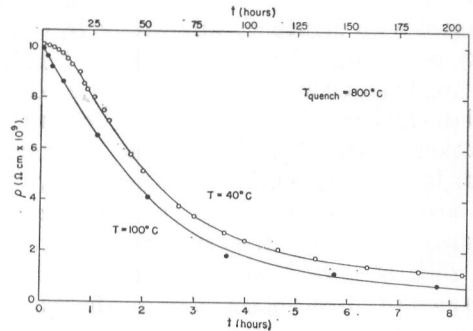


Fig. 1. The resistivity ρ as a function of time of two Au-wires quenched from 800°C and annealed at 100°C and 40°C , respectively. The 8-hour time scale refers to the anneal at 100°C ; the upper time scale to the 40°C anneal.

quenched from 800°C at 100°C . His annealing curve is shown in Fig. 1.

The annealing temperature was deliberately kept high so that no trivacancies and other large vacancy clusters would be formed. Note that one does not obtain the S-shaped curve observed when such a specimen is annealed at 30 or 40°C . Trivacancies can be avoided if the divacancy breaks up before it encounters another vacancy. The condition is:⁴¹

$$\frac{1}{\tau_2} > \frac{1}{\tau_3} \quad (9)$$

where τ_2 is the average time required for

the breakup of a divacancy and τ_3 is the average time required to form a trivacancy. Thus:

$$14\nu_1 \exp[-(E_m^1 + B_2)/kT] \\ > 32\nu_2 c_1 \exp[-E_m^2/kT].$$

In Palmer's experiment $c_1 = 5.3 \times 10^{-5}$, $E_m^1 = 0.82$ eV, $E_m^2 = 0.66$ eV, $B_2 = 0.10$ eV so that at 100°C one finds that the above condition holds. The experimental evidence that no large clusters form is twofold. First, no defect resistivity remains after a long anneal at 100°C . Second, the annealing curve does not follow the characteristic S shape found when annealing at 30°C or 40°C gold quenched from temperatures above $800^\circ\text{C}^{(9)}$.

C. The achievement of the equilibrium ratio of singles to divacancies during annealing

Consider a quenched specimen. The ratio of divacancies to single vacancies has a value appropriate for equilibrium at T^* . If the specimen is then annealed at T where $T < T^*$ the concentration of divacancies will increase. Since the time required to achieve the equilibrium ratio at T is short in comparison with the other characteristic times associated with annealing in a pure metal, it is easy to distinguish this process from others such as the formation of new sinks, or the annealing out at dislocations. There will be a change in the specimen resistivity provided that the resistivity of two single vacancies differs from that of a divacancy. Eqs. (2) and (3) describe the situations. In integrating one finds that

$$\frac{c_1^i - c_1}{c_1^i - c_1^e} = \frac{\text{ctnh } t_0/\tau - \text{ctnh } (t+t_0)/\tau}{\text{ctnh } t_0/\tau - 1}. \quad (10)$$

Here c_1 is the concentration of single vacancies at time t ; c_1^i and c_1^e are the initial and equilibrium concentration of singles. τ is the characteristic time constant for the transient process and is given by:

$$\frac{1}{\tau} = 7\nu_1 \exp[-(E_m^1 + B_2)/kT] \\ \times \sqrt{1 + 48c_0 \exp[B_2/kT]}. \quad (11)$$

t_0 is the integration constant with

$$\text{ctnh } \frac{t_0}{\tau} = \frac{1 + 24c_0 \exp[B_2/kT]}{\sqrt{1 + 48c_0 \exp[B_2/kT]}}.$$

Substituting $E_m^1 = 0.82$ eV, $B_2 = 0.10$ eV⁽¹⁰⁾ and $c_0 = 4 \times 10^{-4}$ one finds that the transient

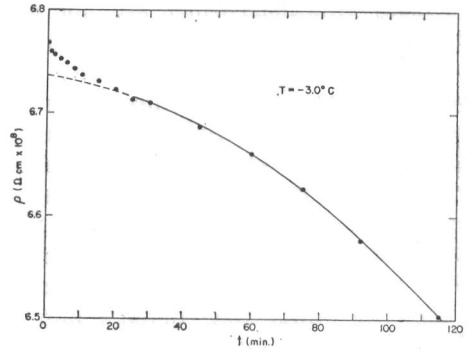


Fig. 2. The resistivity ρ as a function of time of a gold specimen quenched from 1000°C into a salt water bath at -35°C and subsequently annealed at -3°C .

process takes place in a time convenient for measuring (>15 min) at temperatures below 0°C . Fig. 2 gives the result for a wire quenched from 1000°C into a salt water bath at -35°C at a speed of $7 \times 10^5^\circ\text{C}/\text{sec}$ and then annealed at -3°C . An initial decrease in resistivity $\Delta\rho$ is observed which is attributed to this transient process. $\Delta\rho$ is related to the single vacancy concentrations by:

$$\Delta\rho = (c_1^i - c_1) \left(\rho_v - \frac{1}{2} \rho_{2v} \right) \quad (12)$$

where ρ_v and ρ_{2v} are the resistivities of 1 mol of singles and divacancies, respectively. An analysis of this run and similar ones using the above equations gives that the binding energy of a divacancy in gold is: $B_2 = 0.10 \pm 0.03$ eV and that the resistivity of a divacancy is $(4.6 \pm 3)\%$ less than that of two well operated singles⁽¹¹⁾.

At room temperature $\tau \sim 110$ sec. This indicates that by quenching Au in a bath kept in the vicinity of room temperature, the as-quenched concentration of divacancies calculated in Section A cannot be retained long enough to be generally of practical interest. On the other hand in silver, where $B_2 = 0.38$ eV⁽⁷⁾, $\tau \sim 10^6$ sec at room temperature which gives ample time to conserve the as-quenched situation.

§ 3. Conclusion

In the above we hope that we have demonstrated that in certain cases one can arrange matters so that nature is reasonably simple. However, it should be mentioned that there

exist many situations which are not understood as yet. Let us note a few and attempt to describe the kinds of difficulty which arise. In many cases one encounters problems which are essentially nonlinear. To date we do not have much experience in solving such problems. For example, consider the annealing out of voids in a gold specimen quenched from 800°C and annealed at 88°C or 98°C. Vacancies and divacancies are the only migrating defects and they rapidly come into local equilibrium, but if one attempts to describe the way in which they migrate to dislocations the resulting partial differential diffusion equation is nonlinear. Such difficulties we shall call mathematical even though a more profound understanding of the physics of the situation would probably enable us to write down a successful approximate solution.

There are other situations in which our lack of understanding of the physics limits our description of nature. For example we know very little as yet about the details of how dislocations act as sources and sinks for vacancies. Here we need both new experiments and new theoretical calculations.

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- 11 c_1^f was obtained by using the theory described in Section A. One calculates that $T^*=219^\circ\text{C}$ and $c_1^f/c_0=0.965$.

DISCUSSION

Maddin, R.: May I have your view regarding the existence or lack of a repulsive energy before two single vacancies form a divacancy?

Koehler, J. S.: If a repulsive energy of 0.25 eV exists between two vacancies, then divacancies would only be formed during the quench and vacancies and divacancies would anneal separately and independently during time spent at 30°C. This result is not in agreement with the data presented here nor is it in agreement with the experiments of Palmer and Koehler who found that the energy of migration observed in gold quenched from 800°C and annealed at 88°C and 98°C gradually increases from 0.66 eV to 0.77 eV as the vacancy concentration drops by a factor of ten. We do not therefore believe a repulsive interaction exists.

Seeger, A.: Did you have an independent way of establishing that during the -3°C anneal the divacancies come into equilibrium with the singles without losing a measurable fraction of divacancies to sinks?

Koehler, J. S.: The extrapolation of the observed $\Delta\rho$ versus time curve to zero time (back through the transient) enables one to demonstrate experimentally that the loss of voids during the initial transient is quite small.