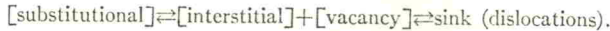


Pressure Dependence of Interstitial-Substitutional Dissociative Diffusion*

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EXPERIMENTAL evidence indicates that noble-metal solute atoms (Cu, Ag, Au) migrate interstitially in Pb.¹⁻³ Because it was expected that the effects of pressure on diffusion would be greater for a vacancy than for an interstitially controlled mechanism, several investigators measured the diffusion constant of Ag⁴ and Au⁵ in Pb under pressure. The results of these experiments were interpreted by supposing that the mechanism for diffusion changed from a vacancy to a predominantly interstitial mechanism with increasing pressure. Earlier, a model for isobaric diffusion in which the solute is distributed between interstitial and substitutional sites was developed and used to interpret the diffusion of copper in germanium.⁶ The objective of this note is to extend this theory to take account of pressure variations.

Below the solubility limit of the noble metals in Pb, we suppose that the concentrations of vacancies, and substitutional and interstitial noble-metal atoms are maintained in a dynamic equilibrium as follows:



We may express this equilibrium in terms of a thermodynamic equilibrium constant $K'(P, T)$:

$$K'(P, T) = C_s/C_i C_v = \exp(-\Delta G/RT), \quad \Delta G = \Delta G_{is} - \Delta G_f^v,$$

where C_i and C_s are, respectively, the interstitial and substitutional concentrations of noble-metal atoms, C_v is concentration of vacancies, ΔG_{is} is the increase in standard molar Gibbs free energy for the transfer of solute atoms from interstitial to substitutional positions, and ΔG_f^v is the standard molar Gibbs free energy for forming vacancies. If it is supposed that the activation energy for migration of a vacancy in Pb is half the activation energy necessary for diffusion (24 kcal/gm atom), then random-walk calculations indicate that with a dislocation density of 10^6 dislocations/cm², the vacancies can equilibrate with sinks in times much shorter than the duration of a typical experiment. This supposition is supported by the observation¹⁻³ that the diffusion constant of Pb is not measurably increased by dissolution of noble metals, which

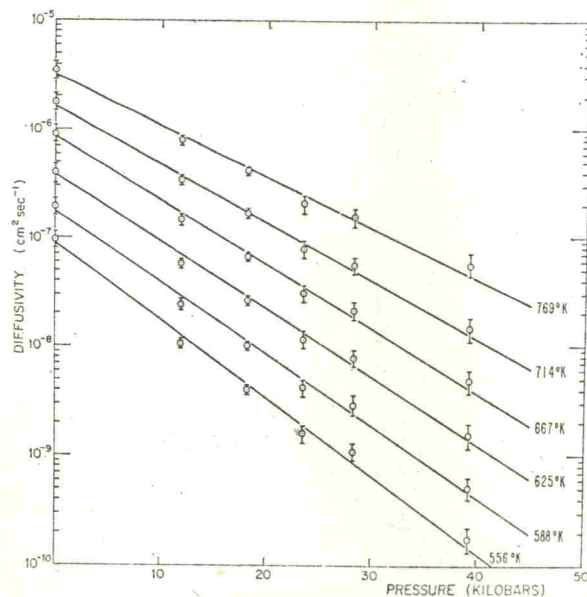


FIG. 1. Pressure dependence of the diffusivity of silver in lead.^{3,4}

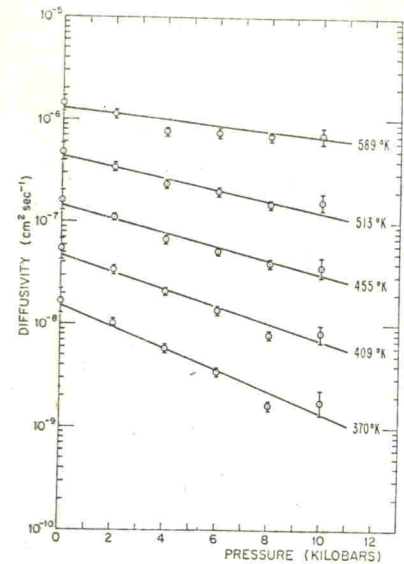


FIG. 2. Pressure dependence of the diffusivity of gold in lead.⁵

implies that the vacancy concentration in the alloy is the same as for pure Pb.

When there is an equilibrium distribution of solute between interstitial and substitutional sites, its effective diffusion constant D_{eff} may be expressed as:

$$D_{\text{eff}} = [C_i/(C_i + C_s)]D_i + [C_s/(C_i + C_s)]D_s,$$

where D_i is the diffusion constant of an interstitial atom, and D_s is the diffusion constant of a substitutional atom. However, our measurements show that the experimentally observed diffusion constant is many orders of magnitude greater than the substitutional diffusion coefficient. Consequently, to a very good approximation, we may write the effective diffusion constant as

$$D_{\text{eff}} = [C_i/(C_i + C_s)]D_i = [1/(K+1)]D_i,$$

where

$$K = C_s/C_i = K' C_v = \exp(-\Delta G_{is}/RT).$$

Taking the derivative of the natural log of the diffusion constant with respect to pressure, ignoring any explicit pressure dependence of the pre-exponential frequency factor in D_i , we have

$$\begin{aligned} \frac{\partial \ln D_{\text{eff}}}{\partial P} &= -\frac{\partial \ln(K+1)}{\partial P} + \frac{\partial \ln D_i}{\partial P} \\ &= -\frac{K}{K+1} \frac{\Delta V_{is}}{RT} - \frac{\Delta V_m^i}{RT} \\ &= -\frac{\Delta V_{is}}{RT} \left(\frac{K}{K+1} \right) - \frac{\Delta V_m^i}{RT}, \end{aligned}$$

where ΔV_{is} is the change in volume occurring when a mole of noble-metal solute atoms passes from interstitial to substitutional positions and is equal to $(\Delta V_s - \Delta V_f^i)$, ΔV_s is the molar formation volume for substitutional noble-metal atoms, ΔV_f^i is the molar formation volume for interstitial noble-metal atoms, and ΔV_m^i is the activation volume for interstitial migration.

Taking the second derivative of $\log D$ vs P and assuming that the activation volumes are independent of pressure, we find

$$\partial^2 \ln D / \partial P^2 = -[K/(K+1)^2](\Delta V_{is}/RT)^2.$$

This equation implies that a plot of $\log D$ vs P should have negative or zero curvature. For Ag diffusing in Pb,^{4,7} a graph of $\log D$ vs P exhibits to within experimental error a constant negative slope (see Fig. 1). The zero curvature implies that $K \rightarrow 0$

FIG. 1. Growth curve of oxide films on GaAs sample oriented (111), sample temperature 500°C; growth factor $35 \times 10^3 \text{ \AA}^2/\text{min}$; oxygen pressure 0.2 Torr.

to other constant due to an electric field and is proportional to the thickness of the film. Thus dY/dt is proportional to the parabolic growth rate of the substrate surface and whether it occurs at the surface or whether it occurs at the interface of the increase of time. The sample growth factor K was 50 V, and a current density of 100 A/cm² was obtained. The oxygen ions were measured by observing the substrate under the appropriate index. The approximate value of K by this method, which is between substrate strength for films capacitance measurement of 3.9. GaAs by heating to β Ga₂O₃.¹ Anesz and Jaininger by Ga₂O₃ with a Ga/As ratio. In contrast, the plasma oxidation are different. It is not yet dissolved or whether on of the oxide seems to be found by Revesz the composition of under the described

diffraction work and operating the

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