Thermal Coefficient of Expansion of an Activated Vacancy in Zinc from High-Pressure Self-Diffusion Experiments*†

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The coefficient of self-diffusion along the principal axes in zinc was obtained over the temperature range 300–400 °C, and over the pressure range 0–9 kbar. The unusually high precision of 2% in the measurement of the vacancy activation volumes was achieved by means of a novel technique that insured temperature reproducibility in the diffusion zone of ± 0.2 °C at high pressure. The activation volumes for diffusion, associated with the basal and nonbasal vacancy mechanisms are found to be temperature dependent, isotropic, and approximately proportional to T. Hence the thermal coefficient of expansion of an activated vacancy is given by $\alpha_v = T^{-1}$, and is about 15 times larger than the thermal coefficient of expansion of the perfect lattice. The activation entropy is pressure dependent, whereas the activation enthalpy is pressure independent to within the experimental uncertainty.

I. INTRODUCTION

A vacancy in a crystalline lattice is characterized by a set of properties that relate to its formation and motion under conditions of thermodynamic equilibrium. Considered as an entity undergoing reversible thermodynamic processes in both its formation and motion, the vacancy's properties are obviously embodied in a knowledge of the temperature and pressure dependence of $\Delta G_f(T, p)$ and $\Delta G_m(T, p)$, the changes in the Gibbs free energy of the crystal associated with the formation and motion of the vacancy, respectively. Thus, the formation enthalpy ΔH_f and entropy ΔS_f are respectively given by $[\partial(\Delta G_f/T)/\partial(1/T)]_p$ and $-(\partial \Delta G_f/\partial T)_p$, whereas similar temperature

derivatives of ΔG_m define the enthalpy and entropy of motion, ΔH_m and ΔS_m. On the other hand, the pressure derivatives $(\partial \Delta G_f / \partial p)_T$ and $(\partial \Delta G_m / \partial p)_T$ give the formation and motional volumes ΔV_f and ΔV_m.

The experiments are by no means trivial to determine precisely the total activation enthalpy $\Delta H(T, 0) = \Delta H_f(T, 0) + \Delta H_m(T, 0)$ from atmospheric radiotracer self-diffusion measurements, [1,2] the quantities $\Delta H_f(T, 0)$ and $\Delta S_f(T, 0)$ directly from combined x-ray and dilatometric measurements,[3,4] and the quantities $\Delta H_f(T, 0)$ and $\Delta H_m(T, 0)$ directly from quenching[5] and annealing kinetics[6] measurements. However, the precision measurement of the total activation volume $\Delta V(T, p) = \Delta V_f(T, p) + \Delta V_m(T, p)$ from self-diffusion measurements at high pressure, and that of $\Delta V_f(T, p)$ and $\Delta V_m(T, p)$ separately from quenching and annealing kinetics measurements under pressure, are indeed formidable owing primarily to the difficulty in making reproducible temperature measurements at pressures up to 10 kbar. Also, various approximations and assumptions regarding the interpretation[7] of quenching data introduce additional uncertainties into the quantities $\Delta V_f(T, p)$ and $\Delta V_m(T, p)$, in marked contrast to the interpretation of self-diffusion data. Thus, one of the most common properties of a thermodynamic system, the coefficient of thermal expansion, has never been measured for a vacancy, prior to the recently reported precision self-diffusion activation-volume measurements in zinc. [8]

The purpose of this paper is to present additional data on activation-volume measurements in zinc to allow a more precise determination of the thermal coefficient of expansion of an activated vacancy, $\alpha_v = (1/\Delta V)(\partial \Delta V/\partial T)_p$, and to further test the theory of Gilder and Chhabildas. [8] In addition, the data are used to determine the effect of temperature and pressure on the activation enthalpy for diffusion, as well as to explore the possible anisotropy in the activation volumes associated with the vacancy jumps in the nonideal hcp zinc lattice.

II. THEORY

Self-diffusion and isotope-effect measurements on zinc[9-11] have indicated that basal and nonbasal vacancy mechanisms are responsible for self-diffusion. Accordingly, the activation volume ΔV_c associated with the nonbasal jump and the activation volume ΔV_b associated with the basal jump are given by[12,13]

$$\Delta V_c = \Delta V_f + \Delta V_m^c = -RT \left(\frac{\partial \ln D_c}{\partial p} \right)_T + RT \, \kappa_c \gamma_c \quad (1)$$

and

$$\Delta V_b = \Delta V_f + \Delta V_m^b = -RT \left(\frac{\partial \ln(D_a - gD_c)}{\partial p} \right)_T + RT \, \kappa_a \gamma_a, \quad (2)$$

where R is the gas constant, T the absolute temperature, g a geometrical factor, and the ΔV_m's, D's, κ's, and γ's are the motional volumes, diffusion coefficients, isothermal linear compressibilities, and Grüneisen constants, respectively, associated with the a- and c-axis directions.

The expressions for the activation enthalpies ΔH_c and ΔH_b associated with the nonbasal and basal vacancy mechanisms are[12]

$$\Delta H_c = -R \left(\frac{\partial \ln D_c}{\partial (1/T)} \right)_p \quad (3)$$

and

$$\Delta H_b = -R \left(\frac{\partial \ln(D_a - gD_c)}{\partial (1/T)} \right)_p . \quad (4)$$

From thermodynamics we have

$$\Delta V = \left(\frac{\partial \Delta G}{\partial p} \right)_T = \left(\frac{\partial (\Delta H - T\Delta S)}{\partial p} \right)_T$$

$$= \left(\frac{\partial \Delta H}{\partial p} \right)_T - T \left(\frac{\partial \Delta S}{\partial p} \right)_T . \quad (5)$$

But, according to one of Maxwell's thermodynamic equations,

$$\left(\frac{\partial \Delta S}{\partial p} \right)_T = - \left(\frac{\partial \Delta V}{\partial T} \right)_p . \quad (6)$$

Therefore, we have

$$\Delta V = \left(\frac{\partial \Delta H}{\partial p} \right)_T + T \left(\frac{\partial \Delta V}{\partial T} \right)_p . \quad (7)$$

Hence $(\partial \Delta H/\partial p)_T$ and $(\partial \Delta V/\partial T)_p$ are, respectively, obtained as the intercept and the slope of the plot of ΔV vs T. Equation (7) may be written as

$$\left(\frac{\partial \Delta H}{\partial p} \right)_T = \Delta V - T \left(\frac{\partial \Delta V}{\partial T} \right)_p$$

$$= \Delta V \left[1 - T \frac{1}{\Delta V} \left(\frac{\partial \Delta V}{\partial T} \right)_p \right]$$

$$= \Delta V (1 - \alpha_v T). \quad (8)$$

Equation (8) is an exact relation, and does not involve the assumption[14-20] that $\alpha_v = \alpha_0$, where α_0 is the coefficient of thermal expansion for the perfect lattice.

III. EXPERIMENTAL PROCEDURE

A. Sample Preparation

Single-crystal rods of zinc about 6 in. long and 1 cm in dia. were grown by the Bridgman method, from 99.999%-pure zinc obtained from Cominco American Inc. After the rods were cut into 1-cm-length disks on an acid string saw, one end of each sample was polished on successively finer grades of emery paper. The surface was etched between