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## Temperature-Dependent Activation Volumes in Zinc\*

H. M. Gilder and L. C. Chhabildas

*Rensselaer Polytechnic Institute, Troy, New York 12181*

(Received 1 March 1971)

Precision measurements of self-diffusion in zinc as a function of pressure indicate that the activation volumes  $\Delta V_c$  and  $\Delta V_b$  respectively associated with the nonbasal and basal vacancy jumps have a temperature dependence given by  $(\partial\Delta V_c/\partial T)_p = (6.2 \pm 1.9) \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$  and  $(\partial\Delta V_b/\partial T)_p = (7.6 \pm 3.4) \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$ . A model calculation based on a Morse-like potential indicates that the frequencies of atomic vibrations in the vicinity of the defect vary with pressure in a way that is consistent with these experimentally measured quantities.

According to the usual assumptions of the validity of reaction rate theory and thermodynamics<sup>1</sup> in describing the diffusion jump of an atom in a crystal, the study of the effect of hydrostatic pressure on the self-diffusion coefficient  $D$  of a pure metal gives information on the sum,  $\Delta V$ , of the volume changes  $\Delta V_f$  and  $\Delta V_m$  that are, respectively, associated with the creation and motion of those defects participating in the diffusion process. On thermodynamic grounds we would expect the activation volume  $\Delta V$  to be temperature dependent, since, according to one of Maxwell's thermodynamic equations,

$$\begin{aligned} (\partial\Delta V/\partial T)_p &= -(\partial\Delta S/\partial p)_T \\ &= -[\partial(\Delta S_f + \Delta S_m)/\partial p]_T, \end{aligned} \quad (1)$$

where  $T$  is the absolute temperature,  $p$  is the pressure, and  $\Delta S$  is the sum of the entropy changes  $\Delta S_f$  and  $\Delta S_m$  respectively associated with the formation and motion of the defect that is re-

sponsible for the volume change  $\Delta V$ . As  $\Delta S$  depends on the way each perfect-crystal normal-mode frequency is changed by the presence and motion of the defect,<sup>2</sup> we would expect  $(\partial\Delta S/\partial p)_T$  and hence  $(\partial\Delta V/\partial T)_p$  to be nonzero, since the pressure derivatives of the perfect and altered frequencies for each mode should in general be different. However, the typical precision of ~10% to which the self-diffusion activation volume has been measured for a variety of metals has always precluded the unambiguous observation of a temperature-dependent activation volume. Curiously enough, in those experiments<sup>4,5</sup> where  $(\partial\Delta S/\partial p)_T$  has been estimated, Eq. (1) has never been invoked to indicate a possibly temperature-dependent activation volume  $\Delta V$ , possibly because the apparent trend of  $\Delta V$  with  $T$  falls within the experimental uncertainty in  $\Delta V$ . It is the primary purpose of this Letter to report recent precision measurements of self-diffusion in zinc as a function of pressure which indicate that

the activation volume changes with temperature. The experimentally measured values of  $(\partial\Delta V/\partial T)_p$  [hence  $(\partial\Delta S/\partial p)_T$ ] are shown to be consistent with the way the estimated ratio of anharmonic to harmonic force constants varies with lattice spacing or pressure.

Self-diffusion and isotope effect measurements on zinc<sup>6-8</sup> have indicated that a basal and nonbasal vacancy mechanism are responsible for self-diffusion. Accordingly, the activation volume  $\Delta V_c$  associated with the nonbasal jump and the activation volume  $\Delta V_b$  associated with the basal jump are given by<sup>9,10</sup>

$$\begin{aligned}\Delta V_c &= \Delta V_f + \Delta V_m^c \\ &= -RT(\partial \ln D_c / \partial p)_T + RT\kappa_c \gamma_c,\end{aligned}\quad (2)$$

and

$$\begin{aligned}\Delta V_b &= \Delta V_f + \Delta V_m^b \\ &= -RT[\partial \ln(D_a - gD_c) / \partial p]_T + RT\kappa_a \gamma_a,\end{aligned}\quad (3)$$

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

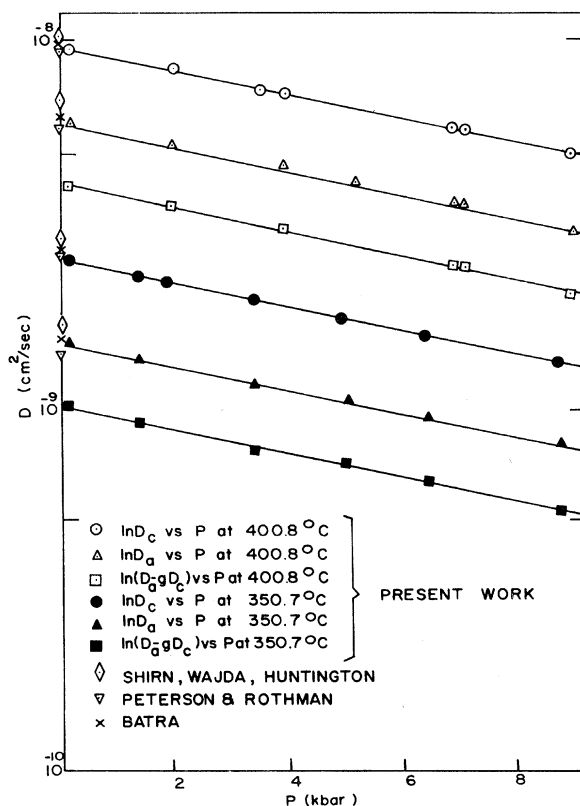


FIG. 1. Isotherms of  $\ln D_c$ ,  $\ln D_a$ , and  $\ln(D_a - gD_c)$  vs  $p$  for temperatures of 400.8 and 350.7°C for zinc.

The self-diffusion coefficients were obtained with Zn<sup>65</sup> by the usual radiotracer, lathe-sectioning technique. A precision of about 2% in the measurement of  $\Delta V$  was primarily achieved by using molten tin as the medium of a temperature bath<sup>11</sup> to provide a totally submerged small pressure vessel containing the zinc single-crystal  $a$ - and  $c$ -axis diffusion specimens with an extremely homogeneous and reproducible ( $\pm 0.1^\circ\text{C}$ ) thermal environment. In addition, since all diffusion anneals of the same temperature had exactly the same duration, warm-up corrections, although affecting the absolute value of the diffusion coefficients by only about 2%, have absolutely no effect on the quantity  $(\partial \ln D / \partial p)_T$  and, hence, the activation volume  $\Delta V$ .

The isotherms of  $\ln D_c$  vs  $p$  and  $\ln(D_a - gD_c)$  vs  $p$  corresponding to temperatures of 400.8 and 350.7°C are shown in Fig. 1. As the isotherms are obviously linear over the entire pressure range of 100-9000 atm, least-squares values of the slopes of lines fitted to the data were used to determine  $(\partial \ln D_c / \partial p)_T$  and  $[\partial \ln(D_a - gD_c) / \partial p]_T$  at both temperatures. After the second terms of Eqs. (2) and (3) were evaluated by recourse to the data of Grüneisen and Goens<sup>12</sup> and Alers and Neighbours<sup>13</sup> (these terms must be retained since they are 2-3% of the first terms), these equations yielded values of  $\Delta V_c$  and  $\Delta V_b$  that appear in Table I. It is apparent that both volumes increase with increasing temperature, and that the changes in both far exceed the limits of error on the changes: i.e.,  $(\partial \Delta V_c / \partial T)_p = (6.2 \pm 1.9) \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$  and  $(\partial \Delta V_b / \partial T)_p = (7.6 \pm 3.4) \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$ . These changes are ten times too great to be accounted for by thermal expansion alone. According to Eq. (1), then, both  $(\partial \Delta S_c / \partial p)_T$  and  $(\partial \Delta S_b / \partial p)_T$  are negative.

We can understand the magnitude and sign of the pressure derivative of the entropy by considering the following expression<sup>2</sup>:

$$\Delta S = R \sum_i \ln(\nu_{ip} / \nu_{id}). \quad (4)$$

The  $\nu_{ip}$  are the frequencies for lattice vibrations in the perfect crystal, and the  $\nu_{id}$  are the frequencies under the conditions where the defect is

Table I. Activation volumes for zinc.

$T$ (°C)	$\Delta V_c$ (cm <sup>3</sup> /mole)	$\Delta V_b$ (cm <sup>3</sup> /mole)
400.8	$4.28 \pm 0.08$	$4.30 \pm 0.14$
350.7	$3.97 \pm 0.05$	$3.92 \pm 0.09$

present and moving. For simplicity we assume an Einstein model in which an oscillator frequency is determined from the curvature at the bottom of the potential well formed from only the pairwise interaction of an oscillator with its fixed first-nearest neighbors. Furthermore, although

zinc is severely stretched along the  $c$  axis, nevertheless, for simplicity we assumed an ideal hcp structure and a direction-independent two-body interaction patterned after the Morse potential. The ion-core interaction energy  $U(r_j)$  between the  $j$ th ion and any of its nearest neighbors is represented by

$$U(r_j) = D[2 \exp\{-3\alpha(r_j - r_0)\} - 3 \exp\{-2\alpha(r_j - r_0)\}], \quad (5)$$

where  $D$  is the dissociation energy of an ion pair,  $r_0$  the equilibrium separation of a pair,  $r_j$  is a general, nonequilibrium separation of the  $j$ th ion and a nearest-neighbor ion, and  $\alpha^{-1}$  is a range parameter. The coefficients "2" and "3" were chosen in favor of the usual<sup>14,15</sup> "1" and "2" to "narrow" the range of interaction and thereby achieve a reasonably good fit to Harrison's potential<sup>16</sup> at a value of  $\alpha = 1.32 \text{ \AA}^{-1}$  and  $r_0 = 2.66 \text{ \AA}$ . Substituting Eq. (5) in Eq. (4) and then differentiating with respect to the pressure  $p$ , we obtain

$$\left(\frac{\partial \Delta S}{\partial p}\right)_T = -\frac{Rr_0}{6}(2\kappa_a + \kappa_c) \sum_{j=1}^{20} \left[ \frac{U_p'''(r_0)}{U_p''(r_0)} - \frac{U_a'''(r_j)}{U_a''(r_j)} \right], \quad (6)$$

where summing over the 20 ions closest to the vacancy is equivalent to including contributions from ions out to the vacancy's third-nearest neighbor. Since  $\Delta V_m$  is typically about 20% of  $\Delta V$ <sup>17,18</sup> we expect that  $(\partial S_f/\partial p)_T \gg (\partial \Delta S_m/\partial p)_T$  under the most likely condition that  $\Delta V_f$  and  $\Delta V_m$  experience comparable fractional changes with changing temperature. Hence,  $(\partial \Delta S_m/\partial p)_T$  is excluded from Eq. (6).

The sum in Eq. (6) was evaluated in terms of the first-, second-, and third-nearest-neighbor displacements  $\delta_1$ ,  $\delta_2$ , and  $\delta_3$ , all directed radially towards or away from the vacancy. The first- and third-nearest neighbors were relaxed inwards while the second-nearest neighbors were relaxed outwards, in accordance with patterns observed for vacancy relaxation in cubic metals.<sup>15</sup> Fourth and more distant neighbors were held fixed. Under these conditions we obtain, to second order in the displacements from equilibrium:

$$\left(\frac{\partial \Delta S}{\partial p}\right)_T = -\frac{Rr_0}{3}(2\kappa_a + \kappa_c)\alpha^3\delta_1^2 \left[ 545 + (36\sqrt{2}\alpha\delta_1)\frac{\delta_2}{\delta_1} + 270\left(\frac{\delta_2}{\delta_1}\right)^2 - 20\sqrt{6}\frac{\delta_3}{\delta_1} - \frac{6\sqrt{6}}{\alpha\delta_1}\frac{\delta_3}{\delta_1} - \frac{30}{\alpha\delta_1} + 30\left(\frac{\delta_3}{\delta_1}\right)^2 \right]. \quad (7)$$

From Eq. (7), for  $\alpha = 1.32 \text{ \AA}^{-1}$ ,  $r_0 = 2.66 \text{ \AA}$ , and  $\delta_1 = 10^{-1}r_0 = 0.266 \text{ \AA}$ , varying  $\delta_3/\delta_1$  from 0 to 0.5 changes  $(\partial \Delta S/\partial p)_T$  by no more than 7%. Hence, the third-nearest neighbors can be considered fixed. When  $\delta_2/\delta_1$  is varied from 0 to 0.5 and  $\delta_1$  is varied from  $5 \times 10^{-2}r_0$  to  $10^{-1}r_0$ ,  $(\partial \Delta S/\partial p)_T$  varies from  $-2 \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$  to  $-11 \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$  according to Eq. (7). Considering the simplifying assumptions made in the calculation, this range of values is in remarkably good agreement, both in sign and magnitude, with the experimentally measured values of  $(\partial \Delta V_c/\partial T)_p = (6.2 \pm 1.9) \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$  and  $(\partial \Delta V_b/\partial T)_p = (7.6 \pm 3.4) \times 10^{-3} \text{ cm}^3/\text{mole } ^\circ\text{K}$ . It should be noted that a Born-Mayer-type potential, according to Eq. (6), would predict  $(\partial \Delta V/\partial T)_p = 0$ , contrary to our experimental results.

Our model can also be used to make an order-of-magnitude estimate of  $(\partial \Delta H/\partial T)_p$ ,<sup>19</sup>  $\Delta H$  being the activation enthalpy for self-diffusion. Since differentiating  $\Delta S$  with respect to  $T$  is equivalent to replacing  $\kappa$  by  $-\alpha$  ( $\alpha$  is either principal-axis coefficient of thermal expansion) in Eq. (6), the

thermodynamic relation  $(\partial \Delta H/\partial T)_p = T(\partial \Delta S/\partial T)_p$  is integrated to obtain

$$\Delta H(T) - \Delta H(T_0) = + \left[ (2\alpha_a + \alpha_c) \frac{|\partial \Delta S/\partial p|_T}{(2\kappa_a + \kappa_c)} \right]^{1/2} (T^2 - T_0^2), \quad (8)$$

where  $T_0$  is some reference temperature above the Debye temperature. As the quantity in the brackets varies by no more than 10% over a wide temperature range, it was assumed to be constant for the integration. The quadratic variation of  $\Delta H$  with  $T$  derived here is in contrast to the linear dependence assumed by Nowick and Dienes.<sup>20</sup> Furthermore, changes in  $\Delta H$  calculated from Eq. (8) can be some five to ten times larger than those of Nowick and Dienes. From zinc thermal-expansion data<sup>21</sup> and our calculated values of  $(\partial \Delta S/\partial p)_T$ , the change in  $\Delta H$  varies from 0.2 to 1 kcal/mole over the range 250 to 400°C. Since atmospheric self-diffusion data for

zinc<sup>6-8</sup> show no change in  $\Delta H$  (to within the experimental uncertainty of  $\pm 0.2$  kcal/mole), it would appear that the combination of relaxation displacements that places  $(\partial\Delta S/\partial p)_T$  towards the low end of the calculated range is most probable. On the other hand, the parameters in Eq. (8) can be varied over reasonable limits to yield changes in  $\Delta H$  of the order of 3 kcal/mole over typical diffusion temperature ranges. This is large enough possibly to account for the presumed<sup>22</sup> curvature in the Arrhenius plot for self-diffusion in gold in terms of a monovacancy mechanism only.

In summary, a model calculation based on a Morse-like potential indicates that the frequencies of atomic vibrations in the vicinity of the defect vary with pressure in a way that is consistent with the observed temperature dependence of the activation volume for zinc. It is expected that more refined measurements for other metals would disclose the same type of behavior.

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## Orthogonality Catastrophe in Metals

D. R. Hamann

*Bell Telephone Laboratories, Murray Hill, New Jersey 07974*

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The overlap of the ground states of a many-fermion system in the absence and presence of a localized potential is recalculated using a method introduced by Rivier and Simanek. Contrary to their claim, the result previously obtained by other methods is recovered.

The calculation of the overlap between the ground states of a fermion gas in the absence and the presence of a scattering potential is the simplest example of a class of related problems which contain infrared divergences.<sup>1</sup> Other ex-

amples occur in the problems of x-ray absorption in metals<sup>2</sup> and of magnetic impurities in metals.<sup>3-5</sup> In a recent Letter<sup>6</sup> Rivier and Simanek (RS) claim to have calculated an exact expression for the overlap which disagrees with that