

$\Delta H$  and somewhat lower in  $D_0$  than the uncorrected isobar results.

Since the isobars in Fig. 8 are essentially parallel, we can determine the relative jump frequencies, defined<sup>4</sup> as  $\Gamma_i = \nu_i e^{\Delta S_i/R} e^{-\Delta H_i/RT}$  for the  $i$ th jump type, by substituting  $\gamma_a a^2 = 1/4 a^2$ ,  $\gamma_c c^2 = 1/2(2)(c)^2 = c^2$ , and  $D_c/D_a = 0.306$  into eq. 10. Thus

$$0.306 = \frac{c^2}{1/4 a^2} \frac{\Gamma_c}{\Gamma_a} = 1.19 \frac{\Gamma_c}{\Gamma_a} \quad (13)$$

or

$$\Gamma_c = 0.257 \Gamma_a \quad (14)$$

Hence, the jump frequency for direct vacancy motion along the  $c$ -axis is only roughly 25% of the frequency of "a" jumps. This result provides considerable information about the details of the jump mechanism in tin.

Rice and co-workers<sup>4-6</sup> have analyzed the conditions for a diffusive jump. Briefly, the atom must have a critical amplitude in the direction of the vacancy, and simultaneously, and also most restrictively, all blocking atoms must move aside with a breathing mode of sufficient amplitude to allow the diffusing atom to pass. These criteria may be visualized for tin in terms of Fig. 7a and 7b. Figure 7b is a view of the  $a$ - $c$  plane looking along the  $a$ -direction in the tin crystal. Suppose that in Fig. 7b the site labeled 1 is vacant. If a "c" jump is to occur (exchange with the site labeled 3), then both atoms labeled 4, plus the two body-centered atoms not shown, must move aside. Thus, both the conditions of sufficient amplitude of the diffusing atom and a suitable breathing mode of the four blocking atoms must be satisfied. But from Fig. 7a it is evident that any one of the atoms labeled 2 may move into the vacancy at 1 without interference from blocking atoms. Hence, the only condition for "a" jumps is that the diffusing atom have sufficient amplitude to effect the jump. Relaxation of the atoms toward the vacancy will modify this picture only slightly, since now a breathing motion is required for the other atoms labeled 2 in Fig. 7a if one of these is to jump. But the required amplitude is small, and should be easily achieved. Thus, "a" jumps are greatly favored, since the frequency of occurrence of the necessary breathing mode in both pairs of blocking atoms involved in "c" jumps is expected to be much lower than the frequency with which the amplitude conditions are fulfilled for either jump. This agrees with (14).

But the activation energies should be different for these jumps, since the jump conditions are different. We use eq. 1 to compare the relative importance of various contributions to  $\Delta H$ .  $\Delta H_f$  is the same for each jump type, since all vacancies are presumed equiv-

alent. The sums  $\sum_{k>l} \Delta H_{kl}$  should be very nearly the same for both jump types. The terms  $U_0$  will be close to equal for each jump type, though perhaps slightly larger for "c" jumps. At first the energy contributions from  $\sum_j U_j$  appear quite anisotropic, since the sum is zero for "a" jumps, but finite for "c" jumps into an unrelaxed vacancy. Relaxation should increase this contribution nearly equally for each type. To determine the anisotropy in  $\Delta H$ , it is necessary to form some estimate of  $\sum_j U_j$  for "c" jumps.

The dynamical theory, as developed by Manley,<sup>23</sup> identifies as the critical variable for each atom  $j$  the difference  $\Delta q_j$  between the maximum attainable amplitude,  $q_{j\max}$ , and the necessary amplitude to just permit the jump,  $q_{j\min}$ . In tin the geometry is such that  $q_{j\min}$  is 0.106 Å. at 25°, and it decreases slightly with temperature. But from Mössbauer measurements in tin<sup>24</sup> the root mean squared vibrational amplitudes of atoms in the  $\langle 100 \rangle$  direction at 300°K. is  $\sim 0.150$  Å. and increases to 0.178 Å. at 400°K. and to 0.204 Å. at 500°K. Apparently, at the diffusion temperatures the root mean squared amplitudes are nearly a factor of two larger than  $q_{j\min}$ , and the atoms  $j$  do not need to acquire extra energy for a diffusive jump. Obviously, they must still satisfy the breathing mode requirement, and this will limit the jump rate. But anisotropy in  $\Delta H$  due to different contributions from  $\sum_j U_j$  will be small, since both jump types require little or no increase over the mean thermal energies for the interfering atoms.

It can still be argued that the activation energies could be quite unequal if the admittedly nonidentical factors  $U_0$  and  $\sum_j U_j$  of (1) were dominant. It has been estimated<sup>6</sup> that the various terms for a simple model have the approximate weights  $\Delta H_f = 20$ -40%,  $U_0 = 30$ -60%,  $U_j = 15$ -25%, and  $\sum_{k>l} \Delta H_{kl} = 5$ -10%.

Recent results of quenching measurements and lattice dilatation studies in Ag,<sup>25</sup> Au,<sup>26</sup> and Cu<sup>3</sup> show that a more probable weight for  $\Delta H_f$  for the noble metals is close to 60%. While tin is far from a noble metal, it seems likely that the formation enthalpy is still close to 50% of the total effect. Thus, anisotropy in the activation energies must be small as observed.

*Entropy.* The activation entropy,  $\Delta S$ , was calculated from the usual relation<sup>1</sup>

(23) O. P. Manley, *J. Phys. Chem. Solids*, **13**, 244 (1960).

(24) A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, *Proc. Phys. Soc. (London)*, **A77**, 129 (1961).

(25) M. Doyama and J. S. Koehler, *Phys. Rev.*, **127**, 21 (1962).

(26) J. E. Bauerle and J. S. Koehler, *ibid.*, **107**, 1493 (1957).

$$\Delta S = R \ln (D_0/\gamma a^2 \nu) \quad (15)$$

The choice of  $\nu$  is difficult and has been related to a normal mode analysis of lattice vibrations by several authors.<sup>4,12</sup> In practice, the Debye frequency is used as the best available estimate. In this experiment the jump rates differing by a factor of 4 can only be the result of differences in  $\Delta S$  and  $\nu$ , and the uncertainty in  $\nu$  is compounded further. Consider three cases:  $\nu_a = \nu_c$  and the  $D_0$  differences are reflected in  $\Delta S$ ;  $\nu_a = 4\nu_c$ , the jump rate difference being almost entirely due to  $\nu$  differences;  $\nu_a = 2\nu_c$ , an intermediate case. These cases are presented in Table VII, with calculations based on  $\nu_a = \nu_\theta$ , where  $\theta_D = 142^\circ\text{K}$ .<sup>27</sup> It is interesting that  $\Delta S_a = \Delta S_c$  if  $\nu_a = 2\nu_c$ . The  $\Delta S$  values do not agree well with Meakin and Klokholm, who apparently used a much different Debye temperature.

Table VII: Activation Entropies

Case	$\Delta S_a$ , e.u.	$\Delta S_c$ , e.u.	Relationships
1	16.6	17.8	$\nu_a = 4\nu_c$
2	16.6	15.1	$\nu_a = \nu_c$
3	16.6	16.4	$\nu_a = 2\nu_c$

Keyes<sup>16</sup> has used continuum theory to write

$$\Delta S = 2(\gamma - \frac{1}{3})\alpha\Delta G \quad (16)$$

where  $\alpha$  and  $\gamma$  are the thermal expansion coefficient and the Grüneisen constant. To a first approximation, this study gives  $\Delta G \simeq \Delta H = 25.3$  kcal. and  $\Delta S = 5.2$  e.u. From this estimate  $\Delta G = \Delta H - T\Delta S = 23.0$  kcal., and  $\Delta S = 4.75$  e.u. This is much lower than the observed  $\Delta S$  values and seems to cast doubt on the applicability of the theory.

*Volume.* It is interesting to note that DeVries, Baker, and Gibbs,<sup>28</sup> in a preliminary report, have found an activation volume for creep in tin of about 30% of the molar volume, in close agreement with the 33% observed in this study. Their results have not been fully published to date so further comment is difficult.

Keyes<sup>16</sup> has also developed the relation

$$\Delta V = 2\left(\gamma - \frac{1}{3}\right)\kappa\Delta G \quad (17)$$

where  $\kappa$  is the compressibility. Using  $\Delta G = 23.0$  kcal., we have  $\Delta V = 5.1$  cm.<sup>3</sup>, in excellent agreement with the observed 5.3 cm.<sup>3</sup>. Hence, the strain energy approach gives quite good agreement for  $\Delta V$ , though the predicted  $\Delta S$  is not good.

We can get some indication as to why no anisotropy in  $\Delta V$  was observed in this study from considering eq.

12a in the Appendix. The  $S_i$  are sums of elastic constants, the same for all  $k$  directions, so anisotropy comes only from the  $M_i^k$  (the  $\gamma RTs_{ij}\delta_{ik}$  term is small, so anisotropy from this source is negligible). But the  $M_i^k$  are defined by eq. 8a in terms of a formation and a motion contribution,  $w_i$  and  $m_i^k$ ; only the latter can be anisotropic. But we have seen that in gold this term is only 22% of the total activation volume, and in general  $w_i \geq m_i^k$  is probably valid. Therefore, any anisotropy in  $m_i^k$  for different  $k$  is largely masked by the isotropic  $w_i$  contribution.

Probably the largest contribution to anisotropy in  $\Delta V_{\text{mob}}$  arises because the blocking atoms must assume a breathing mode before the diffusing atom may exchange with the vacancy. But the previous comments about vibration amplitudes in tin show that this effect will be small at best, since little or no "excess" volume is required. Hence,  $\Delta V_a$  should be almost equal to  $\Delta V_o$ .

From eq. 10a we can get some idea of the magnitude of the  $M_i^k$ . The tin elastic moduli were taken from Mason and Bommel.<sup>29</sup> For the  $a$ -axis isotherm at 225.6° we have

$$4.82 \text{ cm.}^3 = (M_1^1 + M_2^1)(10.3 \times 10^{-13}) + M_3^1(7.8 \times 10^{-13}) \quad (18)$$

so that an upper limit for  $M_i^k$  is  $\sim 5 \times 10^{12}$  ergs =  $10^3$  kcal. The work of Liu and Drickamer<sup>30</sup> on the effect of uniaxial compression on diffusion in zinc can be used in a consistent way<sup>31</sup> to evaluate some individual  $M_i^k$  values. From the elastic data for zinc of Hearmon,<sup>32</sup> we find that  $M_1^3 = 35 \times 10^3$  kcal. and  $M_3^3 = 190 \times 10^3$  kcal. These values are up to two orders of magnitude greater than the upper bounds found for tin and also exceed similar upper limits determined from the hydrostatic pressure results for zinc by the same margins. Two possible explanations of this difficulty are: (1) the effect of pressure is not adequately accounted for by a sum over the individual stress components of the form of eq. 10a; (2) some gross difficulty exists in the experiments. Neither alternative is favored; indeed both may be partially correct.

(27) R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.*, **131**, 529 (1963).

(28) K. L. DeVries, G. S. Baker, and P. Gibbs, *Bull. Am. Phys. Soc.*, [II] **6**, 169 (1961).

(29) W. P. Mason and W. E. Bommel, *J. Acoust. Soc. Am.*, **28**, 930 (1956).

(30) T. Liu and H. G. Drickamer, *J. Chem. Phys.*, **22**, 312 (1954).

(31) See A. W. Lawson, *ibid.*, **22**, 1948 (1954). However, if the stress range is great enough,  $\partial \ln D_k / \partial P_i$  may be evaluated using only uniaxial stress data. This avoids the inconsistency.

(32) R. F. S. Hearmon, *Rev. Mod. Phys.*, **18**, 409 (1946).