

ΔH 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, defined⁴ 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-workers⁴⁻⁶ 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 ΔH . ΔH_i is the same for each jump type, since all vacancies are presumed equiv-

alent. The sums $\sum_{k>1} \Delta H_{ki}$ 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 ΔH , it is necessary to form some estimate of $\sum_j U_j$ for "c" jumps.

The dynamical theory, as developed by Manley,²³ identifies as the critical variable for each atom j the difference Δq_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 tin²⁴ the root mean squared vibrational amplitudes of atoms in the $\langle 100 \rangle$ direction at 300°K. is ~ 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 ΔH 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 estimated⁶ that the various terms for a simple model have the approximate weights $\Delta H_i = 20$ –40%, $U_0 = 30$ –60%, $U_j = 15$ –25%, and $\sum_{k>1} \Delta H_{ki} = 5$ –10%.

Recent results of quenching measurements and lattice dilatation studies in Ag,²⁵ Au,²⁶ and Cu³ show that a more probable weight for ΔH_i 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, ΔS , was calculated from the usual relation¹

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