(000), (1/2 0 1/4), (1/2 1/2 1/2), and (0 1/2 3/4) with unit cell dimensions at 25° of $a = 5.820$ Å., $c = 3.175$ Å., so that $c/a = 0.5456$. Each atom has four nearest neighbors at a distance of 3.016 Å., directed ~15° out of the a-axis plane, and two next nearest neighbors along the c-axis at 3.175 Å.

In this structure two distinct kinds of jump are possible for bulk diffusion *via* vacancies. If in Fig. 7a the vacancy is at the site labeled 1, it may exchange with either of four nearest neighbors labeled 2 or two next-nearest neighbors labeled 3. Only these jumps are considered; other jumps are essentially blocked by the atoms neighboring the vacancy. For convenience, a vacancy jump from site 1 to site 2 shall be called an "a" jump, not exactly in the a-axis direction, and a "c" jump will be the vacancy jump from site 1 to site 3. Note that the "a" jump contains a component in the c-axis direction which contributes to c-axis diffusion, while "c" jumps do not contribute to a-axis diffusion.

In view of the essentially identical energies and volumes associated with diffusion along the different axes, it is attractive to postulate that only one jump, the "a" type, might satisfactorily account for the results of this study. We check this possibility by forming the ratio

$$\frac{D_c}{D_a} = \frac{\gamma_c' c^2 \nu_c' e^{+\Delta S_c'/R} e^{-\Delta H_c'/RT}}{\gamma_a a^2 \nu_a e^{+\Delta S_a/R} e^{-\Delta H_a/RT}} \qquad (10)$$

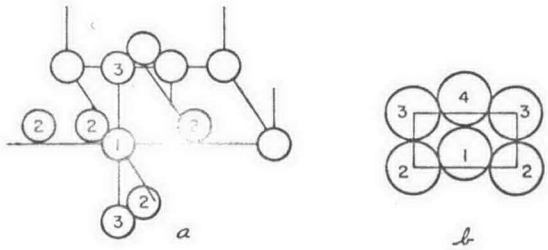
where all terms have their usual meaning. If only "a" jumps are assumed then $\Delta H_a = \Delta H_c'$, $\Delta S_a = \Delta S_c'$, and $\nu_a = \nu_c'$, and (10) becomes

$$\frac{D_c}{D_a} = \frac{\gamma_c' c^2}{\gamma_a a^2} \qquad (11)$$

The component of an "a" jump in the a-axis direction is one-half the length of an a edge of the unit cell. There are four possible jumps of this type, only two of which contribute to diffusion along a given a-axis, so $\gamma_a a^2 = 1/2(2)(a/2)^2 = a^2/4$. All a jumps contain components in the c-axis direction of magnitude $c/4$, so $\gamma_c' c^2 = 1/2(4)(c/4)^2 = c^2/8$. The factor 1/2 in front of each product arises from the definition of the γ-values.[22] Since $D_a/D_c = 2.20$, we have

$$1/2.20 = 0.454 \neq (1/8)c^2/(1/4)a^2 = (1/2)(c^2/a^2) = 0.15 \qquad (12)$$

since the ratio (c^2/a^2) is 0.298. Hence, the observed rate of c-axis diffusion is a factor of three too high to be explained by only "a" jumps. The missing two-thirds of the observed rate must be assigned to "c"-type jumps, so that c-axis diffusion is a combination of both elementary jumps.



Atomic Positons in White Tin

Figure 7. Atomic positions in tin.

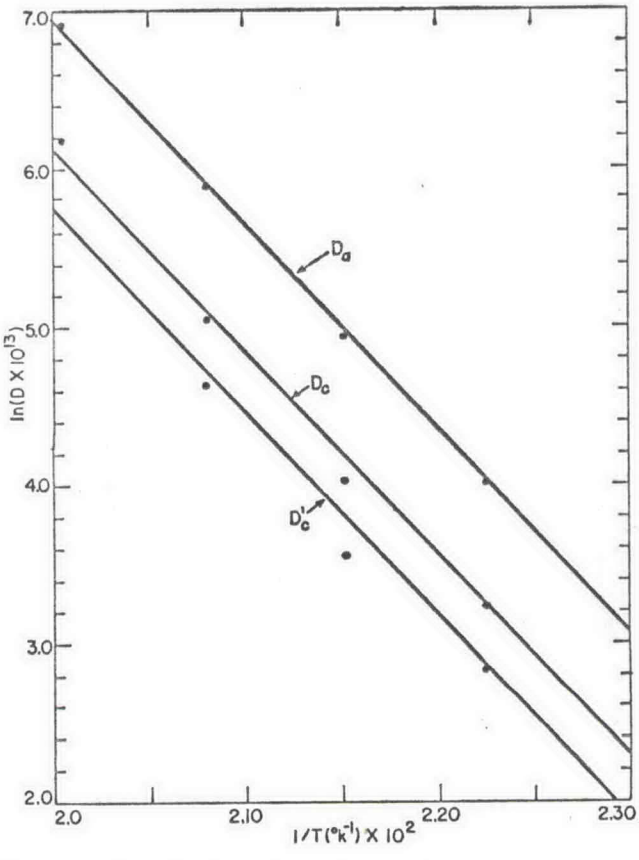


Figure 8. Contributions of a- and c-type jumps.

Similar to Meakin and Klokholm,[10] we compare the diffusion coefficients for "a" and "c" jumps separately by subtracting $0.15D_a$ from each D_c value at the same temperature. This removes the "a"-jump contribution to c-axis diffusion. Figure 8 shows the zero-pressure isobars for D_a, D_c, and D_c', where $D_c' = D_c - 0.15D_a$. Least squares gives $D_0' = 4.64$ cm.²/sec. and $\Delta H_c' = 25.6$ kcal., essentially unchanged in

(22) C. Zener, *J. Appl. Phys.*, 22, 372 (1952).