

$$\Delta H = \frac{\Delta H_m}{\Delta V_m} \Delta V \quad (3)$$

where the subscript *m* refers to fusion. While (2) and (3) hold remarkably well for a large number of metals to 10 kbars⁷ Hudson and Hoffman⁸ have found large deviations for lead at higher pressure. The correspondence between diffusion and melting probably exists only in the limit of zero pressure.

From the foregoing it is evident that vacancy diffusion occurs in metals which crystallize in close-packed structures in which the void volume is a minimum. Anisotropic structures typically have larger void volumes; and if interstitial self-diffusion occurs in metals, those with anisotropic structures should be relatively favored. Since no theoretical calculations for activation energies have been made for such systems, it is necessary to determine the activation volumes, as well as activation energies, to form reliable conclusions about the diffusion mechanism. White tin is anisotropic, with a void volume at 25° of 46.5%, and is thus a favorable metal. Self-diffusion studies in tin at zero pressure have been reported by Fensham⁹ and by Meakin and Klokholm.¹⁰ The results of Fensham are anomalous, giving activation energies which disagree with results for similar metals. Meakin and Klokholm found close agreement with other low melting metals, but could show only that a vacancy mechanism was consistent with their results, not that it was required. This study was undertaken to determine unequivocally the diffusion mechanism in tin.

It is perhaps desirable to ask at this point what is the significance of the quantity $(\partial \ln D / \partial P)_T$ in an anisotropic system. Girifalco and Grimes¹¹ have analyzed the effect of strain on the diffusion relations as developed by Vineyard.¹² Their results are generalized to anisotropic systems in the Appendix, and it is clear that the measured quantity is indeed a volume, related to the usual activation volume in isotropic systems. This result adds confidence in the conclusions drawn from this study.

Experimental

Large single crystals were grown from 99.999% tin¹³ by a modified Bridgman technique. Crystal quality was checked with a modified Laue back-reflection technique, in which the only collimation of the X-ray beam was a 0.10-in. diameter pinhole. This gave a beam which struck about 1 cm.² of the crystal surface. Any crystal defects in this area appeared as irregularities in the X-ray film spots. Only crystals which gave nearly perfect spots were accepted for diffusion studies.

The large crystals were oriented by the usual Laue back-reflection technique. Cubes approximately 1 cm. on an edge and with their faces oriented close to perpendicular to the (100) or (001) axis, principle axes for diffusion, were cut out with a Servomet spark cutter. These cubes were again checked for quality with large-spot X-rays. No difference in quality of faces perpendicular or parallel to the tetragonal (001) axis was detected. Once again only the best crystals were retained. Two faces of each cube were oriented on a small goniometer head by X-rays so that the desired crystal axis and the goniometer axis were parallel to 0.5° of arc. The goniometer head was then aligned optically in a microtome to cut the crystal face perpendicular to the desired axis. Microtoming gave a plane basal surface flat to within 2 μ. The crystal was annealed for 2 hr. to remove the slight cold work introduced by the microtome.

Sn¹¹³ in carrier metal was vapor deposited on the diffusion faces at pressures less than 10⁻⁵ mm. Typically, films less than 1 μ thick and having an activity of close to 10⁵ counts per min. were achieved.

The crystal was sealed in a Pyrex ampoule under vacuum and placed in a wire-wound resistance furnace at the desired temperature for the zero pressure anneals. Temperature was measured with a carefully calibrated iron-constantan thermocouple positioned near the ampoule at the center of an aluminum bronze block which minimized temperature gradients around the ampoule. Temperature was measured to 0.15° and absolute temperature at the crystal was probably correct to within 1°. Correction for finite warm-up rate was applied, in no case being greater than 0.5% of the anneal time. No cooling correction was needed.

High pressure was generated by a liquid hydraulic system of the Bridgman type.¹⁴ Pressure was transmitted by Dow-Corning 200 silicone fluid and measured with a manganin wire coil calibrated against the freezing point of mercury (7640 kg./cm.² at 0°). Automatic pressure control, plus a continuous pressure record, was obtained by monitoring the imbalance of a Wheatstone bridge with a recording potentiometer. Pressure was maintained to within 10 kg./cm.² of the mean

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