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Self-Diffusion in Tin at High Pressure

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Measurements are reported for a-axis and c-axis self-diffusion in tin from 0 to 10 kbars and for temperatures in the range 160–228°. At zero pressure, $D_a = 10.7 \exp(-25{,}100 \pm 800)/RT$ and $D_c = 7.7 \exp(-25{,}600 \pm 1000)/RT$. The activation volume is 5.3 ± 0.3 cm.^{3} g.-atom^{-1} (33% of the g.-atomic volume) for both principal directions and appears to be independent of temperature. The data are most simply interpreted in terms of a vacancy mechanism, in which two distinct kinds of jumps occur.

Introduction

Activation energies ΔH determined from the temperature dependence of the diffusion rate in single crystals of the elementary metals are most satisfactorily correlated with theoretically calculated activation energies for a vacancy diffusion mechanism.[1] Recent work on the pressure dependence, which leads to the activation volume ΔV, has supported this mechanism.[2] The work of Simmons and Balluffi[3] provides near-conclusive evidence for the existence of high concentrations of vacancies in the noble metals and aluminum near their melting points. Hence, a vacancy diffusion mechanism is reasonable in these and similar metals.

Solid-state diffusion has been considered an activated process, with a Gibbs free energy of activation ΔG. For the vacancy mechanism, it is natural to distinguish between contributions to ΔG from the formation of sessile vacancies at equilibrium in the lattice, ΔG_f, and from the additional free energy ΔG_m necessary to move the vacancy from the equilibrium position to the midpoint of the diffusive jump. The activation enthalpy and volume have analogous components; diffusion studies yield only their sum. For close-packed hard spheres, ΔV_f should be 1 molar volume, and ΔV_m should be of this order.[2] Other crystal structures will have smaller motional contributions. Measured values of ΔV range from about 25% of an atomic volume (lithium) to 90% (silver), and are greater than 50% for close-packed structures.[2]

Rice and co-workers[4-6] have developed a dynamical theory of diffusion which, while formally equivalent to activated state theory, avoids the least tenable assumptions of the activated state, and which identifies the important microscopic contributions to the diffusive process. The activation energy is replaced by

$$\Delta H = U_0 + \sum_j U_j + \sum_{k>l} H_{kl} + \Delta H_f \qquad (1)$$

where U_0 is the translational energy a diffusing atom must obtain to successfully effect the jump, $\sum_j U_j$ is the excess energy over the thermal average for any atoms hindering the motion of the diffusing atom to move sufficiently aside for that atom to pass, and $\sum_{k>l} H_{kl}$ accounts for adjustments of the surrounding atoms not specifically included in the jump process. ΔH_f is the formation enthalpy of a vacancy.

Using this approach, Rice and Nachtrieb[5] conclude that a correspondence between diffusion and melting should exist in the form

$$\left[\frac{\partial \ln (D/\gamma a^2 \nu)}{\partial T_m/T}\right]_{T_m} = \text{constant} \qquad (2)$$

and that

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(1) D. Lazarus, "Advances in Solid State Physics," Vol. 10, F. Seitz and D. Turnbull, Ed., Academic Press, Inc., New York, N. Y., 1960, p. 71.

(2) D. Lazarus and N. H. Nachtrieb, "Solids Under Pressure," W. Paul and D. M. Warschauer, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, p. 43.

(3) R. O. Simmons and R. W. Balluffi, *Phys. Rev.*, **117**, 52 (1960); **119**, 600 (1960); **125**, 862 (1962); **129**, 1533 (1963).

(4) S. A. Rice, *ibid.*, **112**, 804 (1958).

(5) S. A. Rice and N. H. Nachtrieb, *J. Chem. Phys.*, **31**, 139 (1959).

(6) A. W. Lawson, S. A. Rice, R. D. Corneliussen, and N. H. Nachtrieb, *ibid.*, **32**, 447 (1960).