purchased from Atomergic Chemetals Co., Carle Place, N. Y.

[22] R. S. Sennet and G. D. Scott, J. Opt. Soc. Am. 40, 203 (1950).

[23] G. Hass, J. Opt. Soc. Am. 45, 945 (1955).

[24] D. Pines, in *Elementary Excitations in Solids* (Benjamin, New York, 1964), p. 144.

[25] R. H. Ritchie, Phys. Rev. 106, 874 (1957).

[26] R. A. Ferrell, Phys. Rev. 111, 1215 (1958).

[27] E. A. Stern and R. A. Ferrel, Phys. Rev. 120, 130 (1960).

[28] C. J. Powell and J. B. Swan, Phys. Rev. 115, 869 (1959); 116, 81 (1959); 118, 640 (1960).

[29] H. Boersch, P. Dobberstein, D. Fritzche, and G. Sauerbrey, Z. Physik 187, 97 (1965).

[30] H. Boersch and G. Sauerbrey, in Ref. 12, p. 386.

[31] P. Von Blanckenhagen, H. Boersch, D. Fritche, H. G. Seifert, and G. Sauerbrey, Phys. Letters 11, 296 (1964).

[32] G. E. Jones, L. S. Cram, and E. T. Arakawa, Phys. Rev. 147, 515 (1966).

[33] E. T. Arakawa, R. N. Hamm, W. F. Hansen, and T. M. Jelinek, in Ref. 12, p. 374.

[34] S. E. Schnatterly and S. N. Jasperson, Phys. Rev. 188, 759 (1969).

[35] O. Hunderi and D. Beaglehole, Opt. Commun. 1, 101 (1969).

[36] O. Hunderi and D. Beaglehole, Phys. Letters 29a, 335 (1969).

[37] D. Beaglehole and O. Hunderi, Phys. Rev. B 2, 309 (1970).

[38] O. Hunderi and D. Beaglehole, Phys. Rev. B 2, 321 (1970).

[39] Y.-Y. Teng and E. A. Stern, Phys. Rev. Letters 19, 511 (1967).

[40] P. A. Fedders, Phys. Rev. 165, 580 (1968).

[41] J. N. Mundy, L. W. Barr, and F. A. Smith, Phil. Mag. 15, 411 (1967).

[42] N. H. Nachtrieb, E. Catalano, and J. A. Weil, J. Chem. Phys. 20, 1185 (1952).

[43] R. A. Ferrel and E. A. Stern, Am. J. Phys. 30, 810 (1962).

[44] J. J. Hopfield, Phys. Rev. 139, A419 (1965).

[45] J. N. Hodgson, in Ref. 12, p. 60.

[46] H. Ehrenreich and H. R. Phillip, Phys. Rev. 128, 1622 (1962).

[47] H. Ehrenreich, H. R. Phillip, and B. Segall, Phys. Rev. 132, 1918 (1963).

[48] H. E. Bennett and J. M. Bennett, in Ref. 12, p. 175.

[49] H. E. Bennett and J. O. Porteus, J. Opt. Soc. Am. 51, 123 (1961).

[50] R. E. Palmer, Ph. D. dissertation (Princeton University, 1971) (unpublished).

[51] R. N. Gurzhi, Zh. Eksperim. i Teor. Fiz. 35, 965 (1958) [Soviet Phys. JETP 8, 673 (1959)].

[52] K. L. Kliewer and R. Fuchs, Phys. Rev. 172, 607 (1968).

[53] M. J. G. Lee, Proc. Roy. Soc. (London) 295A, 440 (1966).

[54] P. Beckmann and A. Spizzichino, in *Scattering of Electromagnetic Waves from Rough Surfaces* (Pergamon, New York, 1963), pp. 67–69, 97, and 98.

[55] D. Pines, in Ref. 24, p. 151.

PHYSICAL REVIEW B VOLUME 4, NUMBER 8 15 OCTOBER 1971

Indium Diffusion in Aluminum

G. M. Hood and R. J. Schultz
Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories,
Chalk River, Ontario, Canada

(Received 22 March 1971)

Six measurements of ^{114}In diffusion in single crystals of 99.999% pure Al have been made in the range 440–660 °C. A least-mean-squares analysis of the data leads to the expression $D = 1.16e^{-(1.27\,\mathrm{eV})/kT}$ cm^2 sec^{-1}. The activation energy is similar to that found for the diffusion of other nontransition solutes in Al and does not therefore appear to reflect an exceptionally large In-vacancy binding energy in Al, such as was found by quenching experiments.

The choice of In for the present study was dictated largely by consistent reports of a relatively large binding energy between vacancies and In atoms in Al.[1,2] (Further references are listed in Ref. 1.)

It is expected, on general grounds, that a large solute-vacancy binding energy will be reflected in the difference between the activation energies ΔQ for diffusion of the solute (Q_i) and for self-diffusion (Q_0) in a given solvent.[3]

In the present work, single crystals of 99.999% pure Al were used. Disks, 1 cm diam by 5 mm thick, were prepared metallographically and annealed under vacuum for 24 h at 620 °C. They were then implanted with 40-keV ^{114}In ions in the CRNL mass separator. The advantages of this technique as a means of forming source layers for diffusion experiments are discussed elsewhere.[4,5] Diffusion anneals were carried out under vacuum. The samples were subsequently sectioned and analyzed for ^{114}In by γ-ray counting techniques. Details of the sample preparation, sectioning, and counting techniques are described in Refs. 4 and 5.

The results are presented in Fig. 1 and Table I. Gaussian profiles were found for all samples, although an anomalous "wiggle" appeared in the first few sections of each sample. For clarity this has been omitted; however, the insert in Fig.

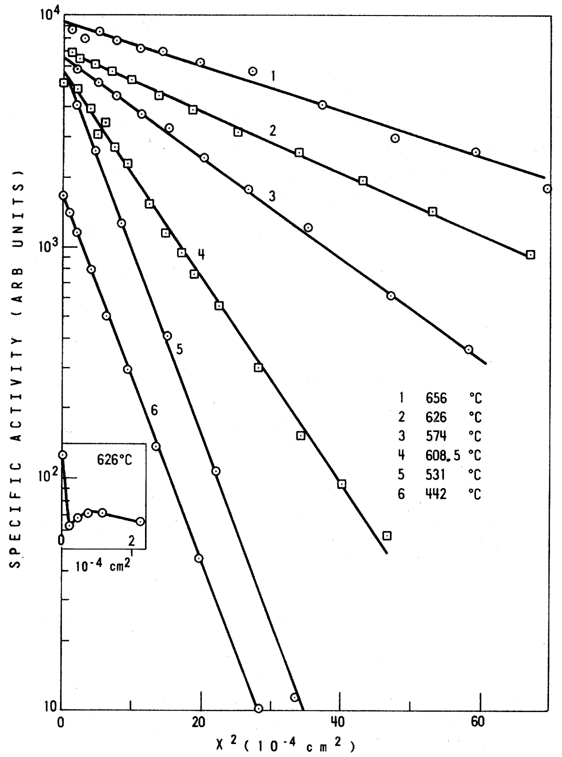

FIG. 1. Penetration profiles for ^{114}In diffusion into Al single crystals. Inset: anomalous near surface distribution for ^{114}In diffusion into Al at 626 °C.

1 is characteristic of the phenomenon. An apparently similar effect has been observed and discussed in relation to Co diffusion in Zr.[6] It may be a precipitation phenomenon associated with a rapidly diffusing solute of limited solubility.

A least-mean-squares analysis of the data of Table I, plotted in Fig. 2, leads to the equation

$$D = 1.16 e^{-(1.27\,\mathrm{eV})/kT}\ \mathrm{cm}^2\,\mathrm{sec}^{-1}$$

for In diffusion in Al.

The activation energy is similar to values found for other nontransition solutes in Al (see Table II and Refs. 7–9) and does not appear to reflect the presence of a large In-vacancy binding energy.

The constancy of the activation energies for diffusion of nontransition solutes in Al and the adoption of $Q_0 = 1.26$ eV for Al self-diffusion has led Peterson and Rothman[7] to speculate that since the resulting ΔQ values are near zero, solute-vacancy binding energies in Al are also likely to be small. However, there is doubt about the best value to use for Q_0. Suggested values tend to lie between a minimum of 1.25 eV, based on NMR measurements,[10] and an upper limit of 1.49 eV from tracer diffusion studies.[11,12]

In addition to questions arising from the best value to adopt for Al self-diffusion there is also a large uncertainty associated with solute-vacancy binding energies in Al.

Concerning the present work, the least ambiguous values for the In-vacancy binding energy in Al should perhaps come from studies on the simplest possible systems. Using this criterion, the investigations of Plumbridge[1] and Duckworth and Burke[2] on dilute binary alloys of In in Al should be considered. The quantitative agreement between the findings of these examinations seems poor.

Duckworth and Burke[2] find the In-vacancy binding energy in Al to be 0.42±0.04 eV, while Plumbridge[1] estimates the binding free energy to lie between 0.18 and 0.21 eV. Some aspects of these studies are discussed below.

Because of the scatter of experimental points

TABLE I. Diffusion coefficients of In in Al.

Temperature (°C)	Diffusion period (sec)	D (cm^{2}sec^{-1})
656 ± 1	5.20×10^3	$(1.9 \pm 0.2) \times 10^{-7}$
626 ± 1	8.4×10^3	$(9.8 \pm 0.4) \times 10^{-8}$
608.5 ± 1	3.6×10^3	$(6.8 \pm 0.3) \times 10^{-8}$
574 ± 1	1.46×10^4	$(3.5 \pm 0.1) \times 10^{-8}$
531 ± 1	7.6×10^3	$(1.7 \pm 0.1) \times 10^{-8}$
442 ± 2	8.9×10^4	$(1.55 \pm 0.05) \times 10^{-9}$

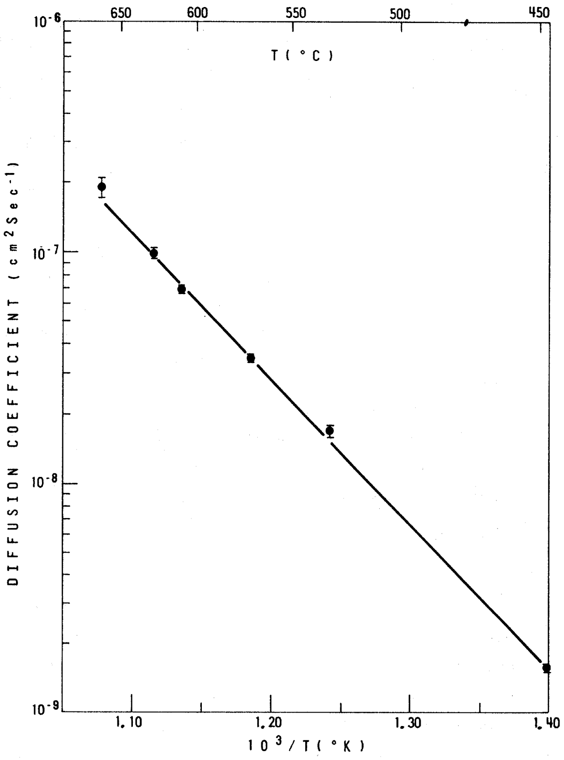

FIG. 2. The temperature dependence of the diffusion of ^{114}In in Al.

TABLE II. Parameters for nontransition solute diffusion in Al.

Solute	Solute valence	Q (eV)	D_0 ($\mathrm{cm}^2\mathrm{sec}^{-1}$)	Ref.
Cu	1	1.40	0.65	7
Zn	2	1.25	0.26	7
Ga	3	1.27	0.49	7
Ge	4	1.26	0.48	7
Ag	1	1.21	0.12	7
		1.22	0.13	8
Cd	2	1.29	1.04	8
In	3	1.27	1.16	This work
Sb	5	1.26	0.09	9
Au	1	1.21	0.13	7
		1.17	0.077	7

shown in Fig. 1 of Ref. 2, any estimate of the In-vacancy binding enthalpy, or entropy, based on the data, must be subject to a very large error. However, a value for the In-vacancy binding free energy $G^B_{\mathrm{In}-v}$ may be estimated within a reasonable degree of accuracy. By considering the data at the lower quench temperature, where possible effects of multivacancy complex formation should be minimized, a figure of 0.35±0.05 eV has been estimated for $G^B_{\mathrm{In}-v}$ at 380 °C.

The interpretation of the experimental work of Ref. 1 depends, in part, on single vacancies being able to migrate rapidly in Al at 0 °C. This is not consistent with the low-temperature quenching experiments of De Sorbo and Turnbull.[13] They indicate that the main recovery stage to be associated with a quench from 500 °C is probably due to divacancy migration. The interpretation of the results should then include an allowance for this effect.

If the values for $G^B_{\mathrm{In}-v}$ obtained from Refs. 1 and 2 are compared, i.e., 0.35 eV at 380 °C (Ref. 1) and 0.20 eV at 0 °C (Ref. 2), then the corresponding values for the binding enthalpy and entropy are 0.1 eV and 4.5k, respectively. Although the value for the binding enthalpy seems reasonable, the large value for the entropy would be expected to make a big contribution to the D_0 factor for In diffusion in Al. The apparent absence of any such contribution probably points to an inconsistency between the findings presented in Refs. 1 and 2. Possibly some of the effects discussed above have some bearing on the discrepancy.

Compared to other solutes listed in Table II, the relatively high diffusivities of In and Cd (two solutes with apparently large binding energies[1,2,14] to vacancies in Al) may indicate that in Al, solute-vacancy binding energies are more obviously related to absolute D values than to individual Q or D_0 parameters. However, the value of such comparisons is questionable when one considers the uncertainty of reported solute-vacancy binding energies in Al.

Obviously further work, aimed at producing reliable and reproducible solute-vacancy binding energies and an unambiguous Q_0 value for Al self-diffusion is required. Additional measurements of solute diffusion parameters, including isotope effects,[15] would also contribute to an understanding of solute-vacancy interactions in Al. A study of the isotope effect for Zn diffusion in Al has recently been made[16] which seems to indicate that the Zn-vacancy interactions in Al may be in excess of 0.1 eV.

Our thanks are due to Dr. D. Santry and O. Westcott for their cooperation with regard to the In implantations and to Dr. M. L. Swanson for useful discussions and comments.

---

[1] W. J. Plumbridge, Phil. Mag. 20, 707 (1969).

[2] F. C. Duckworth and J. Burke, Phil. Mag. 14, 473 (1966).

[3] A. D. LeClaire, Phil. Mag. 7, 141 (1962).

[4] G. M. Hood, Phil. Mag. 21, 305 (1970).

[5] G. M. Hood and R. J. Schultz, Phil. Mag. 23, 1479 (1971).

[6] G. V. Kidson, Phil. Mag. 20, 1047 (1969).

[7] N. L. Peterson and S. J. Rothman, Phys. Rev. B 1, 3264 (1970).

[8] W. B. Alexander and L. M. Slifkin, Phys. Rev. B 1, 3274 (1970).

[9] S. Badrinarayanan and H. B. Mathur, Intern. J. Appl. Phys. 36, 3860 (1965).

[10] F. Y. Fradin and T. J. Rowland, Appl. Phys. Letters 11, 207 (1967).

[11] T. S. Lundy and J. F. Murdock, J. Appl. Phys. 33, 1671 (1962).

[12] M. Beyeler and Y. Adda, J. Phys. 29, 345 (1968).

[13] W. De Sorbo and D. Turnbull, Phys. Rev. 115, 560 (1959).

[14] S. Ceresara and P. Fiorini, Phil. Mag. 19, 105 (1969).

[15] A. D. Le Claire, in *Physical Chemistry, An Advanced Treatise*, edited by W. Jost (Academic, New York, 1970), Vol. X, p. 261.

[16] N. L. Peterson (private communication).