Tracer Impurity Diffusion in Liquid Metals: Zn and Cd in Gallium

S. J. Larsson and P.-E. Eriksson

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

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The diffusion coefficients of ^{65}Zn and ^{115}Cd in liquid Ga have been measured between 27° and 455 °C. The temperature dependence of D can be represented by a linear plot or by an Arrhenius representation with $D_0=2.1\cdot10^{-4}$ cm²/s, $Q=1.60$ kcal/mol for Zn, and $D_0=2.3\cdot10^{-4}$ cm²/s, $Q=1.77$ kcal/mol for Cd. An extrapolation to lower temperatures for Zn in Ga connects to the measurements by Belskii et al. The present results imply that for impurity diffusion in liquid Ga the effects of solute mass are more significant than valence effects.

As a part of a systematic investigation of tracer diffusion in Ga [1–3], we have investigated D_i for divalent impurities ^{65}Zn and ^{115}Cd. The experimental procedure was identical with that of Refs. [2, 3]. The results can be seen in Table 1 and Figure 1. The phenomenological parameters of the Arrhenius representation and of linear representation are expressed in Table 2, listing also the earlier [1, 3, 4] results for comparison. In Fig. 1 the results obtained for Zn in Ga by Belskii et al. [5] are also shown.

It is conspicuous that the linear temperature characteristics of Cd diffusion are nearly identical with those of In. The points obtained for Zn lie only slightly higher than those for the two heavier elements, and considerably lower than those for Ga self-diffusion, although the Zn tracer is 10% lighter than ^{72}Ga. The results obtained in an earlier investigation at low temperatures [5] agree well with the extrapolation of the present Zn series.

Although the divalent impurities have a lower valency than the solvent, and so might be expected to repel "free volume", they exhibit a lower "activation energy" than that of self-diffusion and about the same temperature dependence as trivalent In. Thus electrostatic effects do not play any obviously dominant role in the observed systematics.

Tracer	T (K)	D (cm²/s)
^{65}Zn	323.7	1.68
	369.1	2.47
	397.3	2.72
	417.4	3.07
	470.5	4.18
	473.2	3.93
	520.2	4.58
	595	5.43
	645	5.71
^{115}Cd	300.5	1.21
	314.2	1.32
	325.5	1.42
	364.0	1.98
	400.2	2.97
	413.2	2.95
	443.5	3.28
	462.3	3.12
	505.4	4.11
	522.5	4.45
	570	4.83
	600	4.90
	634	6.17
	681	5.83
	725	7.03

Table 1. Experimental results, diffusion of zinc and cadmium in liquid gallium metal.

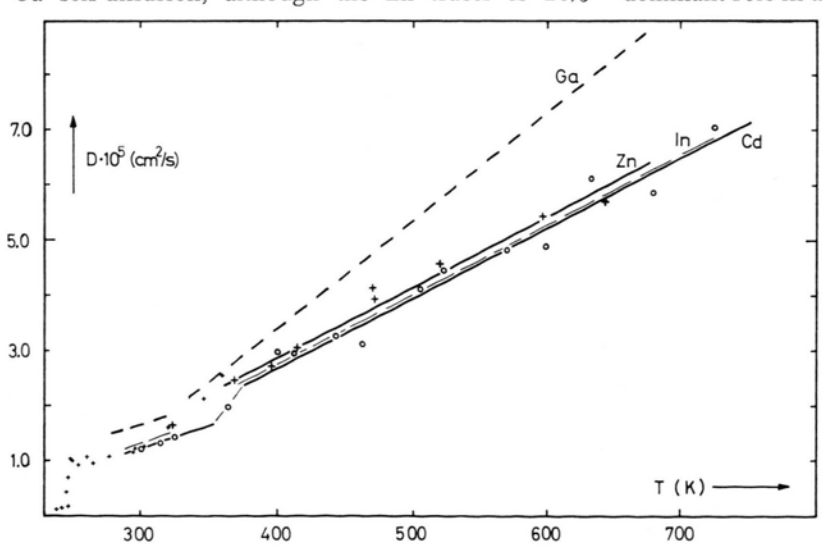

Fig. 1. Linear plot of D vs T for the diffusion coefficients of impurities in liquid Ga. Crosses: ^{65}Zn. Small crosses ^{65}Zn from Ref. 5. Rings: ^{115}Cd. Line with short dashes: ^{72}Ga. Long dashes: ^{114}In.

Reprint requests to Dr. S. J. Larsson, Department of Physics, Chalmers University of Technology, *S-40220 Gothenburg*, Sweden.

Table 2. Parameters of Arrhenius representation $\ln D/D_0 = -Q/RT$ and of linear representation $D = A(T-B)$ for tracer diffusion in Ga.

Tracer	Range (K)	$D_0 \cdot 10^4$ (cm²/s)	Q (kcal/mol)	$A \cdot 10^7$ (cm²/s·deg)	B (K)
^{65}Zn	320−660	2.1	1.60 ± 0.04	1.29 ± 0.08	176 ± 11
^{115}Cd	300−740	2.3	1.77 ± 0.03	1.33 ± 0.06	206 ± 9
^{72}Ga	280−680	3.45	1.85 ± 0.05	2.00 ± 0.04	228 ± 4
^{114}In	290−740	2.0	1.59 ± 0.04	1.24 ± 0.03	176 ± 4

Developing simple model arguments [6, 3] for homovalent diffusion in Ga and In, one has suggested that (at least at temperatures well above the m.p.) the tracer atoms partake in nearly uncorrelated diffusion of single atoms, obeying the inverse root mass law. Thus the ratio of the diffusion coefficients of the impurity (index i) and the solvent (index s) at a given temperature could be expressed as

$$D_i/D_s \approx (M_s/M_i)^{\frac{1}{2}} \quad (1)$$

and the effective masses M were found to be not very different from the respective atom masses m_i and m_s. (A possible exception was implied at the lowest temperatures for the Ga matrix.) Table 3 shows the M_i/M_s values obtained by using Eq. 1 for the present investigation and the earlier results for Ga. It is seen that while ^{115}Cd diffuses practically identically with ^{114}In, i.e. $M_i/M_s = m_i/m_s$ in the middle of the temperature range, the Zn tracer behaves as a much heavier particle, of an approximate mass 110 instead of 65. One explanation may be that the Zn tracer atoms form diatom clusters throughout the studied temperature range, a behaviour also implied for other tracers at lower temperatures.

Table 3. Relations between impurity diffusion and self-diffusion in Ga. m denotes the atom mass of the tracer, M the "effective" mass of the diffusing species, composed of the tracer atom and $p-1$ matrix atoms. Correlation neglected. Values in parentheses: assumption of diatomic Ga-pairs at low temperatures.

Tracer	m_i/m_s	T (°C)	$(D_i/D_s)_{exp}$	$(M_i/M_s)_{calc}$	p_{calc}
^{65}Zn	0.93	650	0.73	1.88	1.95
		450	0.80	1.57	1.64
		300	0.8	1.57 (1.9)	1.64 (3.21)
^{115}Cd	1.65	650	0.71	1.99	1.34
		450	0.76	1.73	1.08
		300	0.76	1.73 (3.3)	1.08 (2.81)
^{114}In	1.64	650	0.72	1.93	1.29
		450	0.78	1.65	1.01
		300	0.82	1.49 (3.0)	0.85 (2.34)

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