Tracer Impurity Diffusion in Liquid Metals: Au in Ga

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The diffusion coefficient of ^{198}Au in liquid Ga has been measured between 35 and 460 °C. The results can be represented by a linear plot of D vs T or by an Arrhenius plot. The latter yields the parameters $D_0 = 4.9 \cdot 10^{-4}\ \text{cm}^2/\text{s}$ and $Q = 2.65$ kcal/mol. However, some distinct departures from the straight line characteristics, showing a considerably higher "activation energy" at the low temperatures, suggest the possibility that clusters composed of two or several atoms may partake in diffusion.

We have studied the diffusion of ^{198}Au in liquid gallium metal, using a long-capillary method first developed for Ga self-diffusion [1] and since applied to several other diffusion studies. Other impurities in Ga whose diffusion has been investigated are In [2], Zn [3] and Cd [3]. The technique employs the liquid counterpart of the thin film geometry common in solid state diffusion measurements. A small solidified droplet of metal, in which the radioactive tracer had been dissolved, is deposited at the closed end of a 10 – 15 cm long capillary, which is then filled with the inactive matrix metal. The subsequent diffusion anneal gives rise to a penetration profile which is linear if the logarithm of the activity is plotted versus the square of the distance from the closed end. In the present case the active droplet consists of Ga containing about 1% of neutron irradiated Au metal.

T (K)	$D \cdot 10^5$ (cm^2/s)
311.1	0.58
312.5	0.74
323.5	0.81
334.5	0.95
349.0	1.20
349.2	0.96
349.7	1.00
370.5	1.28
398.0	1.67
398.2	1.75
431.5	2.45
460.2	2.89
460.2	3.16
461.5	2.78
479.0	3.56
503.2	4.04
544.5	4.15
570	4.86
605	5.49
644	6.32
688	6.80
727	6.78
729	7.23

Table 1. Experimental results.

The experimental results are given in Table 1. The Arrhenius plot in Fig. 1, $D = D_0 \exp\{-Q/RT\}$, and the linear plot in Fig. 2, $D = A(T - B)$, lead to the parameters listed in Table 2. As shown in the table, these parameters exhibit a certain temperature dependence, the observed variations being greater than can be accounted for by experimental inaccuracy only.

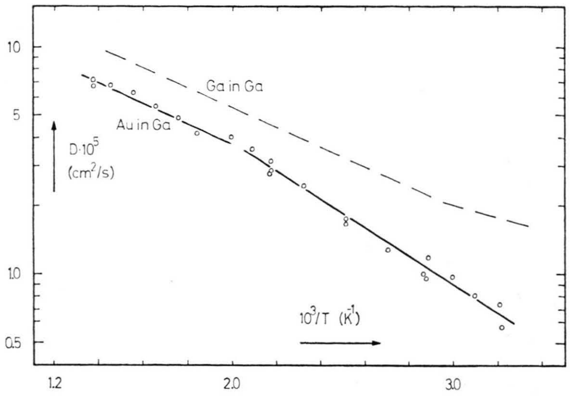

Fig. 1. Arrhenius plot of the diffusion coefficient of ^{198}Au in liquid Ga.

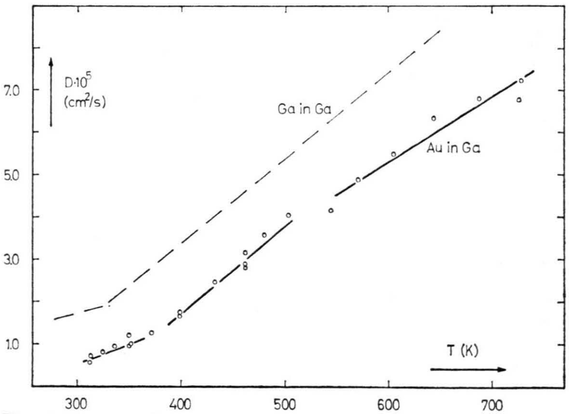

Fig. 2. Linear plot of the diffusion coefficient of ^{198}Au in Ga vs temperature.

Table 2 also lists the observed ratios of Au tracer diffusion to Ga self-diffusion at different temperatures. These ratios are seen to range from low values at the low end of the temperature range to considerably higher and fairly constant values above some 500 K.

According to a model [4] which postulates that all non-vibrational thermal energy in a simple liquid goes to duffusion, neglecting the effects of correlation and of force interaction between the tracer and

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Table 2. Diffusion parameters for ^{198}Au in liquid Ga.

Temp. range (K)	$10^4 \times D_0$ (cm^2/s)	Q (kcal/mol)	$10^7 \times A$ (cm^2/s, deg)	B (K)	D_i/D_s
311–729	4.9	2.65 ± 0.06	1.63 ± 0.04	279 ± 5	0.38 to 0.7
311–500		2.9	0.9 to 1.9		0.38 to 0.7
500–729		2.1	1.5		0.7

free volume, one gets [2]

$$D_i/D_s \cong (M_s/M_i)^{1/2}$$

where the indices pertain to impurity diffusion and to self-diffusion, and where the M-s are to be considered as effective masses of the diffusing species. Evidence from earlier [2, 3] diffusion data in Ga seems to imply that the tracers diffuse mainly as single atoms, except perhaps at temperatures around and below the Ga melting point. If such is the case also for Au in Ga, then one should have $D_{Au}/D_{Ga} = (72/198)^{1/2} \approx 0.6$. As seen in Table 2, a very striking deviation from this value is obtained at the lowest temperatures. These "extra low" diffusion coefficients are here much more conspicuous than the similar tendencies seen [2, 3] for other tracers in Ga. At temperatures below 350 K, the low D-values of Au in Ga imply an effective diffusing mass of at least 3 Au atoms.

Now, Au is distinctly electronegative in Ga, and likely to form stoichiometric clusters with matrix atoms. In the phase diagram [5] of solid Ga-Au, the Au_3Ga compound exists up to about 500 K (while AuGa and $AuGa_2$ appear stable up to still higher temperatures). The mass of Au_3Ga, about 660, could possibly explain the lowest values of D for Au in Ga. At higher temperatures the D_i/D_s ratio rises steeply to values more consistent with the picture of single atom diffusion. If indeed the slow-moving cluster dominates the solubility of Au in Ga at low temperatures, and the single Au atom is dominant in diffusion, then the binding energy of the cluster should figure in the effective "activation energy" of diffusion up to the temperature where the clusters have broken up. A certain support of this may be derived from Fig. 1; the Arrhenius plot shows a distinct "knee" at about 500 K. The difference in slope between the two portions implies a cluster binding energy of the order of 0.8 kcal/mol. In the linear D vs T plot, Fig. 2, the three portions of different slopes would accordingly correspond to the nearly exclusive cluster region, the breaking-up region, and the single atom region.

The cluster hypothesis is seen to present one possible explanation of the exceptional diffusion behaviour of the Au tracer in Ga at the low temperatures. The hypothesis can hardly, however, be taken as proved by the present results. The study of the diffusion of other definitely electronegative solutes in Ga (under preparation) may contribute to further illumination of this problem.

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