e.g., 400 °C, varies over a considerable range,[35] so that with $B_2 = 0.25$ eV, e.g., one obtains $\Delta V_f^1 = 0.80\ V_0$ from the Detert and Ständer data. The value of ΔV_f^1 cited by Tuler corresponds to $B_2 = 0.35$ eV.

The striking feature of the data summarized in Table II is, of course, the spread in the values of the activation volume ΔV_a, ranging roughly $0.6-1.25 V_0$. By contrast, the activation volumes of other fcc metals are consistently less than one atomic volume. Thus, in gold,[36] $\Delta V_a = 0.71\ V_0$; in silver,[37] $\Delta V_a = 0.89\ V_0$; and in lead, $\Delta V_a = 0.71\ V_0$ in one case,[38] and $\Delta V_a = 0.64\ V_0$ in a second case.[39] All of these measurements were made using the radioative-tracer technique.

In the case of aluminum, Butcher, Hutto, and Ruoff first suggested the possibility that the large activation volume which they observed might be due to the dominance of divacancies over monovacancies at high temperatures.[10] The thermoelectric power and resistivity measurements of Bourassa *et al.*[15] were interpreted in terms of a three-defect model comprising the monovacancy, the divacancy, and the vacancy-interstitial bound pair. As indicated in Table II, the formation volume of the divacancy is roughly twice as great as that for the single vacancy. When these values are combined with the motional volumes obtained by Buescher and Emrick,[14] total activation volumes are obtained: $\Delta V_a^1 \leq 0.78\ V_0$ for the single vacancy and $\Delta V_a^2 = (1.13-1.62) V_0$ for the divacancy. These findings have been discussed in detail in the paper by Buescher and Emrick.[14]

The question remains as to why some measurements of ΔV_a yield values consistent with expectations for monovacancy diffusion while others are consistent with divacancy diffusion. Thus, for example, the radioactive-tracer measurements of Beyeler and Adda[11] yield, in the case of aluminum, $\Delta V_a = 1.29\ V_0$, whereas for gold these authors obtained $\Delta V_a = 0.72\ V_0$. Similarly, whereas divacancy effects may be expected to dominate at high temperatures, the creep measurements of Butcher *et al.*[10] were made at relatively low temperatures,

TABLE II. Summary of activation volume results for self-diffusion in aluminum. Superscripts 1 and 2 refer to vacancies and divacancies, respectively.

Method	Ref.	Temp. range (°C)	Specimen purity (%)	Quantity measured	$\Delta V/V_0$
Steady-state creep	9	260–280	99.999	ΔV_a	0.79
Steady-state creep	10	270–290	99.999 [a] 99.9999 [b]	ΔV_a	1.36
Tracer diffusion	11	440–610	not specified	ΔV_a	1.29
Dislocation annealing	12	up to 280	"zone refined"	ΔV_a	0.44–0.87
NMR	this work	390–450	99.99	ΔV_a	0.70
Length change with quenching	16, 17	400	99.99	ΔV_f^1	1.23
Quenched-in resistivity	13	420	99.999	ΔV_f^1	0.62
Thermoelectric power	15	25–600	99.9999	ΔV_f^1	0.54
Thermoelectric power	15	25–600	99.9999	ΔV_f^2	0.96
Resistivity	15	300–400	99.9999	ΔV_f^1	0.60
Resistivity	15	300–400	99.9999	ΔV_f^2	1.45
Annealing of excess quenched resistivity	14	330	99.999	ΔV_m^1	0.18 [c]
Annealing of excess quenched resistivity	14	580	99.999	ΔV_m^2	0.17

[a] Polycrystal wire.
[b] Single-crystal rod.
[c] This value contains some contribution from divacancies.

lower in fact, than the NMR experiments reported here. The dislocation annealing experiments of Norris[12] were also made at relatively low temperatures, but in this case a ΔV_a consistent with monovacancy diffusion was found.

There does appear to be a tenuous correlation between sample purity and ΔV_a value, however. Less pure aluminum appears to correlate with the monovacancy value for ΔV_a. This correlation is not very strong, but the present measurements, as well as those of Norris,[12] were made with aluminum of less than 99.999% purity. In addition, the measurements by Butcher,[9] which yielded $\Delta V_a = 0.79\ V_0$, were very likely made with somewhat less pure aluminum than were the later measurements by Butcher, Hutto, and Ruoff.[10] Finally, the value of ΔV_f inferred from the length-change measurements of Detert and Ständer,[16] as discussed above, ranges down to the monovacancy value depending upon the choice of the divacancy binding energy B_2. These observations suggest that, for reasons which we do not propose to speculate on, the imperfections present in less pure aluminum inhibit the formation of divacancies.

In conclusion, the series of pulsed NMR measurements reported here have obtained a value of the activation volume for self-diffusion in aluminum of $\Delta V_a = (0.71 \pm 0.13) V_0$. This result is consistent with expectations based on monovacancy diffusion in aluminum.

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