Trapping of Positive Muons at Vacancies in Quenched Aluminum

J. A. Brown, R. H. Heffner, M. Leon, and M. E. Schillaci
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545

and

D. W. Cooke
Memphis State University, Memphis, Tennessee 38152

and

W. B. Gauster[(a)]
Sandia Laboratories, Albuquerque, New Mexico 87185
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Evidence is presented for the trapping of positive muons at monovacancies and divacancies in quenched aluminum. The annealing of vacancies as sensed by the muon-spin-rotation effect is compared to positron annihilation measurements on identically prepared samples, showing that whereas positrons are trapped primarily at small vacancy clusters, muons are trapped mainly at monovacancies and diavacancies. Furthermore, the data indicate that it may be possible to study monovacancies and divacancies separately with the muon-spin-rotation technique.

The possibility of trapping of positive muons at vacancies has been proposed on theoretical grounds[1] and has been suggested as a technique to study defects in metals.[2] In this paper we report experimental results on the trapping of positive muons at single vacancies and divacancies in quenched aluminum. Using the technique of muon spin rotation,[3] we compare the μ^+ depolarization data with positron-annihilation (PA) line-shape measurements on identically prepared samples.

In contrast to positrons, trapping of muons at defects in thermal equilibrium at high temperatures has not been observed.[4] The effects of vacancies on muon behavior in nonstoichiometric aluminum compounds have been reported.[5] However, measurements[6] on proton-irradiated Al showed no effects, in contrast to neutron-irradiated Al where depolarization due to defects was seen.[7,8] Unfortunately, the interpretation of vacancy trappings in Refs. 7 and 8 was obscured by the presence of interstitial agglomerates and other defect complexes resulting from the neutron bombardment. Trapping at defects was also observed in deformed Al,[9] but the nature of the "open volume defects" responsible could not be specified. In order to clarify the influence of actual vacancies on the behavior of muons in Al, we have studied quenched samples which contain only vacancies and vacancy clusters but not the interstitial defects that are introduced by irradiation with energetic particles or the large concentrations of dislocations introduced by deformation.

The samples were polycrystalline Marz-grade Al from Materials Research Corporation, specified by the vendor to be 99.9995% pure. Plates 0.1 cm$\times$1.3 cm$\times$5 cm were machined, lightly etched, and annealed in vacuum at ~ 800 K for several hours. The quenching procedure was the same as that described by Wampler and Gauster,[10] except that our sample was quenched from 873 K.

The μ^+-spin-rotation measurements were done at the stopped-muon channel of the Clinton P. Anderson Meson Physics Facility (LAMPF), using the standard transverse-field technique[3] in an applied field of 89 Oe. The sample temperature was controlled in the range of 5 to 300 K. The muon depolarization rate was obtained by fitting the asymmetry in the time-differential μ^+-spin-rotation spectra[3] with both Gaussian and exponential decay functions.

For the PA measurements, two specimens were prepared in a manner identical to that for the μ^+-spin-rotation experiments. The measurement apparatus is described in detail in Ref. 10. Each PA datum point[11] in the inset in Fig. 1 represents the result of a run done at 85 K following annealing for 30 min at the temperature indicated on the abscissa. Both heating and cooling rates for the annealing steps were ~ 100 K min^{-1}, except that cooling from the highest temperatures was done more slowly to prevent any retention of vacancies in thermal equilibrium.

Figure 1 shows the exponential depolarization rate as a function of temperature, with the points numbered in the chronological sequence of measurement. (Point 1, taken at 5 K, is omitted.) Also shown are the data measured earlier[4] for an

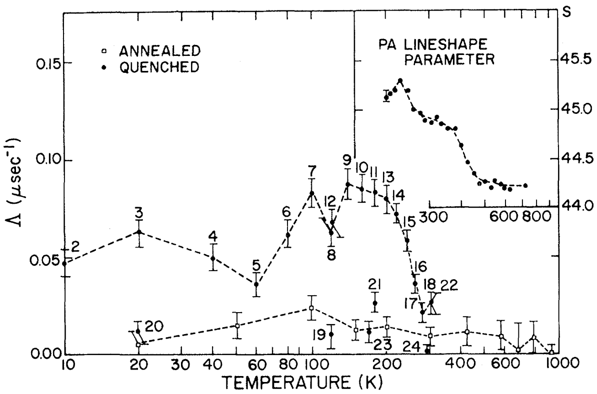

FIG. 1. Temperature dependence of exponential μ^+ depolarization rate for annealed and quenched Al samples, together with positron-annihilation Doppler-broadening line-shape parameter (Ref. 11) as a function of isochronal annealing temperature for quenched Al.

annealed Al sample of the same purity. The value of the muon depolarization rate in quenched aluminum is larger than for fully annealed Al at all temperatures measured, indicating that the observed muon depolarization is due to quenched-in defects. Point 12 shows that the structure below 200 K is reversible, indicating that the defects responsible for this structure are immobile (as would be expected since the quench bath was at 200 K). The abrupt decrease of the depolarization rate observed between 200 and 300 K corresponds to the temperature range in which vacancies are known to become mobile and to anneal at sinks.[10] After the measurement at 300 K, the depolarization rate dropped to the fully annealed value for measurements below 120 K (points 19 and 20), but was still somewhat larger for measurements above 120 K (points 21 and 22). Finally, after a 17-min heat treatment at 500 K, where even vacancy clusters and dislocation loops are known to anneal,[10] the depolarization rate dropped to the fully annealed value for measurements above 200 K (points 23 and 24).

We believe that the depolarization rate observed from approximately 100 to 200 K is due to trapping at monovacancies and divacancies. This conclusion is supported by the maximum value of the Gaussian depolarization rate (σ) of 0.135 ± 0.010 μsec^{-1} which agrees closely with the predicted value for a muon at a substitutional site in an unrelaxed vacancy.[12] The calculated value of σ for a muon in a substitutional site of a divacancy is only a few percent smaller than for a monovacancy so that the measured depolarization rate alone cannot distinguish between occupancy of these two kinds of sites.

Comparison of the μ^+-spin-rotation data with resistivity and PA measurements in the temperature region 100–300 K further supports the conclusion that muons are trapped principally at single vacancies and/or divacancies. The response of the depolarization rate to the annealing of vacancies follows rather closely the decrease of residual electrical resistivity,[10] which indicates a decrease in the total defect concentration. In contrast, the PA data of Fig. 1 show an initial rise in the line-shape parameter[11] S upon annealing above 200 K; only a small drop below the initial value of S has occurred by 300 K. This initial rise in S is due to the trapping of positrons at small clusters of vacancies that form after vacancies become mobile,[10] which is evidence that the fraction of vacancy clusters increases above 200 K. This increase in the number of clusters is accompanied by a decrease in the single-vacancy and divacancy concentration, which in turn produces a decrease in the muon depolarization rate. Thus, while positrons respond most strongly to vacancy clusters, muons respond mostly to single vacancies and divacancies.

Further evidence for this difference of behavior between positrons and muons is seen in the PA measurements above 300 K. The observed effect on the PA line shape for annealing temperatures between 300 and 400 K is due to the trapping of positrons at dislocation loops formed by the growth and agglomeration of the initial vacancy clusters.[10] The positron effect remains large until the dislocation loops anneal out between 400 and 500 K. In contrast to the PA line shape, the μ^+ depolarization rate responds only weakly to the presence of dislocation loops, since at 300 K nearly complete annealing of the μ^+-spin-rotation effect is observed.[13]

In order to demonstrate quantitatively that the interpretation of vacancy trapping is consistent with our experimental results, we have used the diffusion and trapping model of Petzinger, Munjal, and Zaremba[14] to model our data. To explain the structure for $T < 200$ K, we assume three traps, corresponding to the two maxima observed at about 20 and 100 K and to the broad plateau beginning at about 140 K. Only data for $T \leq 200$ K are used since the model is not appropriate for mobile trapping sites. The results of such a model calculation are shown in Fig. 2 along with (Gaussian) data. The fit obtained (Table I), although not unique, demonstrates that a simple

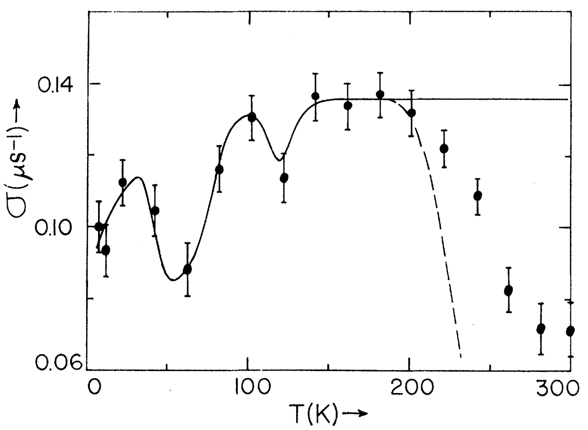

FIG. 2. Temperature dependence of the Gaussian depolarization rate together with the results of the fit to the trapping model described in the text (see Table I). The solid line is for H_3 = 900 meV, the dotted line for H_3 = 350 meV.

TABLE I. Parameters for modeling the temperature dependence of the Gaussian depolarization with the trapping model described in the text. The concentration is C_i, the depolarization rate σ_i, and the binding energy H_i for each trap. The muon hopping rate is parametrized as $\rho_0 = a\exp(-H_0/kT) + d + eT$, where H_0 is the activation energy for diffusion in the high-temperature Arrhenius region. The rate for detrapping is taken as $\rho_i = \rho_0\exp(-H_i/kT)$. The parameters are not uniquely determined by the data (there are too few data points to do so), and no meaningful experimental errors can be assigned to them.

Trap	σ_i (μsec^{-1})	C_i (ppm atomic)	H_i (meV)
1	0.15	1200	28
2	0.13	300	135
3	0.13	200	900

model (random hopping with a rate increasing monotonically with temperature) with a physically realistic set of parameters can be utilized to explain the data in a manner consistent with our interpretation.

We estimate from the measurements of von Guérard, Peisl, and Zitzmann[15] that the concentration of monovacancies and divacancies in our samples after the quench was about 400 ppm with nearly equal concentrations of each. Thus, the parameters shown in Table I agree quite well with the values of the concentrations and depolarization rates expected if we attribute the two higher-temperature traps to monovacancies and divacancies. The fact that the concentrations resulting from the model agree closely with the expected values indicates that the effective trapping radius for these two traps is of the order of one lattice spacing, a reasonable value for small, open, volume defects.

Since one expects the muon to bind more strongly to a divacancy than to a single vacancy, it is reasonable to associate the lower peak at ~ 100 K to monovacancy trapping and the higher peak at ~ 140 K to divacancy trapping. Further studies will be required to confirm this distinction, however. The structure in the depolarization rate at 120 K was not found in previous measurements on neutron-irradiated aluminum,[8] possibly having been obscured by the strong lower-temperature trapping at interstitial clusters.

The onset of annealing of the vacancies for $T > 200$ K prevents a reliable determination of the binding energy of the muon to the third trap. The dotted line in Fig. 2, however, is the result for H_3 = 0.35 eV; this clearly falls off at too low a temperature, and we conclude that the binding enthalpy to this trap is $\geqslant$ 0.4 eV.

The nature of the structure in the data below 40 K is not completely understood; however, its disappearance following annealing (point 20) indicates that it is associated with the quenched-in defects. The fact that the trapping model shows an unphysically large concentration for this trap indicates to us an extended trap which may be due to strains in the polycrystal produced by the defects. A binding enthalpy of a few tens of meV would not be inconsistent with this view.

A recent theoretical work[16] indicates that single protons in Al tend to occupy a vacancy at the center, while other calculations[17] suggest that interstitial sites adjacent to a vacancy are energetically preferred to the vacancy itself. Hydrogen channeling experiments[18] on Al indicate that protons occupy tetrahedral sites apparently associated with vacancies produced during proton implantation. For muons in Al, the σ for such a tetrahedral site is $0.228\sqrt{\frac{5}{3}}$ μsec^{-1} (and is about the same for the octahedral-vacancy site). This is much larger than the observed values; thus the muons appear to be localized at or very near the center of substitutional sites at 100–200 K.

In summary, we present the first experimental evidence for the trapping of muons at quenched-in defects in a metal. In a carefully controlled study with PA and μ^+-spin-rotation measurements on identically prepared samples, we show that in contrast to positrons, muons are trapped predominantly at monovacancies and divacancies in quenched aluminum. Furthermore, the data indicate that one may be able to study monovacancies and divacancies separately, a possibility unique to μ spin rotation.

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[(a)] Present address: Sandia Laboratories, Livermore, Cal. 94550.

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[11]The line-shape parameter S (see Ref. 10) expresses the ratio of low- to high-electron-momentum annihilations, and therefore, the relative amount of overlap between the positron density and the core electrons. Positrons trapped at vacancies have less overlap with core electrons and hence larger S. The value of S characteristically increases with increasing defect concentration until a saturation value is reached; this value is expected to be larger for small clusters of vacancies ($\lesssim 5$ Å) than for single vacancies.

[12]While the Van Vleck lattice sum [J. H. Van Vleck, Phys. Rev. 74, 1168 (1948)] for substitutional site occupancy is 0.109 μsec^{-1} for a polycrystalline average, in low applied fields (as in our experiment), the calculated polycrystal value is increased by a factor of $\frac{5}{3}$ to 0.14 μsec^{-1} by the coupling of the electrostatic field of the muon to the quadrupole moment of the nuclei [O. Hartmann, Phys. Rev. Lett. 39, 832 (1977)].

[13]The lack of sensitivity of the μ^+ to large vacancy clusters may result from several effects: As the clusters agglomerate, the effective concentration of these centers decreases, requiring a higher μ^+ diffusion rate to find these traps. Also, the μ^+ centered in a large vacancy cluster may feel only a small static dipolar field, which depends on the inverse third power of the distance from the μ^+ site to the host nuclei. Finally, it may be that the muon binding energy to a large cluster is too low to produce trapping at temperatures at which the vacancies begin to agglomerate.

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