Muon Depolarization by Paramagnetic Impurities in Nonmagnetic Metals

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The range of metals and temperatures for which positive muon diffusion is measurable can be expanded greatly by doping nonmagnetic metals with paramagnetic ions. In these systems, the diffusivity determines the time needed for the μ^+ to reach the sites of strong depolarization near the paramagnetic ions and hence the depolarization rate of the muon spin rotation signal. For *Au* Gd and *Au* Er we have measured diffusion-induced depolarization for temperatures between 85 and 230 K, and have determined that there is an important short-range component in the muon-ion interaction.

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The problem of light interstitial particle diffusion in solids is of considerable interest, both fundamental and practical. The diffusion of hydrogen isotopes in metals has been studied extensively[1]; in recent years, measurements of positive muon diffusion in metals using muon spin rotation have also been reported.[2] The muon spin rotation experiments have stimulated theoretical interest because the smaller mass of the μ^+ and the generally lower temperatures probed offer the possibility that a wider variety of diffusion mechanisms can be examined.

Information on μ^+ diffusion can be derived from the temperature dependence of the muon depolarization rate, $\Lambda(T)$, in a transverse magnetic field. The technique is described in detail in recent review articles[2]; in brief, the μ^+ precession produces oscillations in the time-differential histogram of decay positrons detected in a fixed spatial direction, and any depolarization dampens these oscillations. In nonmagnetic metals, depolarization is produced by the inhomogeneous magnetic fields of the host nuclear dipole moments. As the muon hops more rapidly with increasing temperature, the field inhomogeneities are averaged, producing the familiar phenomenon of "motional narrowing" of the linewidth, i.e., reduction of $\Lambda(T)$. There are two limitations inherent in this technique, however: (1) muon motion cannot be determined once $\Lambda(T)$ becomes too small, as typically happens at higher temperatures where the muon is moving rapidly; and (2) many metals have negligible nuclear moments, so that muon diffusion cannot be determined from depolarization rates at all.

In this Letter, we report on a new method which overcomes these limitations by doping the metal with small amounts of paramagnetic impurities and measuring the muon depolarization rate produced by interaction with the electronic dipole moments of the impurity ions. This depolarization mechanism is effective only if a muon can move to the vicinity of an impurity within its lifetime, thus providing a rather direct measure of the μ^+ hopping time, τ_h. Because the ionic dipole moment is much larger than the nuclear moment, the doping technique allows the measurement of faster diffusion rates. In addition, these measurements are sensitive to the impurity ion spin-lattice relaxation time, τ_s, and the nature and strength of the impurity-muon interaction.

The measurements were made on polycrystalline Au samples doped with an S-state ion, Gd^{3+}, and a crystal-field–split ion, Er^{3+}. The samples were prepared by repeated arc melting and were annealed at 800 °C for one hour in an inert atmos-

phere. Residual resistivity measurements were consistent with the nominal impurity concentrations, indicating the formation of solid solutions. The experiments were carried out at the Clinton P. Anderson Meson Physics Facility (LAMPF) with use of the standard transverse-field time-differential muon spin rotation method.[2]

Figure 1 shows data taken in Au samples doped with 350 at. ppm Gd. We find that, for several different temperatures $T \lesssim 10$ K and fields $H \lesssim 5$ kOe, $\Lambda(H,T)$ depends on H and T only as the ratio H/T, and the signal is *exponentially damped with time*. This is precisely the behavior predicted[3] for a motionless muon whose line shape is inhomogeneously broadened by a spatially random distribution of slightly polarized magnetic ions. The magnitude of Λ for such a case can be calculated[3] assuming a dipolar interaction and $\tau_s \ll 2\pi/\omega_\mu$, where $\omega_\mu = \gamma_\mu H$ is the muon Larmor precession frequency ($\gamma_\mu = 8.51\times 10^4$/s Oe). One obtains $\Lambda = 1.08\times 10^{-4} H/T$ μs^{-1}, which is also plotted in Fig. 1. From the excellent agreement, we conclude that the muons are relatively immobile in Au at low temperatures and that the long-range part of the muon-ion interaction is dipolar.[4]

Figure 2 shows data up to room temperature in *Au*Gd and *Au*Er with a transverse applied field of 80 Oe. For *Au*Gd, data for a 1230-at.-ppm sample have been plotted with data for a 350-at.-ppm sample, after scaling by the measured concentration ratio. One sees that $\Lambda(T)$ exhibits a linear concentration dependence for $T < 240$ K. Not shown in Fig. 2 are measurements made with a rare-earth concentration of 120 at. ppm, which are also consistent with a linear concentration dependence ($\pm 5\%$) of $\Lambda(T)$ for $T < 240$ K. The structure near room temperature does not have a linear concentration dependence (perhaps indicating impurity clusters) and will not be considered further.[5] In a separate experiment, $\Lambda(T)$ was found to be negligible in the pure host (also polycrystalline); therefore, all of the observed structure is due to interactions with the magnetic ions. The curves are fits to the data as discussed below.

It is instructive to discuss qualitatively the features of the data in Fig. 2 as they relate to the physics. A similar situation exists in NMR studies of superionic conductors doped with paramagnetic impurities.[6,7] For a muon-impurity interaction which is effective only at near-neighbor interstitial sites, the depolarization rate in the temperature region where $\Lambda(T)$ first begins to rise is determined by the time necessary for a muon to diffuse to the vicinity of an impurity: $\Lambda = \kappa\tau_h^{-1}$, where κ is the probability that a muon site is near an impurity. If the interaction is a longer-range dipolar one, $\Lambda \propto \tau_h^{-3/4}$.[7] These expressions hold if the dwell time of the muon at a site (essentially τ_h) is greater than the depolarization time for a muon at rest near an impurity, and $\kappa \ll 1$. Thus, in this region, $\Lambda(T)$ is *independent* of the nature and strength of the interaction, provided that it is reasonably short range. At temperatures well above the peak in $\Lambda(T)$, where the dwell time is shorter, complete depolarization is not possible in a single encounter, and the increased rate of encountering impurities is offset by the decreased depolarization per encount-

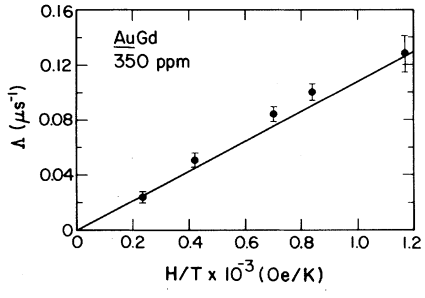

FIG. 1. Muon depolarization rate in *Au*Gd (350 at. ppm.) at several low temperatures ($\lesssim 10$ K) and high fields ($\lesssim 5$ kOe). The straight line represents $\Lambda = 1.08 \times 10^{-4} H/T$ μs^{-1} (see Ref. 3).

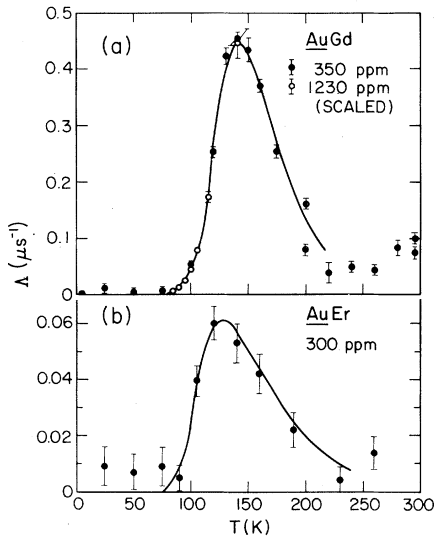

FIG. 2. Temperature dependence of muon depolarization rate in (a) *Au*Gd and (b) *Au*Er at 80 Oe applied field. The rate for the 1230-at.-ppm sample has been scaled by the concentration ratio to demonstrate linearity. Curves are model fits to data as discussed in text.

er. Here $\Lambda = \kappa G \tau_c$, where G is proportional to the square of the interaction strength and τ_c is the correlation time of the interaction. One may take $\tau_c^{-1} = \tau_h^{-1} + \tau_s^{-1}$, so that $\Lambda(T)$ falls off with temperature like τ_h if $\tau_h \ll \tau_s$, or like τ_s if $\tau_s \ll \tau_h$.

Previous models[7] used to describe spin relaxation in the presence of hopping motion and ion relaxation were addressed to the superionic conductor problem. We introduce a model[8] with two improvements over these earlier ones: (1) both long-range (dipolar) and short-range (contact) interactions are treated simultaneously; and (2) the location of and transitions between the important muon sites close to an impurity are more realistically represented. We assume that the muon hops only between adjacent interstitial sites and divide all such sites into shells surrounding an impurity out to a radius corresponding to the mean volume per impurity. Initially, the polarization is uniformly distributed among all interstitial sites. Since the muon hops only between adjacent sites, the transition probabilities per hop time between shells can be determined. Polarization is exchanged among shells according to these probabilities and lost according to whatever depolarization mechanisms are appropriate for each shell (the depolarization for each shell is assumed to be exponential). The point dipolar interaction is effective for all shells. We also include a short-range interaction of strength $A = \gamma_\mu H_x / J$, where J is the ion spin and the contact field H_x is a free parameter. This contact interaction is assumed effective at the innermost shell only. As in the case for hydrogen diffusion at these temperatures, the classical hopping rate is assumed to be given by $\tau_h^{-1} = \nu_0 \exp(-\epsilon/T)$, where ν_0 and ϵ are free parameters. The ion spin-lattice relaxation rate is assumed to have the Korringa form[9] $\tau_s^{-1} = b_s \gamma_s T$, where b_s is a free parameter. Solving the set of coupled rate equations describing the change in polarization for each shell, we find that, after an initial transient (< 0.1 μs), the total polarization decreases exponentially with time, in agreement with the measured signal.

We now discuss the resulting fits quantitatively, noting that the four free parameters of the model are b_s, H_x, ν_0, and ϵ. We assume that the muon occupies octahedral sites only, as in the case of Cu (Ref. 10); similar results are obtained for tetrahedral sites. As noted above, the diffusion parameters ν_0 and ϵ are effectively determined in the temperature region where $\Lambda(T)$ first begins to rise; however, $\Lambda(T)$ is not strictly proportional to τ_h^{-1} because of the presence of the dipolar interaction. For *Au*Gd [Fig. 2(a)], the best fit to all of the data is obtained for $b_s = 6 \pm 4$ Oe/K, $H_x = 24 \pm 10$ kOe, $\nu_0 = 10^{13.5 \pm 0.5}$ s^{-1}, and $\epsilon = 1350 \pm 100$ K. The value of b_s is in reasonable agreement with low-temperature EPR measurements,[11] as might be expected since phonon-induced relaxation should be small for an S-state ion.[12] For temperatures well below the peak ($85 \lesssim T \lesssim 115$ K), $\Lambda(T) \propto \exp(-0.8\epsilon/T)$, indicating that the dipolar interaction dominates in this temperature region, as was also found at the very lowest temperatures ($T \lesssim 10$ K) from the high-field measurements. By contrast a large contact field H_x is required to fit the data in the peak region and beyond. We should caution that the parameters b_s and H_x are correlated, and hence not very well determined. The diffusion parameters ν_0 and ϵ are *not* sensitive to this correlation. The errors specified above represent our best estimate of the effects of statistical errors, correlations, and concentration uncertainties.

For *Au*Er [Fig. 2(b)], we used the same values for the parameters ν_0 and ϵ determined for *Au*Gd. Since the overall splitting due to crystal fields is ~ 100 K,[13] we have assumed for simplicity that all magnetic sublevels are populated at the temperatures of interest and have used $J = \frac{15}{2}$ and $g = 1.20$ (the Landé value), which yields $\gamma_s = 10.6 \times 10^6$/s Oe. The best fit to the data is then obtained for $b_s = 33 \pm 11$ Oe/K and $H_x = 7 \pm 7$ kOe. Again, b_s and H_x are strongly correlated; however, the above value of b_s is much larger than the lower limit set by low-temperature EPR measurements,[11] which is not surprising for a crystal-field–split ion. The fit is excellent, showing that the diffusion parameters deduced for the muon are independent of the ionic species.

We emphasize that this method can be used to greatly expand our knowledge of μ^+ diffusion in nonmagnetic metals. Alrady an interesting host dependence is apparent for the diffusion of muons in Cu and Au. From a comparison of the diffusion parameters in Table I, it seems likely that the diffusion mechanisms for muons in Cu and Au are quite different. The smaller preexponential factor and lower activation energy for muons in Cu suggest significant incoherent tunneling[14]; in contrast, the values for protons in Cu[15] and Au,[16] as well as muons in Au, indicate over-the-barrier hopping.

The present technique can also contribute significantly to our understanding of the muon-ion interaction. At very low temperatures, where the

TABLE I. Diffusion parameters for muons and protons in Au and Cu. The hopping rate is assumed to be given by $\tau_h^{-1} = \nu_0 \exp(-\epsilon/T)$.

	ν_0 (s^{-1})	ϵ (K)	T (K)
μ^+ in Au [a]	$10^{13.5\pm0.5}$	1350 ± 100	85 – 230
p in Au [b]	4.0×10^{12}	2840	770 – 1200
μ^+ in Cu [c]	$10^{7.46\pm0.04}$	551 ± 15	80 – 250
p in Cu [d]	$(1.04\pm0.04)\times10^{14}$	4640 ± 30	720 – 1200

[a]This work.
[b]Ref. 16. No errors are given.
[c]Ref. 14.
[d]Ref. 15.

muon is stationary, we have shown the interaction to be dipolar. However, both the dipolar and Ruderman-Kittel-Kasuya-Yosida[4] interactions are too weak to explain the data at higher temperatures, thus indicating the existence of a short-range (contact) interaction. The following considerations are important in reaching this conclusion: (1) Lattice contraction around the impurity ion can increase the dipolar contribution; however, a 35% reduction in the muon's distance of closest approach to the ion would be required to fit the *Au*Gd data with a dipolar interaction alone. This is an unreasonably large distortion. (2) The presence of the muon near the impurity could affect τ_s; however, our fitted value for b_s does not show a large effect for Gd. (3) Trapping of muons near the impurities can be excluded by the linear concentration dependence measured for $\Lambda(T)$ over the range of the peak. In addition, one would not expect significant trapping at these temperatures.[2]

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