Random anisotropy causes wide distributions of relaxation rates in Tb-Mg-Zn quasicrystals and amorphous DyAg

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''Power-exponential'' zero-field (ZF) muon spin relaxation (μSR), where the power varies with temperature, as observed in icosahedral $Tb_8Mg_{42}Zn_{50}$ and in amorphous (*am*-)DyAg, is shown to be consistent with a wide distribution of relaxation rates by construction of a closed-form relaxation function representing such a distribution that fits the μSR data. This relaxation function is obtained by Laplace transform of a ''double-square'' distribution of relaxation rates, an example of a distribution that is asymmetric about its mean so that its width can be larger than that mean, a property that is necessary to fit the more extremely nonexponential cases. Combination with the results of ^{161}Dy Mössbauer effect measurements in DyAg indicates that this behavior is due to random axial crystalline electric-field (CEF) anisotropy. In addition to creating the random distribution of moment pointing directions in the asperomagnetic ordered state of *am*-DyAg, this creates a wide distribution of splittings between the $J_z=J$ ground doublet and the first excited state, thus causing a wide distribution of rare-earth paramagnetic fluctuation rates, leading to the wide distribution of muon spin relaxation rates deduced above. The contrast of simple-exponential ZF-μSR in *i*-$Gd_8Mg_{42}Zn_{50}$ with double-square-distribution relaxation in the Tb quasicrystal clearly indicates that a CEF mechanism, probably the same one, is causing the nonexponential relaxation in the Tb quasicrystal, as well.

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Zero-field (ZF) muon spin relaxation (μSR, for reviews of the technique see Refs. 1 and 2) that has been phenomenologically characterized as ''power exponential''

$$G_z(t)=\exp[-(rt)^p], \tag{1}$$

with temperature-dependent power $p\leqslant 1$, has been observed in a number of dense-moment disordered magnetic systems [e.g., moderately concentrated $Ag_{1-x}Mn_x$,[3–5] $La_{1-x}Ca_xMnO_3$ (Ref. 6)], and has been difficult to interpret, particularly in the paramagnetic state. The authors have reported varying-power-exponential ZF-μSR in amorphous (*am*-)DyAg from 80 K to room temperature (the asperomagnetic ordering is at 18 K, but below 80 K most of the μSR signal relaxes too rapidly to be resolved),[7] and in icosahedral $Tb_8Mg_{42}Zn_{50}$ from near the spin-glass freezing temperature (which is $\sim$8 K) to at least 160 K.[8] Figure 1 shows an example of nonexponential ZF-μSR spectra in these two materials. In all of these materials, the power p is near 1.0 (simple exponential) at the highest measured temperatures, but drops toward 0.5 or even below that as temperature decreases toward whatever ordering or freezing transition the material undergoes. The relaxation rate r increases in this process, and in the materials of Fig. 1, becomes so large that the signal is lost in the apparatus initial dead time as p approaches 0.5, and p can no longer be reliably determined for temperatures below that.

In the paramagnetic state far above all magnetic freezing temperatures of a material, the electronic moments are expected to be rapidly fluctuating, and the muon spin relaxation function is then expected to be in the fast-fluctuation limit, which is usually exponential. Indeed, the paramagnetic ZF relaxation function in *i*-$Gd_8Mg_{42}Zn_{50}$ is exponential, except perhaps for the few degrees above the freezing temperature ($\sim$6 K). For the temperature-dependent-power cases, it has been argued[3,6] that there is an inhomogeneous distribution of (local) exponential relaxation rates. If this is true, then the complete relaxation function is a sum over a wide variety of muon sites where different sites have slightly different exponential relaxation rates. In the continuum limit, this becomes an integral of exponential relaxation $e^{-\lambda t}$ multiplied by a probability distribution of relaxation rates $P(\lambda)$, that is, the Laplace transform of $P(\lambda)$.[3] The power-exponential relaxation form [Eq. (1)] resembles a ''stretched exponential'' sometimes used in the analysis of bulk response of spin glasses, and researchers analyzing moderately concentrated $Ag_{1-x}Mn_x$ (Refs. 3 and 4) tried to relate the power-exponential form of the muon spin relaxation to stretched-exponential moment-autocorrelation functions suggested for spin glasses, or their nonexponential competitors. In the absence of closed-form Laplace transforms of stretched exponentials for ranges of varying power, rather than at individual, isolated values of p, however, it is not clear if the temperature dependence of the shape observed can be represented in this way. The asperomagnetism of *am*-DyAg also shows that this type of behavior is not limited to spin glasses.

Since all of the cases we are discussing return in their high-temperature limits to simple exponential relaxation, for which $P(\lambda)$ is a delta function, it is reasonable to expect the nonexponential relaxation at lower temperatures to result from $P(\lambda)$ that has the form of a peak with a central or average rate λ_0 and width W_λ, so that the delta function is recovered as $W_\lambda\rightarrow 0$. Some simple functional forms for such peaks do have closed-form Laplace transforms, and it is straightforward to see that they can mimic power-

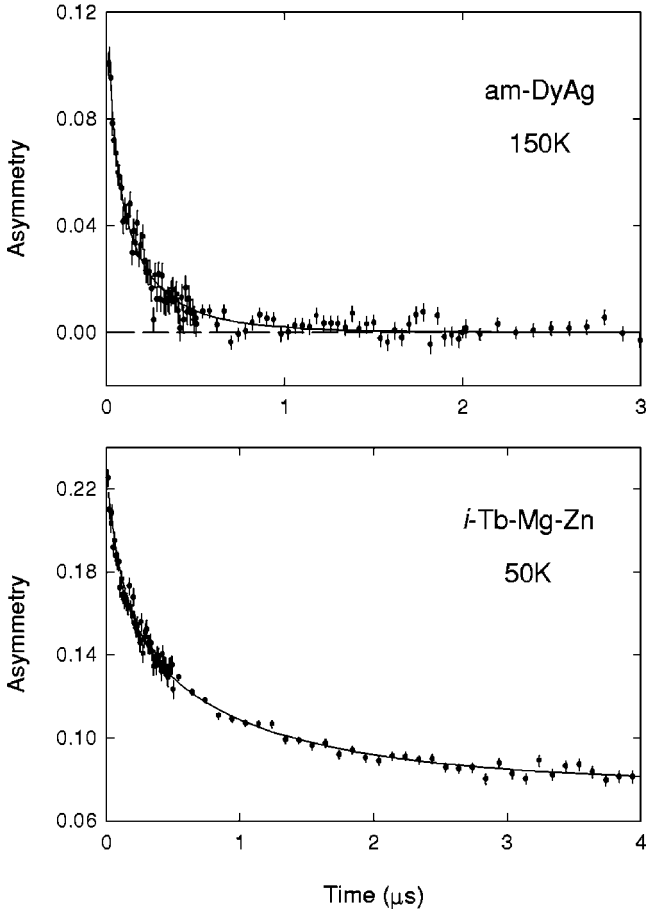

FIG. 1. ZF-μSR asymmetry spectra in the paramagnetic states of amorphous DyAg (top) and icosahedral $Tb_8Mg_{42}Zn_{50}$ at the temperatures indicated, with solid lines showing least-squares fits of the double-square-distribution relaxation function described in the text.

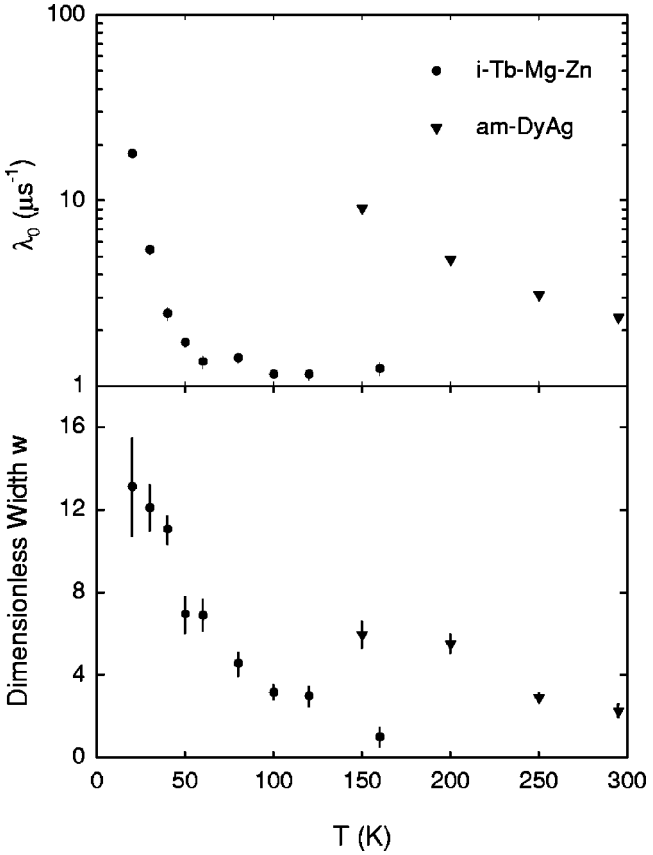

FIG. 2. Temperature dependence of the average relaxation rate λ_0 (top) and dimensionless width w (bottom) of the ''double-square'' relaxation rate distribution, deduced from least-squares fits of $G_{dsq}(t)$ to ZF-μSR in the paramagnetic states of amorphous DyAg (triangles) and icosahedral $Tb_8Mg_{42}Zn_{50}$ (circles).

exponential relaxation for powers from 1.0 down to no lower than ~ 0.7, if the form of $P(\lambda)$ is symmetric about its mean. This limitation arises from the lower bound on the range of the distribution's independent variable λ: only non-negative relaxation rates have any meaning. If the width W_λ is large relative to λ_0, a symmetric distribution would normally have significant probability for negative λ, but that does not represent relaxation at all, and so the line shape would need to be cutoff at zero, at best. Such a sharp cutoff at $\lambda=0$ will (in Laplace transformation) produce $1/t$ (or $1/t$ to a relatively small power) terms in the relaxation function that prevent it from fitting our data for *am*-DyAg or *i*-Tb-Mg-Zn. If symmetric peak shapes are to have low probability at $\lambda=0$, they can only be increased in width by increasing the average as well, so that the dimensionless width $w=W_\lambda/\lambda_0$ will saturate at a finite value even as $W_\lambda \to \infty$. We have found that it is useful to characterize the width of the distribution in terms of the dimensionless quantity w, because only a dimensionless quantity can characterize a relaxation function's shape independent of its relaxation rate.

These arguments suggest that a distribution $P(\lambda)$ that is asymmetric about its mean (and with vanishing amplitude at $\lambda=0$) is necessary to reproduce the entire range of observed ''power-exponential'' muon spin relaxation. We have found that a simple double-square distribution of relaxation rate

$$P_{dsq}(\lambda)=\frac{(w+1)}{(2\lambda_0 w)} \;:\; \frac{\lambda_0}{(w+1)}<\lambda<\lambda_0$$
$$=\frac{1}{(2\lambda_0 w)} \;:\; \lambda_0<\lambda<(w+1)\lambda_0 \qquad (2)$$

[with $P(\lambda)=0$ otherwise] produces by Laplace transform the ZF relaxation function

$$G_{dsq}(t)=\frac{(w+1)e^{-\lambda_0 t/(w+1)}-we^{-\lambda_0 t}-e^{-(w+1)\lambda_0 t}}{2w\lambda_0 t} \qquad (3)$$

which fits our *am*-DyAg and Tb-quasicrsytal ZF-μSR data well at all paramagnetic temperatures, as illustrated by the solid lines in Fig. 1. The temperature dependence of average relaxation rate λ_0 and dimensionless width w for the two materials, deduced from such fits, is shown in Fig. 2. Tem-

peratures where the fit average rates are above 20 μs^{-1} are not shown because in these spectra so much initial asymmetry is lost in the apparatus initial dead time that the fits become unreliable (in particular, the statistical uncertainty in w becomes larger than its estimated value. This occurs for $T \leqslant 90$ K in *am*-DyAg and for $T \leqslant 12$ K in *i*-$Tb_8Mg_{42}Zn_{50}$).

Crucial additional information comes from ^{161}Dy Mössbauer spectroscopy on crystalline (*cr*-) and *am*-DyAg which some of us performed.[9,10] First, it was found that the hyperfine field, which is proportional to the moment on Dy, is nearly the same in the *am*- and *cr*- compounds and in fact very close to the Dy^{3+} ($J=15/2$) free-ion limit. Also, the distribution of hyperfine field magnitude in *am*-DyAg is minimal ($\Delta B/B=0.02$). Second, the spin-relaxation rate (the fluctuation rate of the hyperfine field at the Dy nucleus) is generally an order of magnitude slower in *am*-DyAg than in *cr*-DyAg. The same effect is observed in the μSR studies.[7] The presence of the free ion hyperfine field means that the $|15/2\rangle$ state must be lowest. A cubic crystalline electric field (CEF, for a review, see Ref. 11), as in *cr*-DyAg, will not produce a pure maximum-J_z state, but in a magnetically ordered state, the dominance of the exchange interaction produces such a configuration. In the absence of exchange coupling, the CEF ground state in *cr*-DyAg is the Γ_8^3 quartet. Spin fluctuations are expected to be fast in a Γ_8, while in a pure $|15/2\rangle$ singlet or $|\pm 15/2\rangle$ doublet there can be neither conduction electron nor dipole-dipole relaxation and, in consequence, spin fluctuations are slow. The Mössbauer results correspond well to this picture in *cr*-DyAg: a few K below T_N the exchange coupling splits the Γ_8, creating an isolated singlet maximum-J_z ground state and spin relaxation decreases rapidly with reduced temperature. In *am*-DyAg, in contrast, very slow spin fluctuations were observed well into the paramagnetic regime (i.e., $T \gg T_C$), where there is no significant exchange coupling of spins (which would cause paramagnetic hyperfine splitting). The slowly relaxing $|\pm 15/2\rangle$ doublet must exist independent of exchange splitting. Chappert *et al.*[9] proposed that a $B_2^0 O_2^0$ term, which leads to uniaxial magnetic anisotropy, is dominant in the CEF Hamiltonian. The presence of such a term is a consequence of the disturbance of nearest-neighbor configurations in the amorphous material, which reduces the local symmetry of the Dy ions from cubic to axial. Evidence for this scenario is seen in the observation of a lattice electric-field gradient (efg) in the Mössbauer spectra of *am*-DyAg (which would be absent in cubic symmetry and indeed is not seen in the corresponding data of *cr*-DyAg). It is found in particular that this efg is rather broadly distributed both in size and in direction relative to the angular momentum axis of the Dy ions. Rare-earth amorphous magnets in general are characterized by a distribution of magnetic anisotropy rather than a distribution of magnetic-moment magnitudes.

The Dy spin-relaxation rate in *am*-DyAg deduced from the Mössbauer spectra increases when temperature is raised to ~ 100 K. This is thought to be due to the thermal population of higher CEF states. Above ~ 80 K the Mössbauer relaxation spectra could not be fit well with a single relaxation rate. The inclusion of both a slowly and a much faster relaxing portion was needed, the latter increasing in relative intensity with rising temperature. Thus the Mössbauer results by themselves indicate a distribution of relaxation rates in *am*-DyAg.

For each muon site contributing simple-exponential relaxation to the Laplace transform, the rate (which we assume is in the fast-fluctuation limit) is inversely proportional to the fluctuation frequency ν, and thus proportional to the fluctuation time $\tau = 1/\nu$, of the local field at the muon site:

$$\lambda = \gamma_\mu^2 \langle B_\mu^2 \rangle \tau. \tag{4}$$

In turn, τ should be proportional to the fluctuation time of the magnetic moments on the Dy ions. The experimental results summarized in Fig. 2 show that with decreasing temperature, the muon spin relaxation rates get distributed over a wider and wider range, with an increasing extent of rates corresponding to *slow* Dy spin motion. This temperature-dependent distribution of rates would be difficult to explain in terms of variation in the local environment around the muon stopping site in the amorphous material, which would change $\langle B_\mu^2 \rangle$ (this effect may be present to a small degree, but is unlikely to be smoothly temperature dependent). Instead, the likely cause is the distribution of local surroundings for the Dy ions. This lowers the symmetry of the CEF acting on the Dy ions from cubic to axial and changes the types of CEF levels and their energetic separation. In particular, it creates a rather pure $|\pm 15/2\rangle$ (maximal-J_z) doublet ground state which leads to very slowly relaxing magnetic Dy spins and hence to the appearance of large values of λ. While the ground state is uniform, the separation of the excited CEF states varies, due to the distribution in local symmetry. Because spin relaxation must proceed through the excited states in this case, relaxation rates are sensitive to the varying separation of these excited states and thus a distribution of values of λ can be understood in principle.

There are two spin fluctuation effects contributing to the temperature dependence of the rate distribution shown in Fig. 2. First, spin-lattice relaxation is inherently temperature dependent. Second, there is the effect of thermal population of the higher CEF states. The increasing appearance of large values of λ at low temperatures is explained by the increasing dominance of the $|15/2\rangle$ ground state. These slow Dy relaxation channels (distributed because of the distribution in ground-state separation) must of course always be present, but at higher temperatures the faster relaxation channels due to the population of excited CEF states gain prominence and ''short circuit'' the slow channels. The slow relaxation channels are still there but are not noticeably used by the Dy spins at higher temperatures. In that sense, with rising temperature, the progressively smaller width of the rate distribution and the shift of the mean muon spin relaxation rate to lower values are motional narrowing effects.

The same sort of CEF-induced distribution of magnetic anisotropy strength can be at work in *i*-Tb-Mg-Zn. Tb^{3+} is also a large-J ion ($J=6$) whose J_z substates are susceptible to CEF splitting, and the quasicrystal structure provides a wide variety (though technically not a random selection) of rare-earth sites, confusing the exchange interaction suffi-

ciently that spin-glass freezing, not long range-magnetic ordering, occurs.[12,13] Meanwhile, our observation of only exponential muon spin relaxation in *i*-Gd-Mg-Zn,[8] where the *s*-state ($l=0$) Gd^{3+} ion is immune to CEF effects, strongly suggests that the mechanism of nonexponential relaxation in the Tb quasicrystal must involve CEF, as this random axial anisotropy model does.

In conclusion, we have shown that varying-power-exponential ZF-μSR in amorphous DyAg and *i*-Tb-Mg-Zn quasicrystals is consistent with a wide asymmetric distribution of local relaxation rates in those materials. Combination with ^{161}Dy Mössbauer results for crystalline and amorphous DyAg indicates that a distribution of uniaxial CEF anisotropy that is random in not just direction (to create asperomagnetism in *am*-DyAg), but also in magnitude, creates the inhomogeneous distribution of spin-relaxation rates. This same mechanism explains why ZF-μSR in *i*-Tb-Mg-Zn is varying-power exponential while in *i*-Gd-Mg-Zn it is simple exponential: spherical *s*-state Gd^{3+} is not affected by the CEF.

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