Dynamics of Magnetic Defects in Heavy Fermion LiV_2O_4 from Stretched Exponential ^7Li NMR Relaxation

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(Received 21 March 2005; published 21 October 2005)

^7Li NMR measurements on LiV_2O_4 from 0.5 to 4.2 K are reported. A small concentration of magnetic defects within the structure drastically changes the ^7Li nuclear magnetization relaxation versus time from a pure exponential as in pure LiV_2O_4 to a stretched exponential, indicating glassy behavior of the magnetic defects. The stretched exponential function is described as arising from a distribution of ^7Li nuclear spin-lattice relaxation rates and we present a model for the distribution in terms of the dynamics of the magnetic defects. Our results explain the origin of recent puzzling ^7Li NMR literature data on LiV_2O_4 and our model is likely applicable to other glassy systems.

DOI: 10.1103/PhysRevLett.95.176408 PACS numbers: 71.27.+a, 75.40.−s, 75.50.Lk, 76.60.−k

Heavy fermion (HF, heavy Fermi liquid) behavior has been widely observed at low temperatures T in many metals containing crystallographically ordered arrays of f-electron atoms, which are quite well understood theoretically [1]. In these metals, the current carriers act as if they have a (heavy) mass that is of order 10^2–10^3 times the free electron mass. Only a few d-electron compounds are known to show HF behaviors at low T, e.g., $Y_{1-x}Sc_xMn_2$ with $x \approx 0.03$ [2], LiV_2O_4 [3,4], and most recently $Ca_{2-x}Sr_xRuO_4$ with $x \sim 0.3$–0.5 [5]. There is currently no theoretical consensus on the mechanism for formation of the heavy fermion mass in LiV_2O_4 [6].

An important measurement for establishing Fermi liquid behavior at low T is nuclear magnetic resonance (NMR). For high magnetic purity samples of LiV_2O_4, the ^7Li nuclear spin-lattice relaxation rate $1/T_1$ is proportional to T (the Korringa law for a Fermi liquid) from about 10 K down to about 1.5 K [3,7,8]. In contrast to these results, recent ^7Li NMR measurements of several samples down to 30 mK by Trinkl, Kaps, and co-workers strongly conflict with a Fermi liquid interpretation [9,10]. In particular, nonexponential (stretched exponential) recovery of the nuclear magnetization, non-Korringa behavior in $1/T_1$ versus T, a peak in $1/T_1$ at $\sim$0.6 K, and a strong field dependence of $1/T_1$ were found at low T. In view of the small number of known d-electron HF compounds and the importance of LiV_2O_4 within this small family, it is critical to determine if these results are intrinsic to the pure material, and if not, what they are due to.

Here we present ^7Li NMR measurements on two samples from 0.5 to 4.2 K that were carried out to study the influence of magnetic defects on the low-T HF properties of LiV_2O_4. We confirmed Fermi liquid behavior down to 0.5 K in a high magnetic purity sample. We find that a small concentration (0.7 mol%) of magnetic defects within the spinel structure drastically changes the detected spin dynamics and leads to the above behaviors described in Refs. [9,10], which therefore explain their results as arising from a significant concentration of magnetic defects in their samples. On the other hand, understanding the physics of magnetic defects in LiV_2O_4 is interesting and important in its own right and may further guide and constrain theoretical models for the pure material. A crucial aspect of LiV_2O_4 is the geometric frustration of V spins for antiferromagnetic ordering in the spinel structure. The geometric frustration is likely directly related to the suppression of antiferromagnetic order in pure LiV_2O_4 and the emergence of a heavy electron state instead. A large number of low lying spin excitations emerges and the system becomes ''almost unstable,'' i.e., very susceptible with respect to crystal defects or other perturbations that locally lift the frustration and cause a condensation of the low lying states [11].

We develop a phenomenological description for the observed stretched exponential ^7Li nuclear relaxation in terms of a distribution of $1/T_1$ values and explain the physical meaning of the parameters. We further present a model for defect nucleated dynamical magnetic order in an almost unstable electronic system that can explain this distribution and that provides important insights about the behaviors of magnetic defects in LiV_2O_4. We propose that LiV_2O_4 containing magnetic defects is the first viable candidate to exhibit quantum Heisenberg Griffiths behaviors. The stretched exponential function also describes the kinetics of diverse relaxation phenomena [12], so our model or parts thereof will likely have many applications to other materials and fields.

The two LiV_2O_4 samples measured here were samples #12-1 and #3-3-a2 studied previously in Ref. [13], where their synthesis and characterization were described. The magnetic defect concentration n_{defect} in the two samples was previously estimated from magnetization measurements at low T [13]. Sample #12-1 has $n_{\mathrm{defect}} = 0.01$ mol%, whereas sample #3-3-a2 has $n_{\mathrm{defect}} = 0.7$ mol%. The ^7Li NMR measurements were performed with a Fourier transform (FT) TecMag pulse spectrometer using ^4He (1.5–4.2 K) and ^3He (0.5–1.5 K) cryostats. The ^7Li NMR line shape and the full width at half maximum

(FWHM) were obtained from the FT of half of the echo signal. The ^{7}Li $1/T_1$ was determined by monitoring the recovery of the spin echo intensity following a saturating pulse sequence of $\pi/2$ pulses. The typical $\pi/2$ pulse width was 2 μs. The measurements were carried out at a frequency of 17.6 MHz (magnetic field $H = 10.6$ kOe) so that a direct comparison of our results with the corresponding ^{7}Li NMR data at 17.3 MHz in Refs. [9,10] could be made.

The resonance line for the pure sample #12-1 has a FWHM that is independent of T below 4.2 K whereas sample #3-3-a2 has a much broader line [Fig. 1(a)] that becomes increasingly broad with decreasing T [inset, Fig. 1(a)], indicating an increasing importance of magnetic inhomogeneity in the latter sample with decreasing T. The Knight shift K for both samples is the same and independent of T between 0.5 and 4.2 K, with $K = 0.141(15)\%$ in agreement with previous data [7] above 1.5 K.

Our main experimental results originate from measurements of the influence of magnetic defects on the ^{7}Li nuclear spin dynamics of LiV_2O_4. Figure 2(a) shows representative semilog plots of the time t dependent recovery of the ^{7}Li nuclear magnetization $M(t)$ after initial saturation for magnetically pure sample #12-1 at several T. The data at each T lie on a straight line (shown) with a well-defined $1/T_1$ determined from a fit of the data by $1 - M(t)/M(\infty) = A\ \exp(-t/T_1)$, where the prefactor A is typically 0.9 to 1.1. The resulting $1/T_1$ is plotted versus T in Fig. 3. These data follow the Korringa law for a Fermi liquid ($1/T_1 \propto T$) with a weighted fit giving $(T_1T)^{-1} = 2.46(6)\ s^{-1}\,K^{-1}$. Our results thus further confirm Fermi liquid behavior for pure LiV_2O_4 at low T.

The $M(t)$ for sample #3-3-a2 with $n_{\rm defect} = 0.7$ mol% is shown for representative temperatures in Fig. 2(b). The recovery is drastically different from that of the pure sample, exhibiting strongly nonexponential behavior. Another important feature is that the shape of the recovery curve changes with decreasing T, particularly strongly below 1 K. Following Ref. [10], we fitted the data at each T by the stretched exponential function

$$1 - \frac{M(t)}{M(\infty)} = \exp[-(t/T_1^*)^\beta], \qquad (1)$$

where β is the stretching exponent with $0 < \beta \leq 1$ and $1/T_1^*$ is a characteristic relaxation rate. This function is nonanalytic for $t \to 0$. We therefore employed a low-t cutoff at 15 ms to the fit. The resulting $1/T_1^*(T)$ is plotted as filled squares in Fig. 3 and the fits are shown by the solid curves in Fig. 2(b). The variation of β with T is shown in the inset of Fig. 3. The ^{7}Li NMR $1/T_1^*$ data obtained at 17.3 MHz by Kaps *et al.* [10] are plotted versus T as open squares in Fig. 3. From the totality of the data in Figs. 1–3, we conclude that the data of Kaps *et al.* are not intrinsic to pure LiV_2O_4 but rather are dominated by the influence of magnetic defects.

The nonexponential recovery of $M(t)$ in sample #3-3-a2 suggests that there is a distribution of $1/T_1$ values in this sample for different ^{7}Li nuclei. To check this hypothesis, we performed relaxation measurements in different regions of the NMR spectrum. These are shown in Fig. 1(b) as "hole-burning" experiments. By using a long saturating $\pi/2$ pulse we can irradiate only the central part of the spectrum. The fact that the "hole" disappears gradually

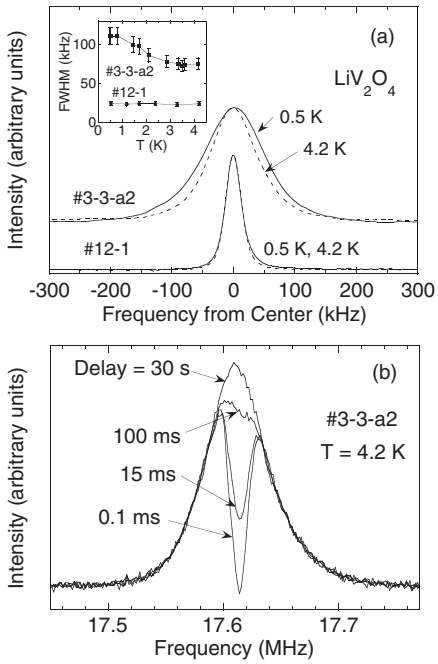

FIG. 1. (a) ^{7}Li NMR line shape at 0.5 and 4.2 K and full width at half maximum peak intensity versus temperature (FWHM, inset) for two samples of LiV_2O_4. (b) Hole-burning spectra at 4.2 K for sample #3-3-a2.

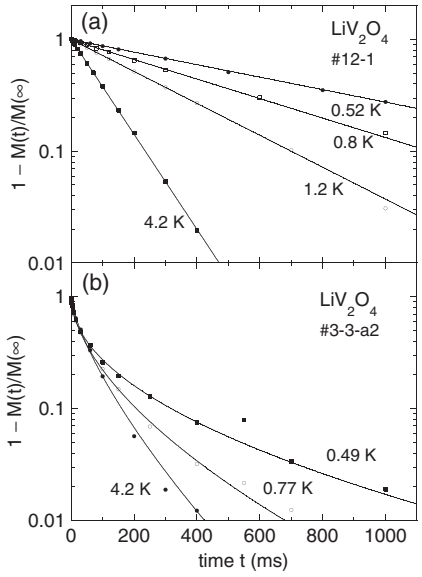

FIG. 2. Recovery of the ^{7}Li nuclear magnetization M vs time t for LiV_2O_4 samples #12-1 (a) and #3-3-a2 (b). The solid curves in (a) and (b) are fits to the data at each T by an exponential and a stretched exponential, respectively.

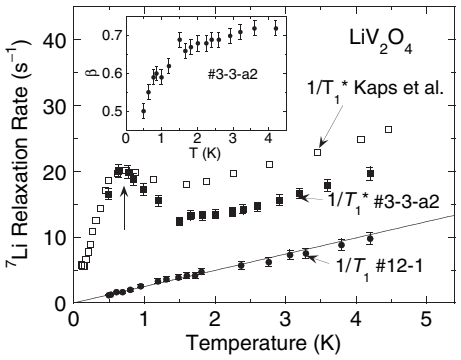

FIG. 3. ^{7}Li nuclear spin-lattice relaxation rates in LiV_2O_4 vs temperature T. The lowest data set of $1/T_1$ vs T is for high purity sample #12-1; the fitted straight line is the Korringa law for a Fermi liquid. The $1/T_1^*$ vs T data sets are for our sample #3-3-a2 (filled squares) and from Kaps *et al.* [Ref. [10]] (open squares). The vertical arrow at about 0.7 K indicates the approximate T of the maxima in $1/T_1^*$. The inset shows the exponent β in the stretched exponential in Eq. (1) vs T.

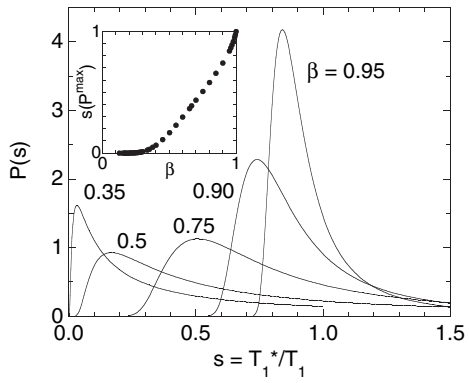

FIG. 4. Probability density $P(s)$ for several stretched exponential exponents β. The inset shows the s values versus β at which $P(s)$ is maximum.

during relaxation without affecting the remaining part of the line shape indicates the absence of spectral diffusion, which means that ^{7}Li nuclei with different Larmor frequencies have no thermal contact over our time scale. Another experiment was done by monitoring the recovery of the part of the echo signal far from $t = 0$. The recovery was found to be nearly exponential and with a $1/T_1$ corresponding to the long-time tail of the stretched exponential in Fig. 2(b). These two experiments together demonstrate that there does exist a distribution of $1/T_1$ values for the ^{7}Li nuclei in the sample at each T on our time scale and that these nuclei or groups of nuclei relax independently. The strong decrease of β with decreasing T in the inset of Fig. 3 must therefore reflect a significant change in the distribution of $1/T_1$ values with T as discussed next.

Our experiments thus demand that we model the stretched exponential relaxation in Eq. (1) as the sum over the sample of a probability distribution P of $1/T_1$ for the various ^{7}Li nuclei. Accordingly we write the stretched exponential function in Eq. (1) as

$$e^{-(t/T_1^*)^\beta} = \int_0^\infty P(s, \beta) e^{-\mathrm{st}/T_1^*} ds, \qquad (2)$$

where $s = T_1^*/T_1$ is the ratio of a particular relaxation rate $1/T_1$ within the sample to the fixed relaxation rate $1/T_1^*$ characteristic of $P(s, \beta)$, and of course $\int_0^\infty P(s, \beta) ds = 1$. For $\beta = 1$, $P(s, 1)$ is the Dirac delta function at $s = 1$. For general β, Eq. (2) shows that $P(s, \beta)$ is the inverse Laplace transform of the stretched exponential. The evolution of $P(s)$ with β for several values of β is shown in Fig. 4. With decreasing β, $P(s)$ broadens and becomes highly asymmetric, and the peak in $P(s)$ becomes finite and moves towards slower rates which is compensated by a long tail to faster rates. The value of s at which $P(s)$ is maximum is plotted versus β in the inset of Fig. 4; this value decreases with decreasing β and approaches zero exponentially for $\beta \lesssim 0.5$. The physical significance of $1/T_1^*$ for $1/3 \lesssim \beta < 1$ is that $1/T_1$ is about equally likely to be less than $1/T_1^*$ as it is to be greater; it is neither the average of $1/T_1$ nor the inverse of the average of T_1. For $s \gg 1$, $P(s, \beta) \sim 1/s^{1+\beta}$, so the average $s_{\mathrm{ave}} = (T_1^*/T_1)_{\mathrm{ave}}$ is infinite. Thus the moments of the distribution depend on the cutoff at large relaxation rates, but this cutoff is irrelevant for the physical interpretation of the long-time relaxation. We see that the measured small values for β at low T in Fig. 3 for sample #3-3-a2 and that of Kaps *et al.* constitute strong evidence for a broad distribution of ^{7}Li $1/T_1$ values at these T.

We now discuss possible physical origins of the $1/T_1$ probability distributions in Fig. 4 and then propose a model that may be applicable to LiV_2O_4 containing magnetic defects. We note at the outset that our NMR measurements were carried out at $H = 10.6$ kOe for which the magnetization of the magnetic defects at $\lesssim 1$ K is significant [13], a situation for which very few calculations of either the average bulk or local electronic spin fluctuations are available. With this caveat, the contribution to the $1/T_1$ of a nucleus located at site $\mathbf{r}$, by fluctuations of electron spins $\mathbf{S}(\mathbf{r}', t)$ with correlation function $q_{\mathbf{r}',\mathbf{r}''}(t) = \langle S_\alpha(\mathbf{r}', 0) S_\alpha(\mathbf{r}'', t)\rangle$, is

$$\frac{1}{T_1}(\mathbf{r}) \propto \int d^3r' d^3r'' A_{\mathbf{r},\mathbf{r}'} A_{\mathbf{r},\mathbf{r}''} q_{\mathbf{r}',\mathbf{r}''}(\omega_n). \qquad (3)$$

Here $A_{\mathbf{r},\mathbf{r}'}$ is the hyperfine interaction between nuclear and electron spins at sites $\mathbf{r}$ and $\mathbf{r}'$, respectively, and $q_{\mathbf{r}',\mathbf{r}''}(\omega_n)$ is the Fourier transform of the correlation function $q_{\mathbf{r}',\mathbf{r}''}(t)$ at the nuclear Larmor frequency $\omega_n = \gamma_n H$. For example, if one had a unique $1/T_1$, a unique $A_{\mathbf{r},\mathbf{r}'}$ with $\mathbf{r}' = \mathbf{r}''$, and a correlation function $q_{\mathbf{r}',\mathbf{r}'}(t) \sim e^{-\varepsilon t}$, one would have $1/T_1 \propto \varepsilon/(\varepsilon^2 + \omega_n^2)$, yielding a peak in $1/T_1$ as ε decreases through ω_n with decreasing T as observed for $1/T_1^*$ at ≈ 0.7 K in Fig. 3. This simplified example suggests that a significant fraction of the magnetic defects drastically slows down below $\sim$1 K.

A distribution of $1/T_1$ could result from a spatial variation in the electron spin dynamics, i.e., $q_{\mathbf{r}',\mathbf{r}''}(t)$, or varia-

tions of the hyperfine interactions. In the latter case, a nonlocal hyperfine interaction $A_{\mathbf{r},\mathbf{r}'} \propto |\mathbf{r}-\mathbf{r}'|^{-3}$, caused by dipolar and/or RKKY interactions, can lead to a broad distribution in $1/T_1$. Depending on whether a given nuclear spin is close to or far away from a local defect that dominates the spin response $q_{\mathbf{r},\mathbf{r}'}(t)$, very different $1/T_1$ values occur. Geometric considerations lead to $P(s,\beta) \propto s^{-3/2}$, i.e., a fixed value $\beta = \frac{1}{2}$ for the stretched exponential which is in direct conflict with our data that show a strongly T-dependent β. A physically more interesting case is when stretched exponential nuclear relaxation is due to dynamical heterogeneity of the magnetic defect spin system, i.e., due to spatially varying $q_{\mathbf{r}',\mathbf{r}''}(t)$. For simplicity we consider the limit of a purely local hyperfine interaction $A_{\mathbf{r},\mathbf{r}'} \propto \delta_{\mathbf{r}-\mathbf{r}'}$. In the limit of strongly disordered spin systems, dynamical heterogeneity with anomalous long-time dynamics was found in numerical simulations above the spin glass temperature [14]. The averaged autocorrelation function was shown to have the Ogielski form $q(t) = t^{-x}\exp[-(\varepsilon^* t)^{\beta}]$, where the energy scale ε^* characterizes the averaged electron spin response. As ε^* becomes smaller than ω_n with decreasing T, $1/T_1^*$ goes through a maximum, located at $T \sim 1$ K in our case, and $q(t)$ immediately yields a stretched exponential relaxation for the nuclear spins. However, these results were obtained in the strong disorder limit in contrast to dilute magnetic defects in LiV_2O_4.

The sensitivity of the HF state with respect to perturbations may be critical to understand the behavior of LiV_2O_4 where n_{defect} is rather small, suggesting the following alternative model for the dynamics. If geometric frustration suppresses long-range order in pure LiV_2O_4, it becomes natural that crystal defects can locally lift the frustration and cause a condensation of dynamic magnetic order in a finite region of volume $\simeq \xi^3$ around the defect. Because of the proximity to an ordered state and long-range electronic spin coupling in metallic systems, we expect ξ to be much larger than an interatomic spacing, in contrast to insulating frustrated systems with only nearest-neighbor interactions [15]. This might help to explain our previous low-T magnetization measurements which indicated that the magnetic defects have large average spins $\sim 3/2$ to 4 [13]. Fluctuations in the local tendency towards order lead to a probability $p(\xi) \propto e^{-c\xi^3}$ for such a droplet [16] and we analyze the system using the ideas of Griffiths physics in disordered magnets [17].

The lowest excitation energies, ε, of a droplet depend on its size ξ. Depending on how $\varepsilon(\xi)$ varies with ξ, different long-time dynamics emerges [18]. If $\varepsilon \propto \xi^{-\psi}$ the distribution function of the droplet energies becomes $p(\varepsilon) \propto e^{-(\varepsilon^*/\varepsilon)^{3/\psi}}$. If $1/T_1 \propto \varepsilon$, this yields $P(s,\beta) \propto e^{-s^{-3/\psi}}$, leading for large times to a stretched exponential relaxation with $\beta = \frac{1}{1+\psi/3}$. Such a behavior occurs in magnets with Heisenberg symmetry [18] where one finds $\beta = \frac{1}{2}$, if the spin dynamics is classical. For lower T, where quantum dynamics of the spins sets in, one finds $\beta = \frac{2-z}{4-z} < \frac{1}{2}$, if the dynamical exponent relating length and time scales obeys $z < 2$. For insulating antiferromagnets, one usually has $z = 1$, giving $\beta = 1/3$.

Probably more appropriate to LiV_2O_4 is the case of itinerant antiferromagnets where one expects $z = 2$, and an even more exotic situation occurs. In this case, $\varepsilon \propto e^{-b\xi^3}$, i.e., large droplets become extremely slow leading to quantum Griffiths behavior $P(s) \propto s^{-\lambda}$ at long times with nonuniversal exponent $\lambda = 1 - c/b$. Now, the nuclear spin relaxes according to a power law $1 - M(t)/M(\infty) \propto t^{-(1-\lambda)}$. It becomes very hard to distinguish at large times power law from stretched exponential behavior with small β at low T. However, there are clear predictions of this scenario which include (given $\lambda > 0$) singular non-Fermi-liquid type specific heat $C/T \propto T^{-\lambda}$, susceptibility $\chi \propto T^{-\lambda}$, and similar results for the field dependence of the magnetization [18], which can all be tested in future experiments.

Discussions with T. Vojta are gratefully acknowledged. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

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