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Search for a spin glass state in $PrAu_2Si_2$ by μSR

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Materials of stoichiometry FT_2X_2, where F is an f-electron ion (rare earth or actinide), T a transition metal, and X a metalloid, generally show long-range magnetic order of fairly localized f-electron moments governed by RKKY and CEF (crystalline electric field) interactions [1]. In cases where F is an 'anomalous' f-electron ion (e.g. Ce or U), more unusual features such as tiny-moment magnetism, superconductivity, heavy-fermion and non-Fermi-liquid behavior occur [2,3]. A spin glass (SG) magnetic ground state was surprisingly discovered in heavy-fermion URh_2Ge_2 [4]. Normal prerequisites for the formation of a SG state are frustration (either geometrical or by competing interactions) and disorder. The compound had the strict 1:2:2 stoichiometry and no simple Rh ↔ Ge site-exchange was detected. Structurally well-ordered materials can still be magnetically frustrated (e.g. Kagomé lattices [5], Gd–Ga Garnet [6]). FT_2X_2 compounds form in two crystallographic structures, the $ThCr_2Si_2$ type (I_4/mmm) or the $CaBe_2Ge_2$ type (P_4/nmm) and a mixture of these two crystallographic structures, which differ only in their T and X positions, was suggested to be perhaps the source of disorder enabling the spin-glass freezing. More recently it was shown that another 'stoichiometric spin glass' exists among the FT_2X_2 materials. Bulk measurements (e.g. susceptibility, electrical conductivity, specific heat, also in applied fields up to 14 T) in $PrAu_2Si_2$ showed the characteristic features of a canonical spin glass with freezing temperature $T_g = 3$ K [7,8]. Neutron diffraction definitely excluded long-range magnetic order, which is present in the analogous compounds $PrAu_2Ge_2$ ($T_N = 11.6$ K) and $PrAu_2(Ge_{1-x}Si_x)_2$ for $x \geq 0.2$ (with $10\ \text{K} \geq T_N \geq 4\ \text{K}$) [9]. It appears that antiferromagnetism evolves into a spin-glass state across the

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$PrAu_2(Ge_{1-x}Si_x)_2$ alloy series. The mechanism leading to the formation of a SG state is particularly difficult to understand in this case and has not been satisfactorily explained to date. Neutron and X-ray diffraction spectra definitely showed that only the $ThCr_2Si_2$ structure is present, but a fraction of approximately 10% displayed site exchange disorder between Si and Au and this non-magnetic disorder was suggested as responsible for the SG ground state, although a detailed model does not exist. Competition between the Kondo effect and the RKKY interaction could play an additional role.

Muon spin relaxation (μSR) is a premier probe of disordered magnetic states [10,11], especially spin glasses [12]. In this paper zero-field (ZF) μSR in a powder sample of $PrAu_2Si_2$ between 100 and 50 K is reported. The compound was synthesized by argon-arc melting of a stoichiometric mixture of the highest-purity elements and subsequently was annealed for one week at 1100 K.

The μSR method is described, for example, in [10, 13]. A beam of positive muons having ~100% spin polarization impinges on the sample. Each muon thermalizes instantaneously (on the time scale of the muon lifetime of 2.2 μs) without loss of polarization. In a conducting solid below room temperature it comes to rest at an interstitial site far from any damage it might have caused during thermalization. The muon magnetic moment then interacts (it Larmor precesses) with the magnetic field $\mathbf{B}_\mu$ produced by atomic and/or nuclear magnetic moments surrounding the muon site.

When the muon decays, a positron is emitted preferentially (asymmetrically) in the direction the muon magnetic moment was pointing at the instant of decay. For zero field (ZF) μSR, positron counters placed backward and forward with respect to the initial muon polarization record the time dependence of the count rate asymmetry $A(t)$. After applying some corrections for experimental conditions, the plot of $A(t)$ (the μSR spectrum), can be expressed as $A(t) = A_0 G(t)$. Here A_0 is the initial ($t = 0$) asymmetry (typically 0.2–0.3) and $G(t)$ the 'μSR response function', that is, the time evolution of the spin polarization of the muon ensemble due to the interaction with $\mathbf{B}_\mu$. The most important correction hidden in $A(t)$ is a factor α which takes into account the inequality of the two positron counters. A value of $\alpha \neq 1$ leads to a (time independent) 'instrumental asymmetry'. It is important to determine α separately. This is usually done by measuring the μSR spectrum in a low transverse field (TF) under the same environmental condition used in ZF-μSR. The TF response function is a damped cosine oscillatory function which, when least squares fit to the data, returns α. With such a procedure one can determine whether a change in asymmetry (e.g. in A_0) is instrumental (not associated with the sample) or based on some physical properties of the sample.

For a frozen disordered system of concentrated magnetic moments the ZF-μSR response takes the form

$$G_{\mathrm{GKT}}(t) = \frac{2}{3}(1 - \Delta^2 t^2)\exp(-\frac{\Delta^2 t^2}{2}) + \frac{1}{3} \quad (1)$$

known as the Gaussian Kubo-Toyabe (GKT) relaxation function [14]. Its characteristic features are an initially-Gaussian decay of asymmetry to a minimum (close to $A = 0$) followed by recovery to the '1/3-tail', meaning that for late times the asymmetry remains time independent at $A_0/3$. The presence of a 1/3-tail is the tell-tale signature of a magnetic state with static moments, be it disordered or ordered. $\Delta = \gamma_\mu B_{\mathrm{rms}}$ is called the 'static width', with γ_μ being the muon gyromagnetic ratio (851.4 μs^{-1}/T). B_{rms} is the root-mean square field of the Gaussian distributed field B_μ assumed to exist in disordered concentrated-moment systems. If the moments begin to fluctuate with rate $1/\tau_f$ the 1/3-tail begins to decay exponentially in time. For fast fluctuation rates ($1/\tau_f \gg \Delta$) the response function should become exponential

$$G_e(t) = \exp(-\lambda t) = \exp(\Delta^2 \tau_f t). \quad (2)$$

Simple long-range magnetic ordering will generate an oscillatory pattern (with damping), even under ZF conditions, having initial amplitude $2A_0/3$ ('spontaneous muon spin precession'). The precession frequency directly gives the mean field at the muon site ($\omega_\mu = \gamma_\mu \langle B_\mu \rangle$) and the damping rate the width of the field distribution. The remaining $A_0/3$ signal decays exponentially below the ordering temperature, becoming time independent in the quasi-static limit $T \rightarrow 0$, i.e. one again sees the 1/3 tail characteristic for static moments.

In ZF, the muon spin polarization in $PrAu_2Si_2$ relaxes monotonically to zero at all temperatures measured, from 50 K down to 40 mK (see Fig. 1). At no temperature is the relaxation well fit as simple exponential decay of polariz-

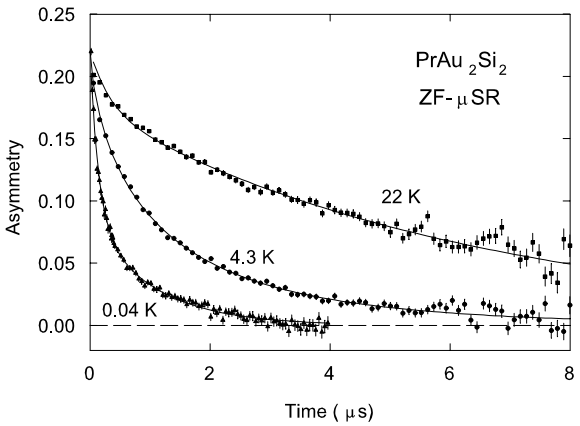

Fig. 1. ZF-μSR spectra of $PrAu_2Si_2$ at the temperatures indicated, with solid lines showing the least-squares fit of the sum of two exponential decays, as described in the text. The useful spectrum time range in the dilution-refrigerator spectrometer (PSI LTF) is limited to 4 μs for technical reasons.

ation, but it is well fit at all temperatures by a muon spin relaxation function consisting of the sum of two pure exponentials, one relaxing more rapidly than the other, representing different muon sites in the material experiencing different typical local fields. In Fig. 1 such fits are shown for spectra obtained at 40 mK, 4.3 K and 22 K. Unfortunately, as temperature is raised above 4.3 K, the fast relaxation is not different enough in rate from the slow relaxation to fully constrain the two amplitude parameters and two relaxation rate parameters of the model: they become progressively more correlated with each other. To overcome such uncertainty, researchers often assume that the ratio of the amplitudes of the two exponential signals should be fixed at a particular value. With this restriction, however, good fits over the entire temperature range could not be obtained. Good quality of fit required that the ratio of amplitudes change with temperature. It was possible to hold the total initial asymmetry, which should be a property of the apparatus, constant at the value 0.22. The deduced temperature dependence of the two relaxation rates and the fast-relaxing signal fraction is shown in Fig. 2. Both relaxation rates rise fairly smoothly as temperature is reduced, and show no indication of any change in behavior near 3 K that might be associated with a spin-freezing transition. The faster relaxation rate only increases by a factor of about two from 50 to 0.04 K. Its relative amplitude increases by a factor of three or more over the same range.

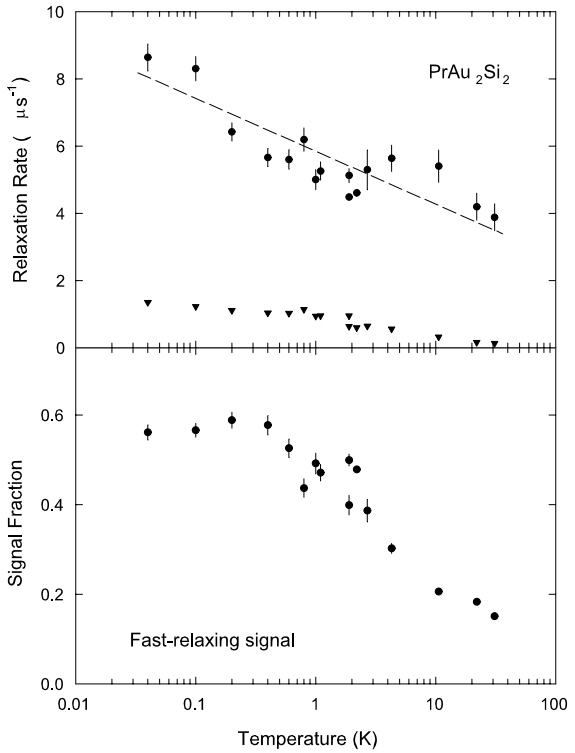

Fig. 2. Temperature dependence of the relaxation rates (upper panel) and fraction in the fast-relaxing signal (lower panel) deduced from two-exponential fits (holding total asymmetry fixed at 0.22) to the ZF-μSR spectra in $PrAu_2Si_2$. Note the logarithmic temperature scale. The dashed line is a guide for the eye.

Independent of the details of the fitting, the important result is that we do not observe any static relaxation function characteristic for a disordered spin frozen state. The monotonic decay to zero spin polarization clearly indicates that the depolarizing agent is still the dynamics of the magnetic moments. Also, we have carefully determined the correction factor α and thus are certain where the spectral baseline (i.e. the position of $A(t) = 0$) is located. We find that the exponential decays fully reach the baseline at later times, meaning that a 1/3-tail is absent. Both these observations, combined with the temperature dependence of the relaxation rates, firmly demonstrate that moment fluctuations slow down with decreasing temperatures as expected in a paramagnet, but without ever reaching a transition point T_g where complete freezing of moments takes place.

In the face of this unusual and unexpected result one may ask whether the muon perhaps is insensitive to the magnetic properties of the compound. This can be excluded. Analogous measurements on antiferromagnetic $PrAu_2Ge_2$ [15] showed spontaneous spin precession, as expected for an ordered magnet, below 12 K, which agrees with T_N found previously from bulk data [9]. The temperature dependence of the precession frequency follows that of the order parameter. For $T \to 0$ a local field $B_\mu(0) \approx 0.2$ T is found. We also studied $PrAu_2(Si_{0.8}Ge_{0.2})_2$, the alloy with the limiting Ge concentration for the presence of long-range (antiferromagnetic) order. We found spontaneous spin precession below $\sim$4.5 K in agreement with $T_N = 4$ K previously reported [9]. The local field for $T \to 0$ is nearly the same as in the pure $PrAu_2Ge_2$ compound showing that the moment on Pr^{3+} is highly localized and thus insensitive to the ligand configuration.

The faster relaxation rate in $PrAu_2Si_2$ at $T \leq 2$ K is $\lambda = \Delta^2\tau_f \approx 8\ \mu s^{-1}$. Using the constancy of $B_\mu(0) \approx 0.2$ T discussed above we may assume that a field of the same magnitude is acting in $PrAu_2Si_2$, leading to $\Delta \approx 17\ \mu s^{-1}$. This, together with the measured relaxation rate allows us to estimate the fluctuation rate $1/\tau_f \approx 36$ MHz. For a free paramagnet one expects a considerably higher rate. For example, in $PrAl_2$ a rate at least one order of magnitude faster was determined from μSR measurements well above the magnetic ordering temperature [16]. On the other hand, in $PrAu_2Si_2$ the estimates above show that the condition for the fully spin-dynamic regime $1/\tau_f \gg \Delta$ is still valid. In summary, moment fluctuations slow down as the temperature decreases, most likely due to increase of spin–spin correlations. In the range of a few Kelvin and below, however, the fluctuation rate approaches a constant non-zero value, preventing spin freezing. Such a behavior of persistent spin fluctuations suppressing magnetic order has

been observed in other materials under the influence of strong Kondo interaction, for example in CeNiSn [17].

We compare our results briefly to those of two other stoichiometric spin glasses where μSR measurements have previously been reported, i.e. in URh_2Ge_2 and in $Y_2Mo_2O_7$. In the cubic pyrochlore $Y_2Mo_2O_7$ where no structural disorder could be detected [18], μSR sees the full range of typical spin-glass behavior, from rapidly-fluctuating moments in the paramagnetic state far above T_g, through a reasonably-sudden freezing transition, to an essentially static magnetic state far below T_g [19]. These results are in full agreement with bulk and neutron diffraction data [20,21]. Only a brief presentation of μSR results for URh_2Ge_2 (where bulk data reported $T_g = 10$ K [4]) is available in the literature [22]. In the paramagnetic state well above the freezing temperature, relaxation is exponential. Rapidly increasing relaxation rate sets in together with power-exponential shape (where power p decreases continuously, for a discussion of this type of behavior, see [23]) as the temperature drops below 20 K. Finally a freezing transition from rapidly fluctuating to slower fluctuations occurs around 9 K, but the form of the μSR response well below the freezing point is not discussed, apart from a statement that no spontaneous oscillation was observed.

In contrast to these two cases, we find no agreement with the bulk data for $PrAu_2Si_2$. The meaning of the peak in bulk susceptibility remains enigmatic in view of the fact that there is no corresponding freezing effect observed in μSR. One might suspect a sample problem. An exploratory susceptibility measurement on the same sample that we performed μSR on, however, showed a peak around 2.2 K [24] in agreement with the published data. The bulk freezing signal is not sample dependent. The possibility that only a fraction of the moments enter a spin-glass-type state can be ruled out as well, since the susceptibility data [8,24] show that this fraction must be substantial, yet the low temperature (spin dynamic) μSR signal has the full amplitude expected, within the accuracy of a few %, i.e. essentially the entire sample volume is involved. It is intriguing, however, that this is roughly the temperature range in which low-temperature 2-site fixed occupancy switches over to temperature-dependent site occupancy (see Fig. 2). At temperatures above 4 K, it is possible to fit the data just as well to power-exponential decay of polarization, which we mentioned for URh_2Ge_2. This is a relaxation function with fewer adjustable parameters, and if this analysis could be extended to the entire temperature range, the associated physical interpretation would be different (see, e.g. [23]). In the present case, however, as temperature drops below 4 K, good power-exponential fits have progressively increasing asymmetry, eventually to unreasonable values. There is no transition point where the relaxation shape 'changes' from power-exponential to two-exponential, because two-exponential decay can fit the data at all temperatures. The physically-simplest interpretation is then to use the two-exponential model only.

Reliable experimental determination of muon stopping sites requires single crystalline materials (see, for example [3]), which were not available. There have been several attempts to determine the stopping sites in materials having the $ThCr_2Si_2$ structure, especially in heavy-fermion compounds (for a discussion see, for example [10]). Unfortunately, the various results differ from each other substantially and no conclusion can be drawn. Generally, the positive muon seeks the largest interstitial hole in a crystal structure. We have developed software to identify the largest interstitial holes in an arbitrary crystal structure (see, for example [25]). When applied to the $ThCr_2Si_2$ structure, however, it provides no clear indications of individual well-defined interstitial holes. This appears to be a very open crystal structure in which muons stop at multiple sites that may depend on composition or even on temperature in one particular sample. At low temperatures the muon is confined to two distinct sites in $PrAu_2Si_2$. Usually a change to more fluid site occupancy at temperatures as low as 2 K should be initiated by a (perhaps subtle) change in crystal structure that may be combined with a change in spin arrangement. To connect such an effect to the distinct susceptibility peak is difficult, if possible at all. Note that this uncertainty about the muon site does not affect our main results concerning moment dynamics and the lack of spin freezing in this material.

In conclusion, we find that our μSR results in $PrAu_2Si_2$ are not in agreement with bulk data. No indication of a transition into a spin frozen state such as a spin glass is seen. The ensemble of magnetic moments in $PrAu_2$ Si_2 shows persistent fluctuations in the 40 MHz range down to dilution refrigerator temperatures. We are unable to explain the origin of the susceptibility peak around 3 K on the basis of the μSR data. Our data confirm the neutron diffraction result of absence of long-range order, in fact μSR even excludes medium to short range order. The exact nature of the magnetic ground state is not resolved.

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