Spin Glass Behavior in URh_2Ge_2

S. Süllow, G. J. Nieuwenhuys, A. A. Menovsky,* and J. A. Mydosh
Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9506, 2300 RA Leiden, The Netherlands

S. A. M. Mentink† and T. E. Mason
Department of Physics, University of Toronto, 60 Saint George Street, Toronto, Ontario, Canada M5S 1A7

W. J. L. Buyers
AECL Research, Chalk River, Ontario, Canada K0J 1J0

(Received 18 September 1996)

URh_2Ge_2 occupies an extraordinary position among the heavy-electron 122 compounds, by exhibiting a previously unidentified form of magnetic correlations at low temperatures instead of the usual antiferromagnetism. Here we present new results of ac and dc susceptibilities, specific heat, and neutron diffraction on single-crystalline as-grown URh_2Ge_2. These data clearly indicate that crystallographic disorder on a local scale produces spin glass behavior in the sample. We therefore conclude that URh_2Ge_2 is a 3D Ising-like, random-bond, heavy-fermion spin glass. [S0031-9007(96)02019-4]

PACS numbers: 75.50.Lk, 61.12.–q, 75.20.Hr

URh_2Ge_2 is a heavy-fermion intermetallic compound ($\gamma \simeq 130$ mJ/mol K^2) for which there has been a long-standing controversy concerning the magnetic ground-state. Usually in the 122 compounds with uranium a simple antiferromagnetic (AF) stacking occurs along the c axis of U moments, ferromagnetically coupled in the a-b planes and directed parallel to c (AF-I structure). In these materials, if the Kondo effect does not dominate, a distinct phase transition takes place to the long-range ordered magnetic ground state. In particular, there has recently been a great deal of systematic study and classification of the various U 122 systems [1] and a standard description (the Doniach model [2]) has emerged which involves the competition between the RKKY interaction, leading to magnetic order, and the Kondo effect which compensates the moments, thereby eliminating the phase transition.

However, URh_2Ge_2 does not belong to this well-understood category. Early neutron scattering experiments [3] on polycrystalline samples did not find magnetic ordering and could not unambiguously determine a unique crystal structure. Two solutions were proposed: (*i*) a structure related to body-centered tetragonal (bct) $ThCr_2Su_2$ ($I4/mmm$), but with lower symmetry ($P4/mmm$) due to randomly distributed Rh and Ge on the Cr and Si sites, and, (*ii*) an atomically ordered $CaBe_2Ge_2$ ($P4/nmm$) unit cell. We repeated the powder neutron diffraction experiments and reached similar conclusions [4]. However, a peak in the static susceptibility χ_{dc} indicated an "antiferromagnetic" transition takes place at 8 K [3]. Other investigations [5] claimed that a drop in the resistivity indicated magnetic order below 2 K. Later, Lloret *et al.* [6] showed that the varying behavior of URh_2Ge_2 is governed by the stoichiometry, which shifts both the χ_{dc} maximum and the resistivity drop. The confusion was complete when the first data on single-crystalline URh_2Ge_2 appeared [7]. Now it was concluded that no long-range magnetic order occurs down to 35 mK, but the maximum detected in χ_{dc} at 11 K and the change in slope of the specific heat at 12 K were tentatively interpreted as arising from crystalline electric field effects.

In these previous investigations an intriguing possibility was overlooked, namely, that spin-glass freezing occurs. But how can a spin-glass state be possible without some kind of randomness or disorder? Intermetallic compounds are customarily thought of as possessing a relatively perfect periodic crystal structure. Motivated by the recent resurgence of interest in spin glasses, especially their formation with f elements and their novel quantum properties [8,9], we have reopened the unsolved case of URh_2Ge_2 by investigating a new single crystal. Our bulk measurements of the ac susceptibility χ_{ac}, static susceptibility χ_{dc}, specific heat c_p, and elastic neutron scattering clearly show this system to be an archetypal spin glass. We propose that the disorder derives from an amalgamation of the $ThCr_2Si_2$ and the $CaBe_2Ge_2$ structures and causes an intermixture of Rh and Ge positions. This in turn creates random bonds which lead to competing magnetic interactions.

A crystal of URh_2Ge_2 was grown using the Czochralski technique in a tri-arc furnace. X-ray Laue diffraction proved the sample to be truly single-crystal, and electron probe microanalysis showed it to be single phase with proper stoichiometry $URh_{2.00\pm0.06}Ge_{1.96\pm0.06}$. Here we report solely on the as-grown crystal. The effect of various heat treatments on the magnetism will be reported elsewhere [4,10]. Measurements of χ_{ac} and χ_{dc} were performed with a Quantum Design SQUID between $T = 1.8$ and 300 K in magnetic fields up to 5 T; c_p was determined using a semiadiabatic heat-pulse method from 1.8 to 30 K in fields up to 6 T. Elastic neutron scattering measurements at low T were performed at the triple-axis spectrometer C5 at AECL using a Ge (1 1 1) monochromator, a sapphire and pyrolytic graphite (PG) filter to reduce higher order contamination in the beam, and the (0 0 2) reflection from PG as an analyzer. The energy resolution as measured with vanadium was $\Delta E = 0.162$ THz, half-width at half maximum. The results of recent μ^+SR experiments will be reported elsewhere [11].

Figure 1 shows the real and imaginary parts of χ_{ac} versus T at different frequencies ω for the 3.5 G driving field $B \| a$ and $B \| c$. Note the sharp cusps in Re(χ_{ac}) at 9.6 K denoting the freezing temperatures T_f and how T_f shifts to higher temperatures with increase of ω. Im(χ_{ac}) appears at a much smaller step whose point of inflection also designates T_f $[\chi''_{ac} \simeq -(\pi/2)\partial\chi'_{ac}/\partial(\log_{10}\omega)]$ and its frequency dependence. By way of the above criteria for χ'_{ac} and χ''_{ac} we can calculate the initial frequency shift of T_f:

$$\delta T_f = \frac{\Delta T_f}{T_f \Delta \log_{10}\omega} = 0.025 \pm 0.005 \qquad (1)$$

for both crystallographic directions. This value is typical for metallic spin glasses, e.g., $\underline{\text{Cu}}$Mn: 0.005 and (La,Gd)($\underline{\text{La,Gd}}$)Al_2: 0.06. In addition to this canonical spin glass behavior [12] the low-T ($T \ll T_f$) forms of χ_{ac} are standard regarding both ω and T dependences. The susceptibilities measured along the c axis are much larger than those in the basal plane, indicating that the preferred spin orientation is randomly up/down parallel to c. Thus there is an Ising-like character to the spin glass freezing.

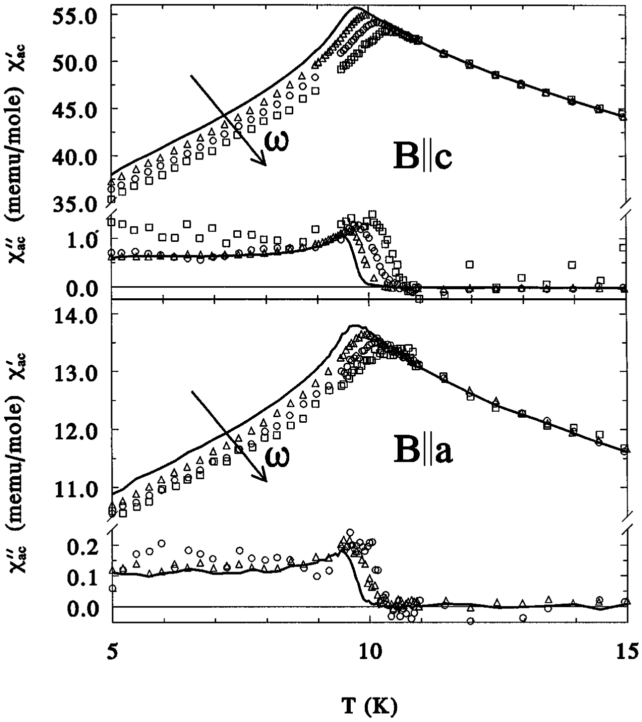

FIG. 1. The frequency dependence of the ac susceptibility (in-phase χ'_{ac} and out-of-phase χ''_{ac}) of URh_2Ge_2 for the two crystallographic directions. (—): 1.157 Hz, (△): 11.57 Hz, (○): 115.7 Hz, (□): 1157 Hz.

Figure 2 displays the zero-field-cooled (ZFC) and field-cooled (FC) magnetization ($\chi_{dc} = M/B$ with $B = 50$ G) for both a and c axes. Here a small maximum appears at 9.3 K with irreversibility starting just below this temperature. Such behavior reveals the static freezing temperature $T_f(\omega \rightarrow 0)$ to be less than T_f at higher frequencies. The maximum in χ_{dc} is smeared out by the application of a static magnetic field B_{dc}. For $T < 9$ K the FC-χ_{dc} is essentially constant and independent of measurement time as expected, while ZFC-χ_{dc} continues to decrease and is time dependent. If on this FC branch we set the field to zero at a constant T, we generate an isothermal remanence magnetization (IRM) which relaxes over many decades of time (not shown) according to the roughly logarithmic time dependence expected for a spin glass [12].

In Fig. 3 we show the magnetic specific heat of URh_2Ge_2 plotted as c_p vs T and c_p/T vs T. We have corrected for the lattice contribution to c_p by subtracting the specific heat of UFe_2Ge_2 which represents a Pauli paramagnetic reference compound. Neither U nor Fe is magnetic and a simple mass scaling was used to correct for the different masses of Fe and Rh [13]. From Fig. 3 it can be seen that c_p is featureless below 10 K, while a broad maximum appears in c_p/T above 10 K, which becomes smeared in an applied magnetic field. At low T, c_p varies between T and T^2 and is independent of field. To determine γ we plot $c_p/T = \gamma + DT^\kappa$, with D and κ as free parameters and γ the intercept. An effective $\gamma \simeq 130$ mJ/mole K^2 is estimated in the limit $T \rightarrow 0$, while $D = 19$ mJ/mole K$^{\kappa+2}$ and $\kappa = 0.91$ [4]. The above properties are typical for a canonical spin glass with the overall curves in Fig. 3 closely resembling those of $\underline{\text{Cu}}$Mn [12].

To further investigate the structural and magnetic properties of as-grown single crystals, we performed elastic

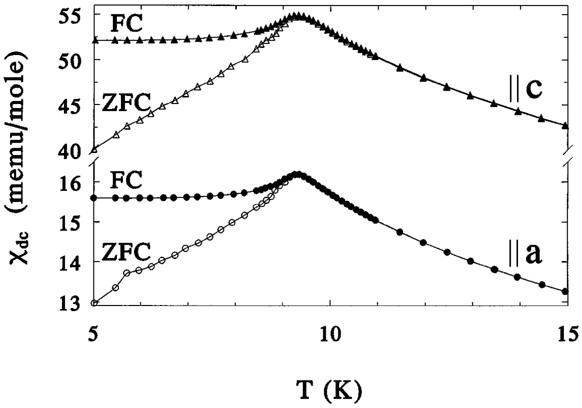

FIG. 2. dc susceptibility χ_{dc} of as-grown single crystal URh_2Ge_2 in a field-cooled (filled symbols) and zero-field-cooled (open symbols) experiment in an applied field $B = 50$ G.

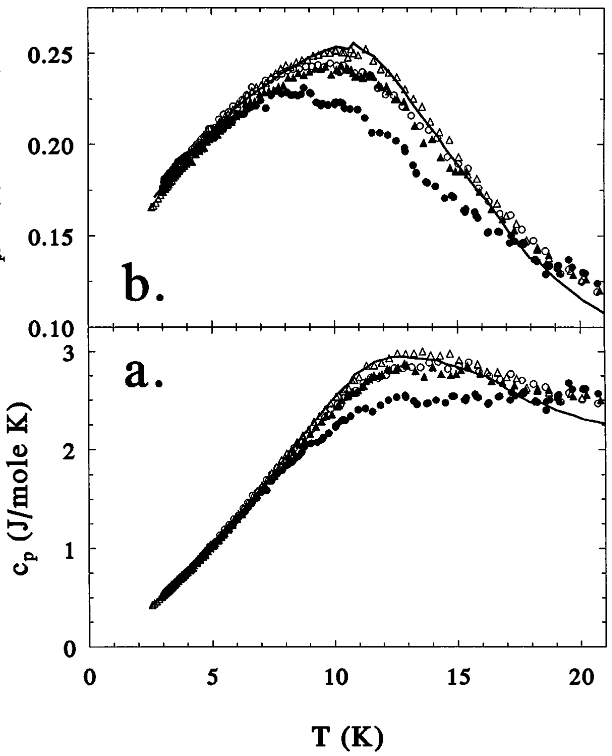

FIG. 3. (a) c_p vs T of as-grown URh$_2$Ge$_2$, corrected for the lattice contribution, in fields of 0 T (—), 3 T (△), 6 T (○) for $B \| a$ and 3 T (filled △), 6 T (●) for $B \| c$. (b) The specific heat from (a), plotted as c_p/T vs T.

neutron scattering measurements, with the crystal oriented in the $(h\,0\,l)$ zone. The lattice parameters at 4.3 K are $a = 4.160$ Å and $c = 9.733$ Å, in good agreement with Ref. [7], and correspond to the correct 122 stoichiometry as found by Lloret *et al.* [6]. The structural intensities, integrated in both a^* and c^* directions, have been reported before [14] and are close to the values calculated for the two suggested structures discussed above. However, anomalously high intensities of the $(0\ l)$ reflections ($l = 2$–7) have been observed. These can only partly be explained by possible extinction or multiple scattering effects, since the crystal is small ($10 \times 3 \times 3$ mm^3) and the difference between measured and calculated intensities of the $(0\ l)$ reflections is an irregular function of l. Moreover, decreases in these intensities occur after annealing the crystal [10], and this indicates better structural order. The small difference in neutron scattering lengths of Rh and Ge does not allow for a straightforward explanation of large intensity differences. We must invoke a more complicated mixture of Rh and Ge atoms, together with a distribution of the free positional z parameters of Rh and Ge, and the presence of a small amount (<5%) of vacancies to account for the increased intensities. Also, the observed weak structural $(1\,0\,0)$ reflection, forbidden in both $P4/mmm$ and $P4/nmm$ symmetries, points to a disordered crystal structure. Certainly the large value of the resistivity at 300 K (as high as 500 $\mu\Omega$ cm) implies a substantial amount of randomness [4,7]. Both powder x-ray data [6,7] and our single-crystal neutron results indicate that the U atoms occupy their regular sites, forming a bct sublattice. Thus the disorder is only on the nonmagnetic ligand sites, leading to the conclusion that URh$_2$Ge$_2$ should be regarded as a three-dimensional "random bond" spin glass.

In Fig. 4 we present the elastic neutron intensity versus T at the $(1\,0\,0)$ position. Superimposed on the small nuclear intensity, weak magnetic scattering is observed that is *not* resolution limited. Much weaker magnetic scattering has also been found at $(1\,0\,2)$, consistent with an easy c axis as derived from the susceptibility data. The lower inset in Fig. 4 shows a scan along $(h\,0\,0)$ at 4.3 K, corrected for background using similar data at 20 K, where the solid line is the momentum resolution measured by removing the PG filter from the incident beam to allow $\lambda/2$ scattering of the strong $(2\,0\,0)$ nuclear reflection. An onset of elastic magnetic scattering occurs at $T_f = 16.2 \pm 0.4$ K. This signals development of magnetic correlations on the time scale set by the energy resolution $\tau > h/\Delta E = 6.0 \times 10^{-12}$ s. We cannot reliably estimate the size of the fluctuating U moment, since this would require integration over all energies and wave vectors. μ^+SR measurements show the onset below 13 K of correlations, which are static on a time scale of 10^{-8} s [11]. In the χ_{dc} and low-frequency ($\omega < 1157$ Hz)χ_{ac}

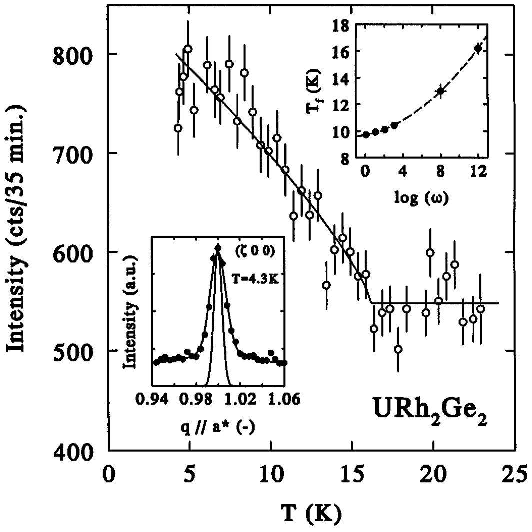

FIG. 4. Elastic neutron scattering at $Q = (1\,0\,0)$ versus temperature, showing the onset of magnetic correlations slower than 10^{-12} s below $T_f = 16.2$ K. The line is a guide to the eye. The lower inset shows a Q scan along $(a^*\,0\,0)$ at 4.3 K, corrected for background provided by similar data at 20 K, with the solid line a fit to Eq. (2), giving the magnetic correlation length. The Q resolution is also indicated. The frequency dependence of T_f, derived from ac susceptibility, μ^+SR, and neutron scattering is shown in the upper inset, over 12 decades of frequency. The line is a guide to the eye.

experiments correlations that are static on a time scale of 10^{-3} s develop only below 10 K. One of the defining characteristics of a spin glass is its frequency dependence of T_f [12]. The upper inset in Fig. 4 collects these data and shows the significant increase of T_f versus $\log(\omega)$ over 12 orders in frequency, firmly establishing the spin-glass nature of URh_2Ge_2. By employing a model assuming exponentially fast decaying spin-spin correlations, $\langle S_R^c S_{R+r_c}^c \rangle \propto \exp(-\kappa_c r_c)$ (with κ_c the inverse correlation length along the c direction), previously used for URu_2Si_2 [15], we can estimate the magnetic correlation lengths in the a (using the same formalism) and c directions. The Fourier-transformed correlation function becomes

$$\langle S_q^c S_{-q}^c \rangle = \langle S^c \rangle^2 \frac{\sinh(\kappa_c c)}{\cosh(\kappa_c c) - \cos(q_c c)} . \qquad (2)$$

The solid line through the Q scan in the lower inset of Fig. 4 is a fit to Eq. (2). This procedure yields magnetic correlation lengths of $\xi_a^m = 45 \pm 5$ Å and $\xi_c^m = 74 \pm 10$ Å, much shorter than for better-ordered URu_2Si_2 [15].

The sensitivity of the crystal structure of URh_2Ge_2 to the Rh/Ge stoichiometry resembles the now well-understood case of isoelectronic UCo_2Ge_2, where the $I4/mmm$ and $P4/mmm$ structures are formed, depending on the exact stoichiometry [1]. In the $I4/mmm$ structure, UCo_2Ge_2 orders as a long-range AF with $T_N = 175$ K. In the $P4/mmm$ structure, with much smaller unit-cell volume, no magnetic order is found down to 0.3 K. The case of URh_2Ge_2, with a c-axis length in between the two extremes of UCo_2Ge_2, thus appears to be even more subtle than UCo_2Ge_2.

The experimental properties of URh_2Ge_2 resemble the "non-Fermi-liquid-like" transport and thermodynamic properties of the *intentionally* diluted system $UCu_{5-x}Pd_x$ [16,17]. A moderately disordered Kondo model, recently proposed by Miranda *et al.* [18] successfully explains the distribution of internal fields as measured by NMR [16]. Without adjustable parameters, it can describe the susceptibility, specific heat, and scaling behavior in ω/T observed by neutron scattering [17]. Recently, indications of possible spin-glass freezing in $UCu_{5-x}Pd_x$ ($x = 1$) were found in magnetization experiments, with $T_f \simeq 100$ mK [19].

In conclusion, all the measured bulk properties of the uranium compound URh_2Ge_2 are those of an archetypal spin glass. Neutron scattering showed that short-range magnetic correlations develop on time scales of 10^{-12} s, in a highly disordered lattice. T_f increases with frequency over twelve decades, providing unambiguous proof for spin-glass behavior. To further explore the exact nature of the structural disorder in this compound, local experimental probes such as EXAFS and NMR are needed. This would allow direct comparison with the disordered Kondo model. Finally, a novel quantum critical point [9] is expected for the metallic quantum paramagnet to metallic spin-glass transition as the freezing temperature is driven towards zero with, e.g., pressure or increased disorder. Such high-pressure experiments seem favorable in URh_2Ge_2 and are presently planned.

This work was supported by the Nederlandse Stichting FOM, and CIAR and NSERC of Canada. The crystal was prepared in FOM-ALMOS. We thank R. L. Donaberger and M. D. Gauthier for technical support.

---

*Also at Van der Waals-Zeeman Laboratory, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands.

†Present address: Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands.

[1] For reviews, see V. Sechovsky and L. Havela, in *Ferromagnetic Materials,* edited by E. P. Wohlfarth and K. H. J. Buschow (North-Holland, Amsterdam, 1988), Vol. 4, p. 309; G. J. Nieuwenhuys, in *Handbook of Magnetic Materials,* edited by K. H. J. Buschow (Elsevier Science, Amsterdam, 1995), Vol. 9, p. 1; T. Endstra, S. A. M. Mentink, G. J. Nieuwenhuys, and J. A. Mydosh, in *Selected Topics in Magnetism,* edited by L. C. Gupta and M. S. Multani (World Scientific, Singapore, 1993), p. 167.

[2] S. Doniach, in *Valence Instabilities and Related Narrow-Band Phenomena,* edited by R. D. Parks (Plenum, New York, 1977), p. 169; Physica (Amsterdam) **91B**, 231 (1977).

[3] H. Ptasiewicz-Bak *et al.*, J. Phys. F **11**, 1225 (1981); Solid State Commun. **55**, 601 (1985).

[4] S. Süllow, Ph.D. thesis, Leiden University, 1996 (unpublished).

[5] J. D. Thompson *et al.*, Phys. Lett. A **110**, 470 (1985).

[6] B. Lloret *et al.*, J. Magn. Magn. Mater. **67**, 232 (1987).

[7] A. J. Dirkmaat *et al.*, Europhys. Lett. **11**, 275 (1990).

[8] Wenhao Wu *et al.*, Phys. Rev. Lett. **67**, 2076 (1991); **71**, 1919 (1993); G. F. Zhou and H. Bakker, *ibid.* **73**, 344 (1994).

[9] N. Read, S. Sachdev, and J. Ye, Phys. Rev. B **52**, 384 (1995); S. Sachdev, N. Read, and R. Oppermann, *ibid.* **52**, 10 286 (1995); A. M. Sengupta and A. Georges, *ibid.* **52**, 10 295 (1995); B. Rosenow and R. Oppermann, Phys. Rev. Lett. **77**, 1608 (1996).

[10] S. A. M. Mentink *et al.* (to be published).

[11] G. J. Nieuwenhuys *et al.* (to be published).

[12] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor & Francis, London, 1993).

[13] T. Endstra *et al.*, Physica (Amsterdam) **163B**, 309 (1990).

[14] S. Süllow *et al.*, in Proceedings of the International Conference on Strongly Correlated Electron Systems, Zürich, 1996 (to be published).

[15] C. Broholm *et al.*, Phys. Rev. B **43**, 12 809 (1991).

[16] O. O. Bernal *et al.*, Phys. Rev. Lett. **75**, 2023 (1995).

[17] M. C. Aronson *et al.*, Phys. Rev. Lett. **75**, 725 (1995).

[18] E. Miranda *et al.*, in Ref. [14].

[19] H. von Löhneysen *et al.*, in Ref. [14].