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Spin-glass behavior in $PrAu_2Si_2$

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We have studied the magnetic properties of pure $PrAu_2Si_2$. The data show the characteristic features of a canonical spin glass with a freezing temperature of $T_F = 3$ K. Thus, $PrAu_2Si_2$ is to our knowledge the first example of a pure rare-earth spin glass with well-localized magnetic moments and without any intentionally introduced disorder. Recently, Süllow *et al.* [S. Süllow, G. J. Nieuwenhuys, A. A. Menowsky, J. A. Mydosh, S. A. M. Mentik, T. E. Mason, and W. J. L. Buyers, Phys. Rev. Lett. **78**, 354 (1997)] discovered heavy-fermion spin-glass behavior in URh_2Ge_2. Our present results reveal that URh_2Ge_2 is not a unique case and that strong hybridization of the localized moments with the band states is not a necessary ingredient but that spin-glass behavior might be a much more widespread phenomenon in ternary RT_2X_2 (R = rare earth/U, T = transition metal, X = Si, Ge) compounds. However, the origin of the frustration, which is necessary to achieve a disordered ground state, still has to be elucidated in this new class of spin-glass compounds. [S0163-1829(99)50610-3]

During the last two decades, the large class (a few hundred different compounds) of RT_2X_2 (R = rare earth, T = transition metal, X = Si, Ge) intermetallics have been the subject of intense research. The magnetic properties in most of these compounds are governed by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and crystal-field (CF) effects, giving rise to various kinds of magnetic order.[1] Also more complex phenomena are found in many Ce and U compounds which reveal heavy-fermion (HF) and intermediate valence behavior including HF superconductivity.[2] Recently, Süllow *et al.*[3] discovered spin-glass (SG) behavior in URh_2Ge_2. Since the necessary conditions to achieve a spin-glass ground state are frustration and disorder, the behavior of URh_2Ge_2 is extraordinary and surprising. Usually, these intermetallics reveal a perfect periodic atomic arrangement leading to a structural stability over a very large temperature range with a strict stoichiometric ratio of 1:2:2. However, two different crystallographic structures are allowed for these compounds, differing only in their T and X positions. They crystallize either in the $ThCr_2Si_2$-type (space group I_4/mmm) (Ref. 4) or the $CaBe_2Ge_2$-type structure (space group P_4/nmm).[5] To explain the spin-glass behavior observed in URh_2Ge_2, Süllow *et al.*[3] proposed an amalgamation of these two structures, leading to a statistical distribution of the Rh and Ge positions. This in turn creates random bonds leading to competing magnetic interactions between only partially quenched moments. As will be shown in the following, URh_2Ge_2 is not a unique case and possible origins of disorder will be critically discussed. Already some years ago, Gschneidner, Jr. *et al.*[6] suggested the possible appearance of nonmagnetic disorder spin glasses in Ce and U compounds. He argued that structural disorder around the *f* atoms causes a distribution of RKKY interactions, yielding a frustrated ground state due to random bonds. Concomitantly, SG behavior and CF effects are responsible for high values of the linear term of the specific heat and therefore are often falsely interpreted as HF compounds.[6] We have studied the magnetic properties of $PrAu_2Si_2$ by x-ray and neutron diffraction, magnetic measurements, heat capacity, and electrical resistance experiments for magnetic fields up to 14 T and temperatures 0.1 K $< T <$ 300 K. The RAu_2Si_2 compounds were investigated previously by x-ray diffraction and magnetic susceptibility measurements down to 4.2 K.[7,8] For $PrAu_2Si_2$, the susceptibility data[8] showed paramagnetic behavior and the x-ray diffraction measurements revealed the $ThCr_2Si_2$-type structure. In particular, it has been reported that atomic disorder of the Au and Si atoms can be excluded.[7,8] Our samples have been synthesized by argon arc melting of the stoichiometric mixtures from commercially available high-purity elements. To assure homogeneity, the ingots were subsequently annealed for one week at $T = 1100$ K and characterized by x-ray diffraction (Guinier, Cu $K\alpha_1$ radiation). All diffraction data were analyzed by the standard Rietveld method[9] employing the FULLPROF program.[10] The x-ray diffraction pattern showed the well known $ThCr_2Si_2$-type structure. The refinement with a corresponding R value of 7% resulted in lattice constants of $a = 4.297(1)$ Å, $c = 10.202(1)$ Å, and lattice parameter $z = 0.368(3)$ Å. These values are in good agreement with the results of the early x-ray studies on $PrAu_2Si_2$.[7,8]

The polycrystalline samples were finely powdered and investigated by neutron diffraction on the multidetector diffractometer DN5 at the Siloë reactor of the Centre d'Etudes Nucléaires (CEN), Grenoble. An incident wavelength of $\lambda = 2.494$ Å has been selected by a pyrolythic graphite monochromator. Diffraction patterns were recorded at $T = 1.5$, 20, and 40 K. The nuclear intensities could be successfully refined with R values of 5% assuming the fully

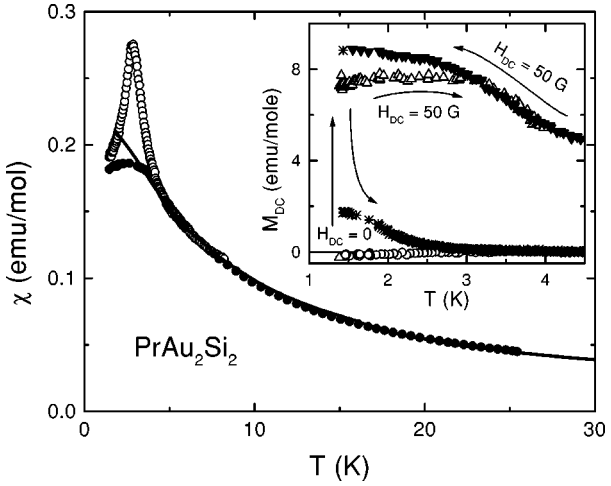

FIG. 1. Temperature dependence of the magnetic susceptibility in a driving field of 0.1 G (open circles), 10 G (full circles), and dc magnetization in an external applied field of 5000 G (solid line) of $PrAu_2Si_2$. The inset shows the field cooled (FC) and zero-field-cooled (ZFC) magnetization in with respect to temperature.

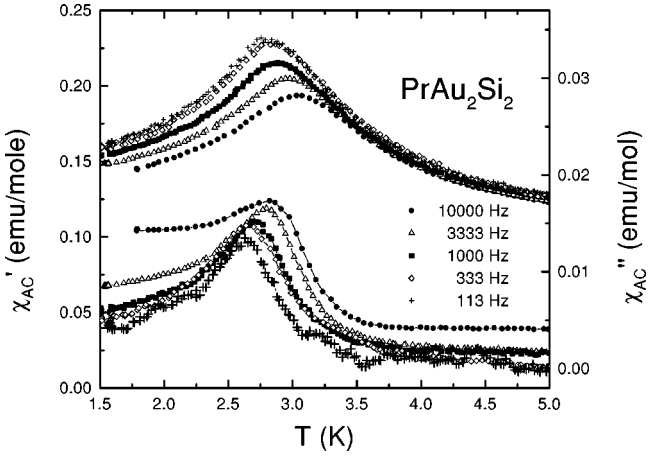

FIG. 2. Real and imaginary part of the magnetic susceptibility of $PrAu_2Si_2$ for different frequencies.

ordered $ThCr_2Si_2$-type structure as described above. By subtracting the high-temperature (paramagnetic) from the low-temperature (usually magnetically ordered) intensities, the nuclear Bragg peaks cancel, leaving the intensities of magnetic origin only. No magnetic Bragg peaks could be observed for $PrAu_2Si_2$ revealing the absence of long-range magnetic order.

To explore the origin of the SG state we searched for disorder of Au and Si. A statistical distribution of Au and Si atoms among the $4(d)$ and $4(e)$ sites of the $ThCr_2Si_2$-type structure most strongly effects the intensity of the (112), but only slightly the intensity of the (200) reflection. Hence, we calculated the experimentally observed intensity ratio $I_{(112)}/I_{(200)}$ and compared it to the ratio of the ideal $ThCr_2Si_2$-type structure. From these values we determined a significant fraction of approximately 10% of our samples displaying disorder between Au and Si.

Magnetic susceptibility measurements have been performed in an ac susceptometer in fields up to 14 T between 1.8 K and room temperature and a superconducting quantum interference device (SQUID) magnetometer in fields up to 7 T and temperatures $1.8\,\mathrm{K} < T < 400$ K. Figure 1 shows the temperature dependence of the magnetic susceptibility. A sharp peak at $T = 2.7$ K is observed with a driving field of 1 G (open circles in Fig. 1). This peak is considerably broadened when increasing the driving field to 40 G. In an external applied field of 5000 G, the anomalous behavior completely disappeared (solid line in Fig. 1). From the high-temperature Curie part of the susceptibility, a paramagnetic moment of $\mu_{eff} = 3.51\mu_B$ with a corresponding Curie-Weiss temperature of $\Theta = -7.05$ K has been determined, in agreement with Ref. 8. The value of the paramagnetic moment is very close to the Pr^{3+}-free ion value of $3.58\mu_B$ and the negative Curie-Weiss temperature points towards antiferromagnetic interactions. It should be noted that the susceptibility can be fitted by a Curie-Weiss behavior starting immediately above T_F. This indicates that the full paramagnetic moment, almost identical with its free ion value, persists almost down to the SG transition.

A characteristic phenomenon of spin glasses is the splitting of the field-cooled (FC) and zero-field-cooled (ZFC) magnetization.[11] In $PrAu_2Si_2$ the irreversibility sets in at $T = 3$ K which defines the quasistatic freezing temperature of a spin-glass system. The cusp of the FC magnetization of $PrAu_2Si_2$ around T_F is not as pronounced as in classical spin-glass systems, e.g., CuMn.[11] The inset of Fig. 1 displays a complete magnetization cycle: First ZFC (open circles), then switching on the field ($B = 50$ G) and heating up in field (open triangles), cooling down again in field (FC, closed triangles) and finally switching off the field and heating up again (stars). If one switches off the field, the remaining signal corresponds to the isothermal remanence magnetization (IRM). At $T = 1.5$ K, we fitted the IRM assuming a stretched exponential decay. We determined a mean relaxation time $\tau = 2 \times 10^3$ s and a stretching exponent $\beta = 0.95$ which signals almost exponential decay.

Figure 2 shows the real and imaginary part of the susceptibility at different frequencies in an excitation field of 50 G. The maximum of χ''_{ac} corresponds to the mean relaxation rate and determines $T_F(\nu)$. The frequency shift of the susceptibility maximum can well be described by an Arrhenius behavior with an energy barrier $E_B/k_B = 147$ K and an attempt frequency $\nu_0 = 3 \times 10^{26}$ Hz. The unnaturally high value of the attempt frequency signals that strong cooperative phenomena are the driving forces for the freezing-in process. These magnetic measurements reveal canonical spin-glass behavior in $PrAu_2Si_2$.

Figure 3 shows the specific heat of $PrAu_2Si_2$ as a function of temperature. A broad maximum can be seen at 3.5 K, which is smeared out in high applied fields. At low temperatures, c_p is independent of field. The extrapolation of the linear part (c_p versus T^2) for $T \to 0$ results in a Sommerfeld coefficient of $\gamma = 102$ mJ/mol K^2. At $T = 10$ K, well within the paramagnetic state, the corresponding magnetic entropy reaches less than half of the value of the full ninefold degeneracy of a $J = 4$ Pr^{3+} ion. The large electronic specific heat in $PrAu_2Si_2$ is usually indicative of heavy-fermion behavior. A similar behavior has been found in $PrCu_2Si_2$ and was interpreted as a realization of the quadrupolar Kondo effect.[12] However, a detailed inelastic neutron scattering study favored an explanation in terms of CF-wave functions only.[13] The enhanced linear part of the specific heat in $PrAu_2Si_2$ is

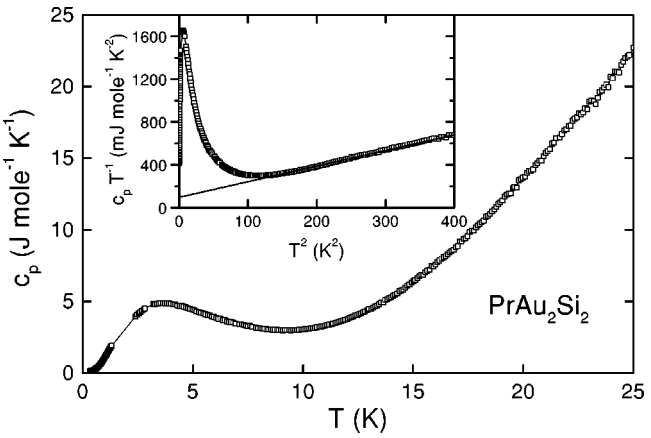

FIG. 3. Specific heat of $PrAu_2Si_2$. In the inset c_p/T vs T^2 and in the lower part c_p vs T^2 is shown.

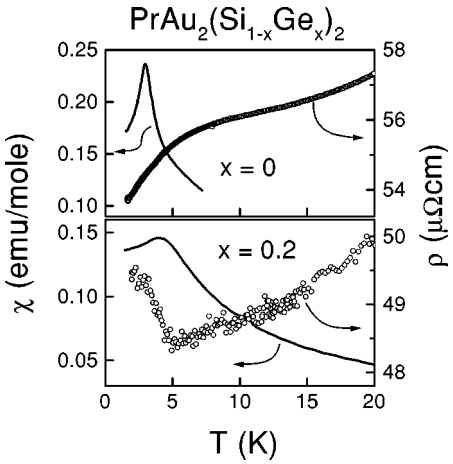

FIG. 4. Temperature dependence of the electrical resistivity and magnetic susceptibility of $PrAu_2Si_2$ and $PrAu_2(Si_{0.8}Ge_{0.2})_2$.

probably caused by magnetic correlations and/or CF effects. The effect of low-lying CF levels as well as the effect of structural disorder leading to similar properties as the formation of a heavy fermion state is described in Ref. 6. The value of the magnetic entropy at $T=10$ K suggests a threefold (quasi-) degenerate state (in tetragonal environment, the $J=4$ state of a Pr^{3+} ion is split into five singlets and three doublets). Inelastic neutron spectroscopic measurements are needed to determine the CF level scheme and further elucidate the magnetic properties of $PrAu_2Si_2$.

To explain the necessary disorder in URh_2Ge_2 which forces a low-temperature spin-glass state, Süllow *et al.* proposed a mixture of the two possible crystallographic structures.[3] Gschneidner, Jr. *et al.*[6] accounts for nonmagnetic atomic disorder in compounds with a perfect periodic lattice of rare-earth or U ions. We want to mention two facts which raise some questions concerning the random bond interpretation: (i) As stated above, in the present case of $PrAu_2Si_2$, only modest disorder of Au and Si ions could be detected with approximately 10% of these ions occupying the other site of the $ThCr_2Si_2$-type structure. It is unclear whether this level of disorder is sufficient to explain a low-temperature spin glass. If so, it demonstrates that even in the case of well-localized spins and a conventional RKKY interaction the local environment plays a crucial role in transferring magnetic interactions to neighboring spins. (ii) We increased the nonmagnetic disorder by substituting Ge for Si. Astonishingly we found that already alloying 15% Ge induces long-range magnetic order. Neutron powder diffraction revealed resolution limited magnetic Bragg peaks for all compounds with still higher Ge concentration.[14] As an example we show in Fig. 4 the temperature dependence of the resistivity and magnetic susceptibility for $PrAu_2Si_2$ and $PrAu_2(Si_{0.8}Ge_{0.2})_2$. Experimentally, due to the competition of the RKKY and the Kondo interaction a peak in the ''magnetic part'' of the resistivity is expected for $T>T_F$. This is what we really observe for $PrAu_2Si_2$. For the Ge-doped system, a strong increase in $\rho(T)$ signals a transition into an antiferromagnetic phase. An increase of $\rho(T)$ at T_N is often observed in rare-earth compounds and indicates that the Fermi surface becomes partly gapped at T_N.

A comparison with other 1:2:2 rare-earth compounds is intriguing. Rossi *et al.*[15] confirmed the particular behavior of RPt_2Si_2 compounds, showing a random distribution of Pt and Si ions, independent of sample preparation conditions (annealed or as grown samples) as has been first reported by Mayer and Yetor.[16] A detailed study later on[17] favored a crystallization into the $CaBe_2Ge_2$-type structure. For $R=$Ce, a new structure type with space group P_4 has been proposed in Ref. 16 and furthermore an amount of disorder at the level of 5% has been found. It is interesting to note that for several rare-earth elements, the corresponding Pt silicides show no sign of long-range magnetic order. In contrast, for the corresponding Au compounds a fully ordered $ThCr_2Si_2$-type structure has been found.[15] A further interesting example are the Ni arsenides.[18] They crystallize in both the $ThCr_2Si_2$- *and* the $CaBe_2Ge_2$-type structures depending on the exact stoichiometry.[18] These compounds are extremely sensitive to any variation of the sample preparation conditions. For nominal concentration, the samples revealed a coexistence of both structures but structural disorder was never observed. Even in that extreme case, the mixture of the two crystallographically allowed structures means a coexistence of two fully ordered phases.[18]

To conclude, the present results reveal unambiguously a spin-glass transition at a freezing temperature of $T_F=3$ K in $PrAu_2Si_2$. It is an example of a pure rare-earth compound with well-localized spins showing SG behavior without any intentionally introduced disorder (neither doping nor rapid quenching nor cold working[19]). We emphasize that most probably the nonmagnetic disorder is responsible for the frustrated ground state. However, it may be that the competition between Kondo effect and RKKY interaction plays in addition a crucial role for the SG transition. There are a number of compounds of this family considered to be nonmagnetic and/or at the border of magnetic order. They should be reexamined on behalf of a possible spin-glass formation. However, the origin of disorder leading to a SG state in 1:2:2 compounds still has to be revealed by future work.

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[1] For review see, for example, A. Szytula and J. Leciejewiz, in *Handbook on the Physics and Chemistry of the Rare Earth*, edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier Science, Amsterdam, 1989), Vol. 12, p. 133.

[2] For review see, for example, N. Grewe and F. Steglich, in *Handbook on the Physics and Chemistry of the Rare Earth,* edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier Science, Amsterdam, 1991), Vol. 14, p. 343; G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).

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