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Random spin freezing in uranium intermetallic compound UCuSi

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Abstract
The results of low-temperature ac susceptibility, dc magnetization, magnetic relaxation, specific heat, and electrical resistivity measurements on the uranium intermetallic compound UCuSi, a hexagonal $CeCd_2$-type non-magnetic atom disorder system, are reported. The results establish that a spin-glass state is formed in this compound at low temperature. Some dynamical parameters characterizing the spin freezing state of this system, such as static spin freezing temperature T_s, critical exponent $z\nu$, and activation energy E_a, are determined from dynamical analysis of the ac susceptibility data. The observed properties are discussed based on a magnetic cluster model.

1. Introduction

Spin-glass (SG) behaviour found in some non-magnetic atom disorder (NMAD) systems with concentrated magnetic atoms has attracted much attention in recent years. In these compounds, the magnetic atoms form a fully periodic lattice but the remaining non-magnetic atoms exhibit some disorder in their arrangement in the ligand sites. Such a structural character, i.e., geometrical order of magnetic atoms and chemical disorder of non-magnetic atoms, is clearly different from that in amorphous or diluted metallic SG materials. Thus, how to understand the origin of SG behaviour in these compounds is a very interesting problem. The uranium equiatomic compound UCuSi was reported to be an NMAD system with the hexagonal $CeCd_2$-type crystal structure (space group $P\bar{3}m1$) [1]. To the best of our knowledge, only three research works on this system with respect to its physical properties have been reported to date [2–4]. The evident bifurcation between field-cooled (FC) and zero-field-cooled (ZFC) dc susceptibilities was first observed by Tran *et al*, and thus UCuSi was considered to be a new concentrated SG material (with SG transition temperature $T_f \sim 52$ K), even though a similar behaviour can also be manifested by a ferromagnet with a strong domain-wall-pinning effect [2]. This viewpoint is supported by the neutron diffraction results, where no long-range magnetic order was observed at 4.2 K [3]. Otherwise, strong sample dependence of magnetic properties of UCuSi was reported by Pechev *et al*. Some SG behaviours were observed only for their nonstoichiometric sample (namely $UCu_{0.84}Si_{1.16}$ with AlB_2-type structure and $T_f =$ 43 K) [4]. To obtain the definitive evidence for the formation of SG state in UCuSi, we have systemically measured the ac susceptibility $\chi_{ac}(T)$ at various frequencies, dc magnetization $M(T)$ in various magnetic fields, magnetic relaxation $M(t)$ at different temperatures, high field magnetization $M(H)$, electrical resistivity $\rho(T)$ and specific heat $C(T)$ on a well annealed UCuSi sample. In this paper, we present our detailed experimental results, and discuss the observed properties in terms of a cluster glass model.

2. Experimental details

A polycrystalline sample of the UCuSi compound was prepared by arc melting of high-purity uranium (3N), copper (5N) and silicon (6N) elements in purified argon atmosphere. The button was flipped over and remelted several times to ensure homogeneity. The reaction product was then wrapped in tantalum foil and annealed in an evacuated silica tube at 650 °C for 168 h. X-ray powder diffraction was performed at room temperature with Cu Kα radiation to check the sample quality and to determine the crystal structure. We found that the obtained UCuSi sample shows the AlB_2-type derivative structure. The diffraction lines can be indexed based on the hexagonal $CeCd_2$-type structure model (space group $P\bar{3}m1$) with U atoms on the 1a sites and Cu and Si atoms statistically distributed over the 2d sites. No impurity phase can be detected. The ac susceptibility, low-field dc magnetization, and magnetic relaxation were measured using a SQUID magnetometer. A high-field magnetization experiment up to 115 kOe was carried out at 5 K using a vibrating sample magnetometer (VSM). The adiabatic heat pulse method was employed for specific heat measurement. The electrical resistivity measurement was performed using a standard four-terminal dc method.

3. Experimental results and analysis

The temperature dependence of magnetization $M(T)$ of UCuSi was measured in various applied magnetic fields (H) employing both the ZFC and FC conditions. In this paper we call M/H the dc susceptibility and denote it as χ $(=M/H)$. Figure 1 presents the $\chi_{ZFC}(T)$ and $\chi_{ZFC}^{-1}(T)$ data up to 300 K in a field of $H = 100$ Oe. Above 110 K, the reciprocal susceptibility curve could be well fitted using the Curie–Weiss law $\chi = C/(T-\theta_p)$ (dashed line of figure 1), where C is the Curie constant and θ_p the paramagnetic Curie temperature. From this fit, the effective magnetic moment and the paramagnetic Curie temperature are determined to be $\mu_{eff} = 2.99\mu_B$ per U ion, and $\theta_p = 22.7$ K, respectively. The obtained μ_{eff} value is smaller than that ($\mu_{eff} \sim 3.6\mu_B$/U) expected for a free U ion with f^2 or f^3 electronic configuration, suggesting the itinerant behaviour of 5f electrons and/or Kondo effect in this compound. The positive sign of θ_p suggests the ferromagnetic exchange interaction to be dominant. With decreasing temperature, the $\chi_{ZFC}(T)$ curve shows a sharp peak near $T_0 \sim 46$ K, suggesting a certain kind of magnetic phase transition at this temperature.

The temperature dependence of FC and ZFC susceptibility of UCuSi was also measured in various magnetic fields around the transition temperature. As shown in figure 2, the FC curve is reversible, traces the same path independent of the time of the measurement, and has a tendency to approach a constant value at low temperature. In contrast, the ZFC curve separates from the FC one at a characteristic temperature T_{ir} (indicating the appearance of magnetic irreversibility), and exhibits an irreversible behaviour dependent on the elapsed time and the cooling and heating history below T_{ir}. Up to 10 kOe, a cusplike maximum can be

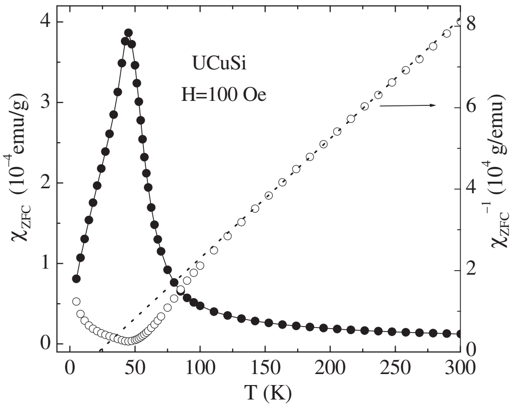

Figure 1. DC susceptibility χ $(=M/H)$ and reciprocal susceptibility χ^{-1} $(=H/M)$ as a function of temperature for UCuSi measured in the ZFC mode in a magnetic field of 100 Oe. The dashed line shows the fitting result using the Curie–Weiss law.

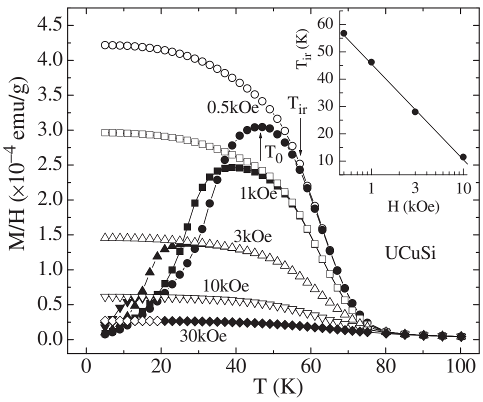

Figure 2. DC susceptibility χ $(=M/H)$ data for UCuSi measured in the FC (open symbols) mode and in the ZFC (closed symbols) mode in various magnetic fields. The inset shows the field dependence of the characteristic temperature T_{ir}.

observed in the $\chi_{ZFC}(T)$ curve at a strongly field dependent temperature T_0. With increasing H, the peak in the $\chi_{ZFC}(T)$ curve loses intensity and broadens and both T_0 and T_{ir} shift to low temperatures. As the typical features of SG materials, the magnetic irreversibility (manifesting as a bifurcation between the $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ curves) and the strong field dependences of peak position and peak intensity in $\chi_{ZFC}(T)$ signify the formation of the SG state in the UCuSi sample. It is interesting to note that similar bifurcation between $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ curves has also been observed by Tran *et al* and has been considered to originate from the SG freezing effect [2]. However, their data reveal that T_{ir} is almost identical with T_0 (denoted as T_f in [2]), $\chi_{FC}(T)$ tends to be nearly constant below T_f, and the field dependence of T_f between 0.5 and 5 kOe follows approximately the Almeida–Thouless law (AT line: $T_f \propto -H^{2/3}$) [5, 6] as usually observed in a canonical SG system. A finding of emphasis here is that the characteristic temperature T_{ir} for our UCuSi sample is evidently larger than T_0 under low applied fields. In addition, the variation of T_{ir} with H does not follow the Almeida–Thouless law; a logarithmic function seems to be much better for describing the $T_{ir}(H)$ behaviour in the field range

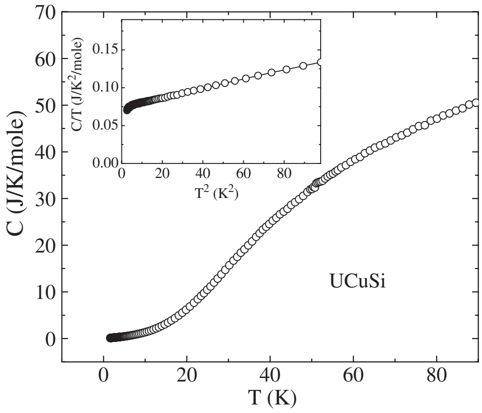

Figure 3. Temperature dependence of specific heat $C(T)$ of UCuSi. The inset shows the plot of C/T versus T^2.

measured (see the inset of figure 2). In this sense, our UCuSi sample is different from the canonical (simple) SG materials; its magnetic properties could be more accurately described as cluster glass behaviours (see the following).

In order to confirm whether or not a long-range magnetic order occurs around T_0, where ZFC susceptibility shows an evident peak, the temperature dependence of specific heat between 1.6 and 90 K was measured in this study. It is clear from figure 3 that the specific heat increases monotonically with T, and no singularity can be detected at T_0 ($\sim$46 K). This result suggests the absence of long-range spatial magnetic order in the vicinity of T_0, consistent with the neutron diffraction results [3]. Thus, the observed sharp peak in the $\chi_{ZFC}(T)$ curve at T_0 as well as the thermomagnetic irreversibility below T_0 can be considered to originate from the random spin freezing in a SG state. Note that, to take more experimental data around T_0, the parameters used in the specific heat measurement program were changed when the specific heat was measured near T_0. This operation results in the small 'blip' in the data around 50 K. At low temperatures, the C/T versus T^2 plot (inset of figure 3) yields for $T \rightarrow 0$ K a large Sommerfield coefficient ($\gamma \sim 75$ mJ (mol-U)$^{-1}$ K^{-2}) like that usually observed in a common SG material or a heavy-fermion compound, suggesting the influence of NMAD structure and possible Kondo effect in this compound. It is well known that, for spin glasses, the *magnetic specific heat* usually makes a broad contribution around the temperature exceeding T_f (spin freezing temperature) by about 20–40%. For UCuSi, the magnetic contribution to the observed total specific heat is not determined in this work, because no specific heat data of a corresponding nonmagnetic compound can be used to estimate the lattice contribution at present. On the other hand, since the low-temperature magnetic specific heat of an SG system is also linear in T, the lattice contribution can also be calculated over the entire temperature range using the Debye temperature (θ_D) roughly estimated from the slope of the C/T versus T^2 plot at low temperatures. However, this method is used very little, because it neglects the crystal-field effect and the obtained θ_D value depends strongly on the temperature range of the data used in the fit. Thus the calculated lattice specific heat in this method has a large uncertainty.

Figure 4 shows the electrical resistivity measurement of UCuSi down to 0.5 K. With decreasing temperature, a broad peak is observed around 50 K, which may result from SG freezing and/or the coherent Kondo state as usually observed in uranium compounds. Note that the appearance of a broad maximum in $\rho_m(T)$, the *magnetic part* of resistivity, around the spin freezing temperature is one of the characteristic features of the diluted metallic spin glasses [7].

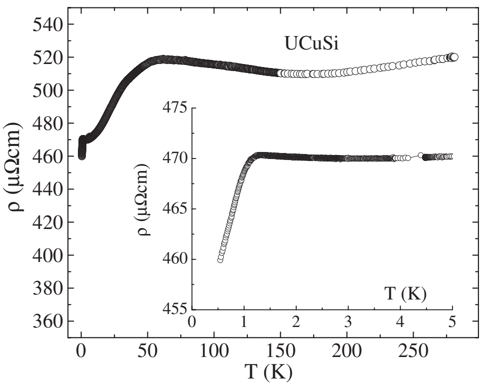

Figure 4. Temperature dependence of electrical resistivity of UCuSi. The inset shows the low temperature part.

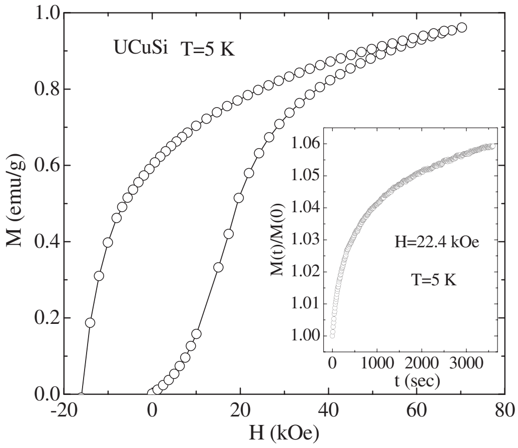

Figure 5. Magnetization $M(H)$ up to 70 kOe measured at 5 K for UCuSi. The inset displays the magnetization $M(t)$ as a function of time t (plotted as $M(t)/M(0)$ versus t) in a magnetic field of 22.4 kOe measured at the same temperature for the same sample.

Such a behaviour is also a common feature of uranium compounds and usually attributed to the transition from a single Kondo-ion-like scattering at high temperature to a coherent Kondo state at low temperature. The surprise is that, when the temperature is further decreased down to 1.2 K, the $\rho(T)$ curve manifests a sudden drop (see the inset of figure 4 with the expanded scales), like that usually observed for a superconductor or a long-range magnetic order system at the Curie or Néel point. To confirm whether this drop is intrinsic to this compound or is of impurity origin, $\rho(T)$, $C(T)$ and $\chi(T)$ measurements at much lower temperatures in applied magnetic field are necessary and in progress. In this paper, we concentrate mainly on the spin freezing behaviour appearing at higher temperatures.

Magnetization $M(H)$ and magnetic relaxation $M(t)$ measurements shown in figure 5 for UCuSi also reveal the typical features of the SG state: at 5 K, $M(H)$ increases monotonically with increasing H up to 70 kOe, while an evident hysteresis effect and a remanent magnetization of about 0.6 emu g^{-1} is detected when H is returned from 70 kOe to zero. Actually, the high-field magnetization measured at 5 K by using a VSM reveals that

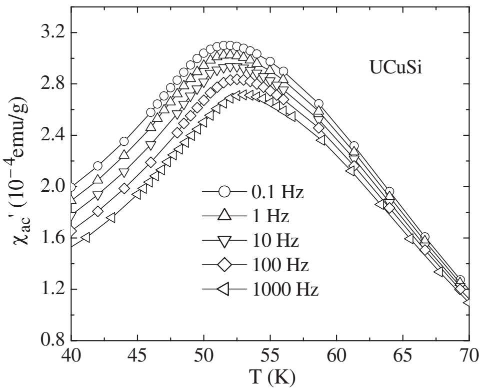

Figure 6. Real component ($\chi'_{ac}(T, \omega)$) of the ac susceptibility of UCuSi versus temperature at various frequencies.

the complete saturation of $M(H)$ is not achieved up to 115 kOe (not shown here). From figure 5 the coercive field H_C of UCuSi is determined to be 16 kOe at 5 K. At this temperature we investigated the magnetic relaxation behaviour of the UCuSi sample by measuring the time dependence of magnetization in a constant field $H = 22.4$ kOe ($\gg H_C$). The sample was first cooled in zero field from 200 to 5 K, then a field of 22.4 kOe was applied, and the recording started immediately just as the field stabilized ($t = 0$). As seen from the inset of figure 5, $M(t)$ increases continuously as a function of time t. After waiting for one hour, $M(t)$ is still far from saturation. For this sample, magnetic relaxation on macroscopic timescales has also been observed by measuring the isothermal remanent magnetization $M_{IRM}(t)$ at different temperatures below T_{ir} when there are changes of the magnetic field (not shown here). Note that the occurrence of long-time magnetic relaxation behaviour *even in an applied magnetic field much larger than the coercive field* is one of the distinctive features of SG materials [8–10].

In order to obtain the definitive evidence for an SG state in UCuSi, the frequency dependence of ac susceptibility was measured. The results of the in-phase component $\chi'_{ac}(T, \omega)$ for different frequencies $0.1 \leqslant \omega/2\pi \leqslant 1000$ Hz in the temperature range between 40 and 70 K are shown in figure 6. It is clear that the χ'_{ac} curve exhibits a pronounced maximum that shifts towards higher temperatures with increasing frequency. This is the most typical behaviour characterizing SG materials. In this work, the frequency dependent spin freezing temperature T_f is defined as the peak point in χ'_{ac} curve, which increases from 51.7 K at $\omega/2\pi = 0.1$ Hz to 53.2 K at $\omega/2\pi = 1000$ Hz. The frequency shift rate of the peak position is determined to be $\delta T_f = \Delta T_f/(T_f \Delta \log \omega) = 0.007$. This value is much smaller than those determined for typical superparamagnets and comparable to the values reported for many SG systems (for most spin glasses the δT_f values are usually observed from a few thousandths to a few hundredths) [11]. To estimate the dynamical parameters characterizing the SG state of this UCuSi sample, we have fitted the obtained $T_f(\omega)$ data to the standard expression $\tau_{max} = \tau_0[(T_f - T_s)/T_s]^{-z\nu}$ (critical slowing down) [12, 13] and to the Vogel–Fulcher law [14, 15] $\omega = \omega_0 \exp[-E_a/k_B(T_f - T_{vf})]$. It is known that the typical value of critical (dynamical) exponent $z\nu$ is about 4–12 for different SG materials [11]. The fit using the equation of critical slowing down yields $z\nu = 7.43$ and the static freezing temperature $T_s = 51.1$ K, while the fit using the Vogel–Fulcher law yields the Vogel–Fulcher temperature $T_{vf} = 48.0$ K and the activation energy $E_a \approx 2.34\ k_B T_s$ for our UCuSi sample. Here, a characteristic value of $\tau_0 = 2\pi/\omega_0 = 10^{-13}$ s was used [16–18]. These results clearly indicate the formation of the SG state in the UCuSi sample.

It is commonly accepted that both randomness and frustration of magnetic moments are necessary to produce an SG state [11]. Random spin freezing behaviour in diluted metallic SG material (RKKY spin glass) is generally explained to originate from the random distribution of magnetic atoms, which causes frustration of magnetic moments by the medium of interatomic distance dependent RKKY exchange interaction. For an NMAD compound, however, since the magnetic atoms form a fully periodic lattice, random change of the distance between magnetic atoms does not exist. Recently, we have put forward a cluster-glass model to explain the SG behaviour found in a new NMAD SG system U_2AuGa_3 [19]. We believe that a similar mechanism is also essential to the random spin freezing state in UCuSi. As described above, our UCuSi sample is also an NMAD system, which shows the hexagonal $CeCd_2$-type crystal structure with a complete order of U atoms on the 1a sites and a random distribution of Cu and Si atoms on the 2d sites. The disorder of non-magnetic Cu and Si atoms in the crystal lattice could destroy the long-range magnetic correlation between U atoms and results in the formation of individual spins or finite-size granules with net magnetic moments (magnetic clusters). At low temperature these randomly distributed clusters could interact with each other, causing the formation of frustrated magnetic moments as in the case of diluted metallic SG material. In this sense, the UCuSi sample should be considered as a cluster glass. This viewpoint is supported by the above-mentioned dc susceptibility measurements which show that the low-field ZFC susceptibility curve separates from the FC one at a characteristic temperature T_{ir} clearly larger than the peak point T_0 in $\chi_{ZFC}(T)$ curve (maybe due to the influence of superparamagnetism), and a logarithmic function can well describe the variation of T_{ir} with applied field instead of the Almeida–Thouless law. Note that, for most canonical SG materials, T_{ir} is almost equal to T_0 even for very low magnetic field, while the variation of T_{ir} with H follows the Almeida–Thouless law [9, 11].

Summarizing, we have investigated the magnetic, transport and thermal properties of the uranium intermetallic compound UCuSi. At low temperatures, the up-shift of the ac susceptibility peak with increasing frequency, the down-shift of the ZFC dc susceptibility peak with increasing magnetic field, the long-time magnetic relaxation behaviour, and the clear irreversible magnetism are observed. These features suggest the occurrence of random spin freezing in this UCuSi sample as usually observed in an SG material. In particular, to characterize the spin freezing state, static spin freezing temperature T_s, critical exponent $z\nu$, and activation energy E_a of UCuSi are determined in this work from the dynamical analysis of the ac susceptibility data. Moreover, specific heat measurement provides a new evidence for the lack of long-range magnetic ordering in the vicinity of T_s. In low field, irreversible magnetism is found to happen at the temperature T_{ir} clearly larger than the peak temperature in the $\chi(T)$ curve, and the variation of T_{ir} with H does not follow the Almeida–Thouless law. These behaviours could be understood in the framework of a magnetic cluster model. It is interesting to note that magnetic properties of UCuSi seem to depend strongly on its deviation from the stoichiometry, in particular in the vicinity of the composition 1:1:1 as advocated by Pechev *et al* [4]. Similar strongly sample dependent magnetic properties have been reported for UCuGe [2, 20, 21]. In this sense, further experimental works on UCuSi starting from the challenge of high-quality single-crystal growth are necessary.

References

[1] Zygmunt A 1976 *Proc. 2nd Int. Conf. on Electronic Structure of Actinides (Wrocław, Poland)* p 335
[2] Tran V H and Troć R 1990 *J. Magn. Magn. Mater.* **86** 231
[3] Leciejewicz J, Szytula A and Zygmunt A 1991 *J. Magn. Magn. Mater.* **97** 219
[4] Pechev S, Chevalier B, Darriet B and Etourneau J 1999 *J. Alloys Compounds* **282** 44

[5] Almeida J R L de and Thouless D J 1978 *J. Phys. A: Math. Gen.* **11** 983
[6] Pöttgen R P, Tran V H, Hoffmann R D, Kaczorowski D and Troc R 1996 *J. Mater. Chem.* **6** 429
[7] Ford P J and Mydosh J A 1976 *Phys. Rev.* B **14** 2057
[8] Majumdar S, Sampathkumaran E V, Eckert D, Handstein A, Müller K H, Saha S R, Sugawara H and Sato H 1999 *J. Phys.: Condens. Matter* **11** L329
[9] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
[10] Folks L and Street R 1994 *J. Appl. Phys.* **76** 6391
[11] Mydosh J A 1993 *Spin Glass: An Experimental Introduction* (London: Taylor and Francis)
[12] Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435
[13] Gunnarsson K, Svedlindh P, Nordblad P, Lundgren L, Aruga H and Ito A 1988 *Phys. Rev. Lett.* **61** 754
[14] Vogel H 1921 *Z. Phys.* **22** 645
[15] Fulcher G S 1925 *J. Am. Ceram. Soc.* **8** 339
[16] Tholence J L 1980 *Solid State Commun.* **35** 113
[17] Prejean J J 1978 *J. Physique* **39** C6 907
[18] Dho J, Kim W S and Hur N H 2002 *Phys. Rev. Lett.* **89** 27202
[19] Li D X, Yamamura T, Nimori S, Yubuta K and Shiokawa Y 2005 *Appl. Phys. Lett.* **87** 142505
[20] Tran V H, Zaleski A J, Troć R and du Plessis P de V 1996 *J. Magn. Magn. Mater.* **162** 247
[21] Li D X and Shikawa Y 2002 *J. Nucl. Sci. Technol.* (Suppl.3) 164