Spin-cluster glass state in $U(Ga_{0.95}Mn_{0.05})_3$*

Dong-Hua Xie(谢东华)[1,2], Wen Zhang(张文)[2], Yi Liu(刘毅)[2], Wei Feng(冯卫)[2], Yun Zhang(张云)[2], Shi-Yong Tan(谭世勇)[2], Xie-Gang Zhu(朱燮刚)[2], Qiu-Yun Chen(陈秋云)[2], Qin Liu(刘琴)[2], Bing-Kai Yuan(袁秉凯)[2], and Xin-Chun Lai(赖新春)[2,†]

[1] *Beijing Institute of Technology, Beijing* 100081, *China*
[2] *Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang* 621700, *China*

(Received 28 October 2015; revised manuscript received 4 December 2015; published online 25 February 2016)

We report the study of a low temperature cluster glass state in 5% Mn-doped UGa_3 heavy fermion compound. This compound transforms from a paramagnetic state to a spin-cluster glass state, which is confirmed by measuring the dc susceptibility and magnetization. The ac susceptibility exhibits a frequency-dependent peak around T_f, which provides direct evidence of the cluster glass state. By analyzing the field-dependent magnetization and frequency-dependent ac susceptibility in detail, we deduce that this compound forms a spin-cluster glass state below T_f.

Keywords: spin-cluster glass, $U(Ga_{0.95}Mn_{0.05})_3$, magnetic properties

PACS: 75.50.Lk, 75.40.Gb, 65.40.Ba **DOI:** 10.1088/1674-1056/25/4/047502

1. Introduction

The uranium compounds of the UX_3 series (X: a group-IIIA or IVA element in the periodic table) present various interesting magnetic behaviors from an enhanced, Pauli-like paramagnetism (UAl_3, USi_3, and UGe_3), through local spin fluctuations (USn_3), to a local-moment ordering (UPb_3). A great variety of magnetic properties in the UX_3 series are commonly attributed to a hybridization effect between the 5f-electron states of uranium and the s, p, d electronic states of neighboring atoms. The antiferromagnetic compound UGa_3 ($T_N = 67$ K),[1–3] crystallizing in the $AuCu_3$ structure, locates a special position at the onset of magnetic order among the UX_3 phase. The substitution of the group-IIIA (or group-IVA) element for Ga atoms in UGa_3 exhibits interesting magnetic properties through the changes of the hybridization between the uranium 5f electronic states and the conduction electronic states of gallium. For example, with increasing Sn concentration, the f electrons in the $UGa_{3-x}Sn_x$ system undergo a transition from the itinerant antiferromagnetic state to a typical spin fluctuation state, and finally localize for $x \sim 1$.[4] While in $UGa_{3-x}Ge_x$, the substitution of Ge atoms gradually suppresses the long range magnetic order, and reaches the quantum critical point at $x \sim 0.6$, which presents non-Fermi liquid behavior.[5]

Similarly, the hybridization effect would be changed by the substitution of UGa_3 in the transition metal for Ga atoms since it not only changes the order degree of the occupied atom, but also prominently changes the exchange interactions through changes of environment (the valence electrons and the U–U distance). This concept motivated us to investigate the properties of Mn-doped UGa_3, which present the spin-cluster glass (SCG) state at a low temperature. This compound plays an important role in better understanding the f-electron contributions to the magnetism in uranium compounds.

2. Experiment

Single crystals of $U(Ga_{0.95}Mn_{0.05})_3$ were grown by the Ga self-flux method.[6,7] The raw materials of U (99.8%), Mn (99.999%), and Ga (99.9999%) were mixed together according to the ratio of U:Mn:Ga = 1:(0.5∼2):10. The feed, placed in an alumina crucible and sealed in an evacuated quartz tube, was heated in a resistance furnace up to 1200 °C, held at this temperature for 24 h and then slowly cooled down to 600 °C at a rate of 1 K/h. Then, the single crystals were separated from the flux by means of centrifuging at 600 °C. The obtained crystals were a cube shape with a maximum dimension of 2 mm×2 mm×3 mm.

The actual compositions of the obtained crystals were determined by utilizing energy dispersive x-ray (EDX) microanalysis. All the single crystals prepared by different ratios present the same atomic ratio of U:Ga:Mn, which is 1:2.85:0.15. X-ray diffraction (XRD) was performed on the single crystals and their crushed powder by a diffractometer in a range from 10° to 90°. The frequency-dependent ac-susceptibility and low-field magnetization were measured by using a quantum design physical properties measurement system (PPMS). Specific heat experiments were performed in a temperature range of 2 K–200 K on the PPMS using the relaxation method.

*Project supported by the Natural Science Foundation of China Academy of Engineering Physic (Grant No. 2014A0301013) and the National Natural Science Foundation of China (Grant Nos. 11304291 and 11504342).

†Corresponding author. E-mail: laixinchun@caep.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

3. Results and discussion

Figure 1(a) shows the powder and single crystal XRD patterns for both $U(Ga_{0.95}Mn_{0.05})_3$ and UGa_3 samples, which can be indexed on the basis of $AuCu_3$ type structure (Fig. 1(b)). All the powder diffraction peaks of $U(Ga_{0.95}Mn_{0.05})_3$ shift to a high angle compared with UGa_3 due to the small ionic radius of Mn^{3+}. The calculated lattice parameters of $U(Ga_{0.95}Mn_{0.05})_3$ and UGa_3 are 4.2354 Å and 4.2560 Å, respectively.

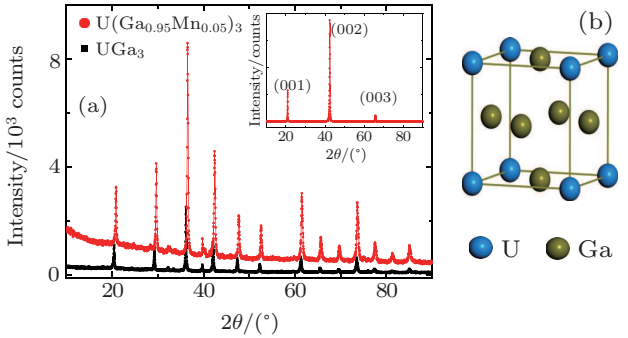


Fig. 1. (color online) (a) Room temperature XRD patterns of the powder of UGa_3 and $U(Ga_{0.95}Mn_{0.05})_3$ single crystals after grinding. The inset shows the XRD pattern of the corresponding single crystal, showing mainly the *c*-axis orientation featured with very sharp peaks. (b) Schematic diagram of UGa_3 unit cell.

The values of the dc susceptibility χ ($\chi = M/H$) of $U(Ga_{0.95}Mn_{0.05})_3$ measured in the zero-field-cooled (ZFC) and field-cooled (FC) modes under various applied magnetic fields are shown in Fig. 2. At low fields (e.g., 100 Oe, 1 Oe = 79.5775 A·m^{-1}), the magnetic susceptibility exhibits a sharp increase below 60 K, and an irreversibility behavior is manifested by the bifurcation between the $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ curves below 41.7 K. Those phenomena, together with results of ac susceptibility, suggest the formation of the SCG state in the $U(Ga_{0.95}Mn_{0.05})_3$ sample below T_{ir}. By increasing the magnetic fields, the cusp in the $\chi_{ZFC}(T)$ curve at T_a loses its intensity and broadens, and both T_a and T_{ir} shift to a lower temperature. These phenomena are typical of spin glass behaviors. In canonical spin glass (SG) systems, the cusp in $\chi_{ZFC}(T)$ is governed by SG dynamic transition and the magnetic irreversibility generally starts at the temperature slightly lower than T_a.[8,9] The obvious difference between T_{ir} and T_a in $U(Ga_{0.95}Mn_{0.05})_3$ suggests the existence of short-range interactional clusters with different sizes. When the system is cooled down from the high temperature in a zero or nonzero field, magnetic moments of the different size spin clusters in $U(Ga_{0.95}Mn_{0.05})_3$ may be frozen in the directions energetically favored by the strong Ruderman–Kittel–Kasuya–Yosida (RKKY) action or by the external field. There would be a competition between the RKKY action and the external field acting on the spin moment. The RKKY action is predominant at $T < T_a$ and the external field is predominant at $T > T_a$. Thus, the broad cusp at T_a marks a crossover region where the RKKY action energy and the energy caused by the external field are comparable to each other.

Above 60 K, the reciprocal susceptibility curve can be well fitted by the Curie–Weiss law $\chi = C/(T - \theta_p)$ (inset of Fig. 2), where C is the Curie constant and θ_p is the paramagnetic Curie temperature. From this fit, the effective magnetic moment and the paramagnetic Curie temperature are determined to be $\mu_{eff} = 1.54\mu_B$/U, and $\theta_p = 43.7$ K, respectively. The obtained μ_{eff} value is much smaller than that of a free U ion with f^2 ($\mu_{eff} \sim 3.58\mu_B$/U) or f^3 ($\mu_{eff} \sim 3.62\mu_B$/U) electronic configuration, suggesting the itinerant behavior of 5f electrons and/or Kondo effect in this compound. The positive sign of θ_p suggests that the ferromagnetic exchange interaction is dominant.

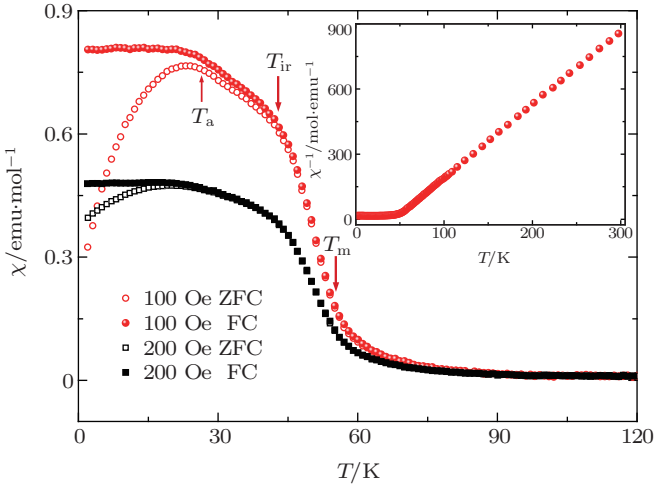


Fig. 2. (color online) DC susceptibility χ ($\chi = M/H$) data for $U(Ga_{0.95}Mn_{0.05})_3$ measured in the FC (closed symbols) mode and the ZFC (open symbols) mode in various magnetic fields. T_a is denoted by the temperature where $\chi_{ZFC}(T)$ reaches a maximum and T_{ir} is the temperature where $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ start to separate from each other. T_m is defined as the temperature where the susceptibility sharply increases. The inset displays the temperature dependence of the inverse molar magnetic susceptibility.

Figure 3(a) shows the dc isothermal magnetizations for $U(Ga_{0.95}Mn_{0.05})_3$ at various temperatures. The dependence of magnetization on the applied magnetic field at 80 K presents a characteristic linear behavior of the paramagnetic state. However, the magnetization below 60 K exhibits a sharp jump at very low field ($H < 500$ Oe) followed by a monotonic increase in the high field range without reaching saturation up to 9 T, which provides strong evidence of the existence of the SCG state. By increasing the applied field, the frozen net moment part tends to be saturated, whereas the cluster glass part increases linearly and results in the unsaturation of magnetization. In addition, the small magnetic hysteresis loop (S-type curve) below 60 K shown in Fig. 3(b) also indicates the existence of a frozen net moment in the $U(Ga_{0.95}Mn_{0.05})_3$ sample.

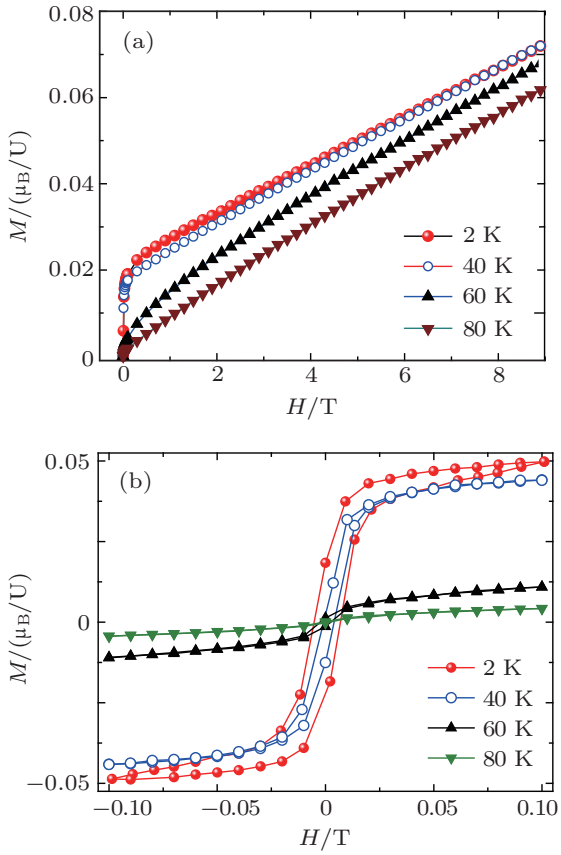


Fig. 3. (color online) (a) Magnetizations up to 9 T and (b) the hysteresis curves measured at various temperatures for $U(Ga_{0.95}Mn_{0.05})_3$ single crystal.

Figure 4 displays the in-phase χ'_{ac} and the out-of-phase χ''_{ac} components of the ac susceptibility for $U(Ga_{0.95}Mn_{0.05})_3$ at various frequencies $f = \omega/2\pi$. Both χ'_{ac} and χ''_{ac} curves exhibit the characteristic pronounced maxima whose amplitudes and positions strongly depend on the applied magnetic field frequency. These features further confirm an SG state in $U(Ga_{0.95}Mn_{0.05})_3$ below T_f. Here, T_f is defined as the temperature corresponding to the peak position in the χ'_{ac} curve. The frequency shift rate $\delta T_f = \Delta T_f/(T_f \Delta \lg \omega) = 0.019$ for $U(Ga_{0.95}Mn_{0.05})_3$ falls in a range between canonical spin glasses (e.g., $\delta T_f \sim 0.005$ for CuMn alloy)[10] and non-interacting ideal superparamagnetic systems ($\delta T_f \sim 0.1$).[11] This value is comparable to those of a nonmagnetic atom-disorder SG system, such as U_2PdSi_3 ($\delta T_f = 0.020$),[12,13] URh_2Ge_2 ($\delta T_f = 0.025$),[14] and U_2AuGa_3 ($\delta T_f = 0.01$).[15]

The dynamical parameter, relaxation time τ, follows the conventional power-law divergence of critical slowing down,[8,9]

$$\tau = \tau_0 \left(\frac{T_f - T_{SG}}{T_{SG}} \right)^{-z\nu}, \tag{1}$$

where τ is the dynamical fluctuation time corresponding to the measured frequency ($\tau = 1/(2\pi f)$), τ_0 is the spin flipping time of the relaxing entity, z is the dynamic scaling exponent, ν is the critical exponent, T_f corresponds to the peak in the χ'_{ac} curve at a given measuring frequency, and T_{SG} represents the infinitely slow cooling dc (equilibrium) value of T_f ($f \to 0$). The value of T_{SG} is obtained by extrapolating the plot of T_f versus f to $f = 0$, which gives $T_{SG} = 40.9$ K. We rewrite Eq. (1) as

$$\ln(\tau) = ln\tau_0 - z\nu \ln\left(\frac{T_f - T_{SG}}{T_{SG}} \right). \tag{2}$$

The ln–ln plot of relaxation time τ versus $[(T_f - T_{SG})/T_{SG}]$ is shown in Fig. 5(a). The solid line in Fig. 5(a) represents the best fitting result of Eq. (2). The slope and intercept of the plot yield $z\nu = 4.6(2)$ and $\tau_0 = 1.5 \times 10^{-10}$ s. Many experimental results give the typical value of $z\nu$ between 4 and 12 for various spin glass systems,[16] while $z\nu$ is usually around 2 for conventional phase transitions.[9] Moreover, the value of τ_0 is much larger than that of canonical spin glass (10^{-13} s),[9,16] which means a slow spin flip process in $U(Ga_{0.95}Mn_{0.05})_3$ caused by the strongly interacting clusters rather than individual spins. Hence, $T_f \approx 41.7$ K (the maximum in χ'_{ac} at 11 Hz) can be defined as a cluster spin freezing temperature below which the clusters will be randomly frozen.

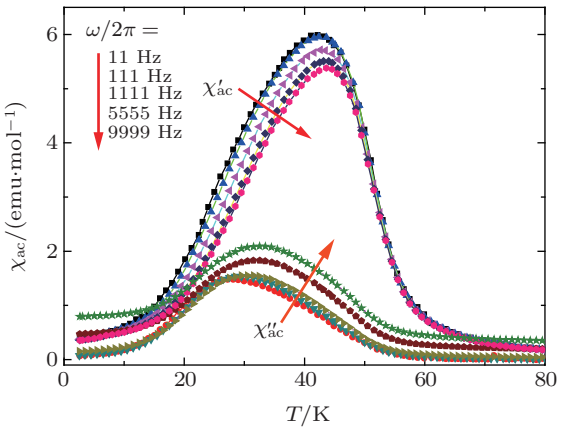


Fig. 4. (color online) In-phase (χ'_{ac}) and out-of-phase (χ''_{ac}) components of the ac susceptibility versus temperature in an applied ac field of 10 Oe at various frequencies for $U(Ga_{0.95}Mn_{0.05})_3$.

The frequency dependence of freezing temperature T_f can be obtained using the empirical Vogel–Fulcher law:[16–20]

$$\omega = \omega_0 \exp\left(-\frac{E_a}{k_B (T_f - T_0)} \right), \tag{3}$$

where ω_0 is the characteristic attempt frequency, T_0 is the Vogel–Fulcher temperature (representing the inter-cluster interaction strength), and E_a is the average activation energy, and k_B is the Boltzmann constant. We rewrite Eq. (3) as

$$T_f = \frac{1}{\ln(\omega_0/\omega)} \cdot \frac{E_a}{k_B} + T_0. \tag{4}$$

A plot of T_f versus $100/[\ln(\omega_0/\omega)]$ is shown in Fig. 5(b). The solid line in Fig. 5(b) represents the fit to Eq. (4). Here, we have used the value of attempt frequency $\omega_0 = 1/\tau_0$. The determination of characteristic time constant $\tau_0 = 1.5 \times 10^{-10}$ s, has been discussed before. The slope and intercept of the plot yield $T_0 = 380$ K and $E_a/k_B \approx 68.5$ K ($E_a \approx 1.7 k_B T_f$) for our $U(Ga_{0.95}Mn_{0.05})_3$ sample. The nonzero value of T, arising

from the interaction between spins, suggests a cluster spin-glass behavior in the $U(Ga_{0.95}Mn_{0.05})_3$ compounds. Furthermore, the result that T_0 is very close to T_f suggests that the RKKY interaction is relatively strong in the compound. According to the Tholence criterion, $\delta T_{Th} = (T_f - T)/T_f$, we obtain $\delta T_{Th} = 0.088$ for $U(Ga_{0.95}Mn_{0.05})_3$, which is comparable to that of the RKKY spin-glass system (e.g., $\delta T_{Th} = 0.07$ for CuMn system).[19] Therefore, these phenomena indicate that $U(Ga_{0.95}Mn_{0.05})_3$ has an RKKY spinglass behavior, similar to $PrRhSn_3$.[21]

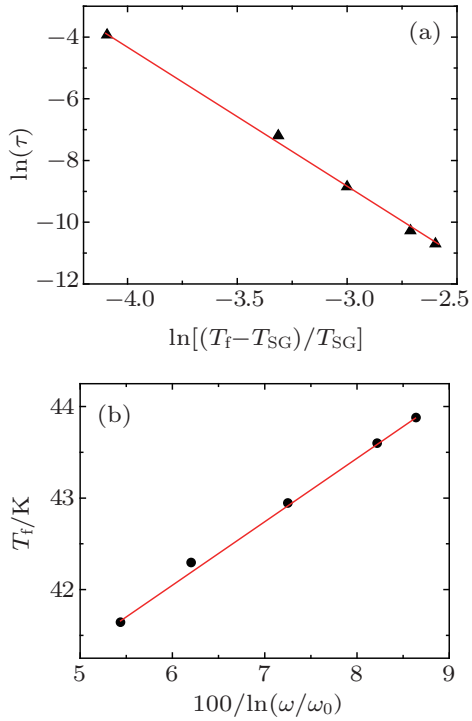


Fig. 5. (color online) (a) Relaxation time of freezing temperature plotted as $\ln(\tau)$ versus $\ln[T_f - T_{SG}]/T_{SG}]$. The solid line represents the fit to the power-law divergence. (b) The frequency dependence of freezing temperature plotted as T_f versus $100/\ln(\omega_0/\omega)$. The solid line represents the fit to Vogel–Fulcher law.

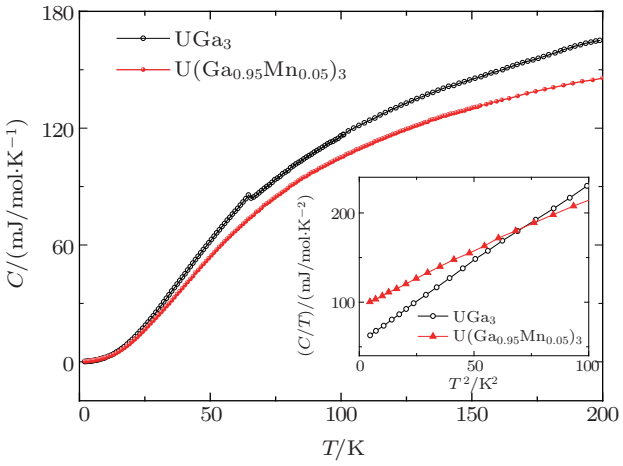


Fig. 6. (color online) Temperature dependences of the specific heat $C(T)$ for $U(Ga_{0.95}Mn_{0.05})_3$ and UGa_3. Inset shows C/T versus T^2 plot.

Figure 6 shows the temperature dependences of the specific heat for $U(Ga_{0.95}Mn_{0.05})_3$ and UGa_3 below 200 K. A λ-type anomaly for UGa_3 is found to be at 67 K corresponding to the antiferromagnetic transition. However, no anomaly was observed in specific heat of $U(Ga_{0.95}Mn_{0.05})_3$ around T_f. This indicates that no long-range magnetic order exists in this SCG system. The specific-heats of $U(Ga_{0.95}Mn_{0.05})_3$ and UGa_3 in a temperature range of 2 K–10 K follow the $C_p(T) = \gamma T + \beta T^3$ as shown in the plot of C_p/T versus T^2 (see the inset of Fig. 6). By fitting the experimental data, the electron specific heat coefficient γ of $U(Ga_{0.95}Mn_{0.05})_3$ is obtained to be 90 mJ/mol·K^{-2}, which indicates that its electron effective mass is much larger than that of UGa_3. The enhancement of electron effective mass for $U(Ga_{0.95}Mn_{0.05})_3$ is caused by the spin-cluster glass state resulting from the presence of atomic disorder, as for other nonmagnetic atom-disorder spin glass compounds Ce_2CuGe_3[22] and Ce_2CuSi_3.[23]

It is generally accepted that both randomness and frustration of magnetic moments are essential to produce the spin glass state.[9] As for $U(Ga_{0.95}Mn_{0.05})_3$, the magnetic U atoms form a fully periodic lattice, the 3d half-filled Mn atom and non-magnetic Ga atom randomly occupy the ligand site. The disorders of Mn and Ga atoms in the lattice can destroy the long-range magnetic correlation between U atoms and introduce individual spins or spin clusters with net magnetic moments by the local RKKY interaction. In addition, the Mn atom may have a local magnetic moment which has not been completely screened by the conduction electrons in this compound. Within one layer, U atoms and Mn atoms may form triangles of the nearest neighbors and no single configuration of the spins is extraordinarily favored. Therefore, the combination of the site randomness of Ga/Mn ions and frustration of magnetic moments resulting from the competing ferromagnetic and antiferromagnetic interactions between U ions easily leads to the randomly distributed spin-clusters in $U(Ga_{0.95}Mn_{0.05})_3$.

4. Conclusions

The ac and dc magnetic susceptibilities, isothermal magnetization, and specific-heat data of $U(Ga_{0.95}Mn_{0.05})_3$ single crystal provide conclusive evidence of SCG behavior below the characteristic freezing temperature $T_f = 41.7$ K. Irreversible magnetism behaviors in ZFC and FC, and a frequency-dependent anomaly in the ac susceptibility reveal a spin-glass behavior with a freezing temperature T_f. The sharp increase in dc susceptibility, a small jump at the very small field in the isothermal magnetization below T_m and no anomaly in the specific heat support the presence of clusters with frozen moments. We deem that the disorders of Mn and Ga atoms in the crystal lattice and frustration of magnetic moments lead to the random distribution of spin-clusters below T_f.

Acknowledgment

The authors thank Prof. Huiqiu Yuan, Dr. Lin Jiao and Dr. Fei Du for their scientific discussion.

References

[1] Dervenagas P, Kaczorowski D, Bourdarot F, Burlet P, Czopnik A and Lander G H 1999 *Physica B* **269** 368
[2] Kaczorowski D, Klamut P W, Czopnik A and Jezowski A 1998 *J. Magn. Magn. Mater.* **177–181** 41
[3] Kaczorowski D, Hauser R and Czopnik A 1997 *Physica B* **230–232** 35
[4] Kaczorowski D, Troć R, Badurski D, Böhm A, Shlyk L and Steglich F 1993 *Phys. Rev. B* **48** 16425
[5] Gofrky K and Kaczorowski D 2003 *Acta Physica Polonica B* **34**
[6] Xie D H, Lai X C, Chen Q Y, Zhang Y Z, Xu Q Y and Luo L Z 2014 *Rare Metal Mater. Eng.* **43** 646
[7] Schoenes J, Barkow U, Broschwitz M, Oppeneer P M, Kaczorowski D and Czopnik A 2000 *Phys. Rev. B* **61** 7415
[8] Binder K and Young A 1986 *Rev. Mod. Phys.* **58** 801
[9] Mydosh J A 1993 *J. Bio. Phys.* **19** 310
[10] Mydosh J A 1996 *J. Magn. Magn. Mater.* **157–158** 606
[11] Dormann J, Bessais L and Fiorani D 1988 *J. Phys. C: Solid State Phys.* **21** 2015
[12] Li D X, Shiokawa Y, Haga Y, Yamamoto E and Onuki Y 2002 *J. Phys. Soc. Jpn.* **7** 418
[13] Li D X, Nimori S, Shiokawa Y, Haga Y, Yamamoto E and Onuki Y 2003 *Phys. Rev. B* **68** 172405
[14] Süllow S, Nieuwenhuys G J, Menovsky A A, Mydosh J A, Mentink S A M, Mason T E and Buyers W J L 1997 *Phys. Rev. Lett.* **78** 354
[15] Li D X, Yamamura T, Nimori S, Yubuta K and Shiokawa Y 2005 *Appl. Phys. Lett.* **87** 142505
[16] Souletie J and Tholence J L 1985 *Phys. Rev. B* **32** 516
[17] Fulcher G I 1925 *J. Am. Ceram. Soc.* **8** 789
[18] Vogel H 1925 *J. Am. Ceram. Soc.* **8** 339
[19] Tholence J L 1984 *Physica B+C* **126** 157
[20] Tholence J L 1993 *Solid State Commun.* **88** 917
[21] Anand V K, Adroja D T and Hillier A D 2012 *Phys. Rev. B* **85** 014418
[22] Tien C, Feng C H, Wur C S and Lu J J 2000 *Phys. Rev. B* **61** 12151
[23] Hwang J S, Lin K J and Tien C 1996 *Solid State Commun.* **100** 169