Random spin freezing in single crystalline Ce$_2$CuSi$_3$

D. X. Li $^1$, S. Nimori $^2$, S. Ohta$^3$, Y. Yamamura $^3$ and Y. Shikama $^1$

$^1$ Institute for Materials Research, Tohoku University, Oarai, Ibaraki, 311-1313 Japan
$^2$ Tsukuba Magnet Laboratory, National Research Institute for Metals, Tsukuba, 305-0003 Japan
$^3$ Institute for Materials Research, Tohoku University, Sendai, 980-8577 Japan

E-mail: dxli@imr.tohoku.ac.jp

Abstract. We present the results of ac and dc susceptibility, magnetization and magnetic relaxation measurements performed on single crystalline Ce$_2$CuSi$_3$, a hexagonal AlB$_2$-type nonmagnetic atom disorder compound, with the magnetic field applied along two typical crystallographic directions, i.e. $H \perp c$-axis and $H//c$-axis. For both the directions, spin-glass state is confirmed to form at low temperature with almost the same spin freezing temperature $T_f$ (~2.07K), initial frequency shift $\delta T_f$ (~0.015) and activation energy $E_a/k_B$ (~10.04 K) in zero dc field. Strong magnetic anisotropy is also found to be a significant feature of this compound. The experimental results and the dynamical analyses suggest that spin-glass behavior is intrinsic to the title compound.

1. Introduction

Random spin freezing occurring in rare earth or uranium ternary intermetallic compounds has been of interest in recent years, and numerous studies on fundamental physical properties have confirmed the existence of typical spin-glass (SG) behaviors in many compounds. Among them hexagonal nonmagnetic atom disorder (NMAD) compounds $R_2MX_3$ ($R$=rare earth or U, $M$=transition metals, $X$=Si, Ga and Ge) are particularly interesting due to their special structure and diversified magnetism. SG behavior in many $R_2MX_3$ systems was found to be diversified according to the degree of disorder. We have observed the simple SG behavior in U$_2$PdSi$_3$ with disordered arrangement of all Pd and Si atoms [1] and the cluster glass behavior in U$_2$IrSi$_3$ with disordered arrangement of partial Ir and Si atoms [2], while no SG behavior is detected in U$_2$FeSi$_3$ with ordered arrangement of all Fe and Si atoms [3]. Moreover, the levels of crystallographic disorder in some NMAD compounds could be changed by improving the quality of the sample such as heat treatment under different conditions. For examples, the SG or SG-like behavior observed in polycrystalline NMAD compounds U$_2$NiSi$_3$ and Gd$_2$PdSi$_3$ disappears in their single crystalline samples [4]. After an annealing treatment single crystalline URh$_2$Ge$_2$, which in its as-grown form is found to be a heavy-fermion SG, is transformed into a long-range antiferromagnetically ordered heavy-fermion compound [5]. In this sense, to obtain an intrinsic and complete physical picture of a SG material, investigation on high quality sample including single crystal is necessary. As a continuation of our research work on NMAD SG systems, we have successfully prepared a single crystal of Ce$_2$CuSi$_3$, a typical NMAD compound existed some controversies concerning with its magnetic ground state [6-8], and carefully measured the ac and dc susceptibilities, magnetization and magnetic relaxation effect on this sample with the magnetic field ($H$) applied along two typical crystallographic directions, i.e. $H \perp c$-axis and $H//c$-axis. In this paper,
we present the experimental and dynamic analysis results, which indicate that formation of SG state and anisotropic magnetic properties are intrinsic to Ce$_2$CuSi$_3$.

2. Experimental

A single crystal of Ce$_2$CuSi$_3$ has been grown by the Czochralsky technique from a stoichiometric melt using high purity starting materials. X-ray powder diffraction shows the disordered hexagonal AlB$_2$-type structure for this sample (space group $P6/mmm$ with Ce atoms on the Al- and Cu and Si atoms statistically distributed over the B-sites) without impurity phases. A cube-shaped sample used in this work was cut by an electro-discharge machining. The ac and dc susceptibilities, magnetization and magnetic relaxation were measured by means of a SQUID magnetometer between 1.8 and 300 K in fields up to 70 kOe.

3. Results and discussion

We have measured the temperature dependences of dc susceptibility $\chi (=M/H)$ of Ce$_2$CuSi$_3$ in $H=100$ Oe applied for $H \perp c$ and $H//c$ under zero field-cooled (ZFC) and field-cooled (FC) conditions (not shown here). The $\chi$ value at low temperatures is much larger for $H \perp c$ than for $H//c$, while the $\chi_{ZFC}^{-1}(T)$ curve illustrates evident different temperature dependences for $H \perp c$ and $H//c$. In the case of $H//c$, $\chi_{ZFC}^{-1}(T)$ curve shows a broad bend around ~120 K with some negative curvature, whereas for $H \perp c$ similar bend is observed in the $\chi_{ZFC}^{-1}(T)$ curve around ~30 K. At higher temperatures, a Curie-Weiss law can be used to fit the $\chi$ data approximately. The best fits of the data above 180K to Curie-Weiss behavior yield the effective moments of $\mu_{eff}=2.64$ and 2.65 $\mu_B$/Ce, and the paramagnetic Curie temperatures $\theta_p=-167.7$ and 15.9 K for $H//c$ and $H \perp c$, respectively. The large difference between the $\theta_p$ values indicates the drastic influence of the magnetic anisotropy.

Anisotropic magnetic behavior of Ce$_2$CuSi$_3$ can be observed also in the field dependence of magnetization $M(H)$ measured at 1.8 K (not shown here), which shows a rapid increase with increasing $H$ at low field side, and achieves a value of 1.13 $\mu_B$/Ce at $H=70$ kOe for $H \perp c$. In the case of $H//c$, however, $M(H)$ increases monotonically up to 70 kOe, here a value of $M=0.54$ $\mu_B$/Ce is observed. For both the directions, $M(H)$ values at $H=70$ kOe are much smaller than 2.14 $\mu_B$/Ce, the expected saturation values for Ce$_2$CuSi$_3$. This may arise due to the possible canted structure of the Ce magnetic moments as well as the presence of magnetocrystalline anisotropy. These anisotropic magnetic properties mentioned above are similar to those reported early in the literature, and can be explained by taking into account crystalline electric effect [8].

In this work, we are mainly focus attention on low temperature magnetic behavior of the Ce$_2$CuSi$_3$ single crystal. Figure 1(a) shows the temperature dependences of FC and ZFC susceptibility of the single crystalline sample between 1.8 and 5 K in $H=10$ Oe. In the case of $H \perp c$, A pronounced peak is observed in $\chi_{ZFC}(T)$ at $T_m=2.03$ K, below which, $\chi_{ZFC}(T)$ is smaller than $\chi_{FC}(T)$. The irreversible magnetism characterized by the difference between the $\chi_{ZFC}$ and $\chi_{FC}$ curves is a typical

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Figure 1. The temperature dependences of FC (○) and ZFC (●) susceptibility of Ce$_2$CuSi$_3$ in a field of 10 Oe (a), and the temperature dependences of the real component ($\chi'_ac$) of the ac susceptibility of Ce$_2$CuSi$_3$ at various frequencies in an ac field of 5 Oe applied for $H_{ac}//c$ (b) and $H_{ac} \perp c$ (c).
feature of SG system. Similar SG-like behavior is also observed for \( H//c \). Note that in the case of \( H//c \), difference between the \( \chi_{pc}(T) \) and \( \chi_{Zpc}(T) \) curves is evident only at the temperatures below \( T_m \). For \( H//c \), however, this difference can be observed clearly even at the temperatures much higher than \( T_m \). This is most likely to result from the stacking faults and/or twinning effects that could be formed during the crystal growth and would cause tiny regions of ferromagnetic behavior along the \( c \)-axis [9]. Clearly, magnetic behavior in the basal plane indicates the simple SG nature, and that along the \( c \)-axis suggests the coexistence of the SG effect and short range magnetic correlation.

In order to confirm the SG effect, we performed an ac susceptibility measurement on the single crystalline Ce\(_2\)CuSi\(_3\) sample at frequency range 0.1 Hz \( \leq \omega/2\pi \leq 1000 \) Hz with an ac field \( H_{ac} = 5 \) Oe. Figures 1(b) and 1(c) show the temperature dependences of real component (\( \chi'_{ac} \)) of the ac susceptibility between 1.8 and 2.8 K for \( H_{ac}/c \) and \( H_{ac}/c \), respectively. In the case of \( H_{ac}/c \), \( \chi'_{ac} \) exhibits an evident peak with amplitude and position depending on the frequency of the applied ac field. As \( \omega \) increases, the peak position in \( \chi_{ac}(T,\omega) \) shifts to high temperatures and the peak amplitude decreases. This is a typical behavior characteristic of SG materials and consistent with our earlier results observed for a polycrystalline sample [7] suggesting the formation of the SG state in the single crystal. In this work, the peak temperature in \( \chi_{ac}(T,\omega) \) at \( \omega/2\pi = 0.1 \) Hz is defined as the spin freezing temperature \( (T_f = 2.07 \) K) of Ce\(_2\)CuSi\(_3\). The initial frequency shift \( \delta T_f \) calculated as \( \delta T_f = \Delta T_f/(T\Delta \log \omega) \) is 0.014 comparable to the typical values for most spin glasses [10]. Taking \( \alpha_0/2\pi = 10^{-15} \) Hz [11], the best fits of the \( T_f(\omega) \) data to the Vogel and Fulcher empirical law [12], \( \omega = \omega_0 \exp[-E_a/k_B(T_c-T)] \), and to the conventional critical slowing down model [13], \( \tau_{\max} = \tau_0 [(T_f - T_c)/T_c]^{-\nu} \), yield the dynamical parameters \( E_a/k_B \) (activation energy), \( T_c \) (static freezing temperature) and \( \nu \) (critical exponent) to be 9.84 K, 1.97 K and 10.52, respectively. Note that many experimental results give \( \nu z = 4-12 \) for different SG systems, while \( \nu z \) is usually around 2 for conventional phase transitions [10]. In the case of \( H_{ac}/c \), \( \chi_{ac}(T,\omega) \) shows the similar behavior. Using the analysis method mentioned above, the values of characteristic parameters \( E_a/k_B \), \( T_c \) and \( \nu z \) are also estimated, and there is no significant change in these values comparing with the corresponding data obtained for \( H_{ac}/c \).

It is well known that long time magnetic relaxation is also characteristic of SG materials. We carried out the relaxation measurements on Ce\(_2\)CuSi\(_3\) at different temperatures with and without the applied field, respectively. The results are show in Fig. 2 by plotting the data of \( M(t)/M(0) \) as a function of time \( t \). To measure the relaxation behavior in \( H=10 \) Oe, the sample was first cooled in zero field from 20 K to the desired temperature, then a fields of 10 Oe was applied and \( M(t) \) was measured in this field for about 1 h. To measure the relaxation behavior in zero field, the sample was first cooled in 10 Oe from 20 K to the desired temperature, then the field was switched off and \( M(t) \) was recorded in zero field. It is clear from Fig. 2 that, in any case, the decay of \( M(t) \) is remarkably slow, nonsaturation magnetization in 10 Oe and nonzero remanence in zero field can be observed even after 1 h. Using a logarithmic function, \( M(T, t)=M(0, T) - S(T) \ln(t+t_0) \), the \( M(t) \) data can be fitted very well over the full time range studied, with three \( T \)-dependent fitting parameters: initial zero-field magnetization \( M(0, T) \), magnetic viscosity \( S(T) \) and characteristic time \( t_0(T) \). For \( H//c \), fitting the data obtained at \( T = 1.8, 1.85 \) and 1.9 K to this equation yields the values of \( S = 10.864 \times 10^{-4}, 8.681 \times 10^{-7} \) and

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small magnetic clusters (small granules with net magnetic moments), which interact with each other at small magnetic clusters (small granules with net magnetic moments), which interact with each other at

We have confirmed the formation of random spin freezing state in single crystalline Ce$_2$CuSi$_3$ by ac susceptibility, dc magnetization and magnetic relaxation measurements, which suggest that the SG behavior is intrinsic to this compound. For $H_{ac}/c$ and $H_{ac}\perp c$, the ac susceptibility measurements reveal almost the same spin freezing temperature $T_f$, while the frequency dependence of $T_f$ yields almost the same dynamical parameters ($E_a$, $T_S$ and $v$) characteristic of the random spin freezing state. The FC and ZFC dc susceptibility, magnetization as well as magnetic relaxation measurements, however, show evident anisotropic magnetic features. At the same temperature and the same magnetic field, the values of ac and dc susceptibilities, magnetization and magnetic viscosity are much larger for $H\perp c$ than for $H//c$. It seems that magnetic behavior in basal plane is characteristic of a simple SG state, and that along the c-axis originates from the combined effects of random spin freezing and short range magnetic correlations. The existence of short range magnetic correlations may be due to the stacking faults and/or twinning effects [9]. Considering that Ce$_2$CuSi$_3$ is a NMAD compound, long-range magnetic correlations between Ce atoms could be destroyed by the statistical distribution of the Cu and Si atoms at crystallographically equivalent lattice sites. This disordered arrangement of nonmagnetic atoms could also result in the formation of individual and randomly distributed spins or small magnetic clusters (small granules with net magnetic moments), which interact with each other at low temperatures and freeze in along random directions leading to the formation of SG state.

4. Conclusions

We have confirmed the formation of random spin freezing state in single crystalline Ce$_2$CuSi$_3$ by ac susceptibility, dc magnetization and magnetic relaxation measurements, which suggest that the SG behavior is intrinsic to this compound. For $H_{ac}/c$ and $H_{ac}\perp c$, the ac susceptibility measurements reveal almost the same spin freezing temperature $T_f$, while the frequency dependence of $T_f$ yields almost the same dynamical parameters ($E_a$, $T_S$ and $v$) characteristic of the random spin freezing state. The FC and ZFC dc susceptibility, magnetization as well as magnetic relaxation measurements, however, show evident anisotropic magnetic features. At the same temperature and the same magnetic field, the values of ac and dc susceptibilities, magnetization and magnetic viscosity are much larger for $H\perp c$ than for $H//c$. It seems that magnetic behavior in basal plane is characteristic of a simple SG state, and that along the c-axis originates from the combined effects of random spin freezing and short range magnetic correlations. The existence of short range magnetic correlations may be due to the stacking faults and/or twinning effects [9]. Considering that Ce$_2$CuSi$_3$ is a NMAD compound, long-range magnetic correlations between Ce atoms could be destroyed by the statistical distribution of the Cu and Si atoms at crystallographically equivalent lattice sites. This disordered arrangement of nonmagnetic atoms could also result in the formation of individual and randomly distributed spins or small magnetic clusters (small granules with net magnetic moments), which interact with each other at low temperatures and freeze in along random directions leading to the formation of SG state.

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