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2009 J. Phys.: Condens. Matter 21 026006

(http://iopscience.iop.org/0953-8984/21/2/026006)

J. Phys.: Condens. Matter **21** (2009) 026006 (7pp) doi:10.1088/0953-8984/21/2/026006

Ferromagnetic ordering and weak spin-glass-like effect in Pr_2CuSi_3 and Nd_2CuSi_3

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Received 17 June 2008, in final form 22 October 2008
Published 9 December 2008
Online at stacks.iop.org/JPhysCM/21/026006

Abstract

We present the results of the temperature dependences of ac and dc susceptibilities, high-field magnetization, magnetic relaxation, specific heat, and electrical resistivity of Pr_2CuSi_3 and Nd_2CuSi_3, compounds previously shown in the literature to exhibit interesting properties. It is observed that the investigated compounds undergo a ferromagnetic phase transition at a characteristic temperature T_C (= 9.8 K for Pr_2CuSi_3 and 5.6 K for Nd_2CuSi_3), where zero-field-cooled dc susceptibility shows a rapid increase followed by a sharp peak just below T_C. Below T_C, the magnetization curve displays an open hysteresis loop and a steep rise at low fields, while irreversible magnetism and long-time magnetic relaxation effects can be observed. Furthermore, near T_C both the real and imaginary components of the ac susceptibility show a large peak with a small frequency shift of the peak position, and a sharp anomaly appears in the specific heat and electrical resistivity curves. These unusual features observed for Pr_2CuSi_3 and Nd_2CuSi_3 strongly suggest the formation of huge ferromagnetic clusters accompanied by a very weak spin-glass-like effect in both samples. The obtained results are discussed by comparing them with the data reported for other 2:1:3 intermetallic compounds and some alloyed compounds with different stoichiometry.

1. Introduction

Ternary intermetallic compounds with general formula R_2MX_3 (R = rare earth or U, M = transition metals, X = Si, Ge, Ga, In) have become the subjects of intensive studies during the last decade. Many members of the R_2MX_3 compounds have AlB_2- or $CaIn_2$-type crystal structures, which consist of R and M–X layers alternating along the *c*-axis, and possible crystallographic disorder within M–X positions. Various magnetic ground states with complicated magnetic structures originating from such distinctive crystal structures have been found for R_2MX_3 systems in recent years. The typical examples are the uranium-based compounds U_2MSi_3, which show numerous unusual magnetic properties strongly related to the crystal structure of the sample. Compounds U_2MSi_3 with M = Pd, Pt, Au, Ir and Rh are found to show spin glass (SG) or cluster glass behavior below their respective spin freezing temperature T_f [1–5]. The crystal structures of these compounds are confirmed to be the derived AlB_2-types with completely or partially disordered M and Si atoms at B crystallographic sites. In contrast, for U_2MSi_3 with M = Fe, Ru, and Os, which crystallize in the U_2RuSi_3-type structure with a perfectly ordered arrangement of M and Si atoms, no SG behavior can be observed [2, 3, 6, 7]. On the other hand, interesting magnetic properties were also observed in rare-earth 2:1:3 compounds, such as typical SG behavior in Ce_2NiGe_3 [8], Ce_2CuGe_3 [9], Ce_2AgIn_3 [10] and Nd_2AgIn_3 [11], ferromagnetic order in Nd_2MSi_3 (M = Rh, Pd, Pt) [12–14], antiferromagnetic order in Tb_2AgIn_3 [15] and R_2CuIn_3 (R = Nd, Dy, Ho) [16], and coexistence of SG state and long-range magnetic order in Dy_2PdSi_3, Tb_2PdSi_3, and Tb_2CuIn_3 [17–20] etc. In general, it is accepted that the SG state in some R_2MX_3 compounds originates from the random arrangement of the nonmagnetic atoms, and thus these systems

are usually called nonmagnetic atom disorder (NMAD) spin glasses.

Rare-earth copper silicides R_2CuSi_3 (R = rare earth elements) form another family in ternary 2:1:3 intermetallic compounds. In this family, apart from Ce_2CuSi_3 [21] and Eu_2CuSi_3 [22] which were found to show cluster glass and ferromagnetic behavior below the spin freezing temperature $T_f = 2.7$ K and the Curie temperature $T_C = 37$ K, respectively, research work on physical properties was reported only for Pr_2CuSi_3 in 1997 [23] and for Nd_2CuSi_3 in 1998 [24] by Tien *et al*. The former was classified as an SG material exhibiting ferromagnetism at $T_C = 10$ K, and the latter was considered to have an antiferromagnetic transition at $T_N = 5$ K and SG properties below 5 K. For both Pr_2CuSi_3 and Nd_2CuSi_3, irreversible magnetism manifesting itself as the difference between the field cooling (FC) and zero-field cooling (ZFC) magnetization was observed below T_C/T_N in a low field, and larger specific heat coefficients (γ) of the T-linear term were estimated from the specific heat measurements. On the other hand, based on the x-ray diffraction patterns, Pr_2CuSi_3 and Nd_2CuSi_3 were considered to crystallize in the hexagonal AlB_2-type structure with strong site disorder among Cu and Si atoms. Thus compound Pr_2CuSi_3 was classified as an NMAD spin glass [23].

Very recently the electron diffraction observation performed by Yubuta *et al* [25] clearly indicates the existence of Cu–Si superstructure in our Pr_2CuSi_3 and Nd_2CuSi_3 samples (similar to that reported for U_2IrSi_3 [26]) suggesting the ordered distribution of Cu and Si atoms, although it could not be confirmed within the limit of the x-ray diffraction technique. In this sense, the SG behavior reported to exist in these compounds is extraordinary and interesting in physics, because it is hard to understand the presence of randomness and frustration (the necessary conditions to form the SG state) in a compound with ordered crystal structure [27]. Moreover, irreversible magnetism is not always the sign of SG behavior, it is also a common feature for magnetic materials with long-range magnetic order [28]. These motivate us to carry out detailed magnetic property measurements on the two compounds, including the temperature dependence of ac susceptibility at various frequencies that could offer a good criterion for distinguishing a canonical SG from an SG-like material. In this paper we will mainly present the experimental results, and discuss the observed anomalous magnetic behaviors by comparing our data with those obtained for other 2:1:3 systems and some alloyed compounds with different stoichiometry.

2. Experimental details

Polycrystalline samples of about 3.5 g for Pr_2CuSi_3 and about 4 g for Nd_2CuSi_3 were prepared by melting high-purity starting elements in a four-electrode arc furnace. The buttons were flipped and remelted several times to ensure homogeneity, and then annealed at high temperature (500 °C × 168 h + 750 °C × 168 h for Pr_2CuSi_3, 950 °C × 480 h for Nd_2CuSi_3) in evacuated sealed quartz tubes. Both x-ray powder diffraction measurement and electron diffraction observation are used to check the sample's quality and examine the crystal structure. The samples used for x-ray powder diffraction, electron diffraction, and magnetic measurements are cut from the same annealed button. The ac susceptibility $\chi_{ac}(T)$, dc magnetization $M(T)$, and magnetic relaxation $M(t)$ measurements were performed in a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Using a hybrid magnet, the high-field magnetization was measured at 4.2 K by means of a sample extraction method up to 280 kOe, and the absolute value of the magnetization was calibrated using the data measured by a SQUID. The adiabatic heat pulse method and a standard four-terminal dc method were employed for specific heat $C(T)$ and electrical resistivity $\rho(T)$ measurements, respectively.

3. Experimental results and analysis

The x-ray powder diffraction measurements of the Pr_2CuSi_3 and Nd_2CuSi_3 samples were performed at room temperature with Cu Kα radiation. Although the diffraction lines can be indexed based on the disordered hexagonal AlB_2-type structure model (space group $P6/mmm$) with Pr/Nd atoms on 1a sites and Cu and Si atoms statistically distributed over the 2d sites, the electron diffraction patterns and the high-resolution image obtained by Yubuta *et al* prove clear evidence for the presence of a Cu–Si superstructure in both the Pr_2CuSi_3 and Nd_2CuSi_3 samples suggesting the ordered arrangement of Cu and Si atoms (the detailed experimental and analytical results will be published elsewhere) [25]. Similar superstructure had been confirmed to exist in the compound U_2IrSi_3 [26]. In fact, powder x-ray diffraction measurements, in many cases, cannot find the existence of superlattices due to the limit of the x-ray technique. Based on these results, it seems to be more reasonable to consider the Pr_2CuSi_3 and Nd_2CuSi_3 samples as crystallographic ordered compounds (with the structure derived from the hexagonal AlB_2-type) than NMAD systems. With this structural image in mind we show the magnetic property measurements of our Pr_2CuSi_3 and Nd_2CuSi_3 samples and discuss the experimental results in the following.

The temperature dependences of dc magnetization $M(T)$ of Pr_2CuSi_3 and Nd_2CuSi_3 were measured in the FC mode and in the ZFC mode between 1.8 and 300 K. Figures 1(a) and (b) show the ZFC data in a field of $H = 100$ Oe plotted as $M(T)/H$ versus T (hereafter, we call $M(T)/H$ dc susceptibility and note it as $\chi(T)$). At high temperatures, the observed $\chi_{ZFC}(T)$ behavior can be fitted using the Curie–Weiss law with the values of the Curie–Weiss temperature $\theta_p = 7.5$ and 5.9 K and the effective magnetic moment $\mu_{eff} = 3.59\ \mu_B$/Pr and $3.68\ \mu_B$/Nd for Pr_2CuSi_3 and Nd_2CuSi_3, respectively (see the insets of figures 1(a) and (b)). At low temperatures, a large and sharp peak is observed at T_m just below the temperature ($T_C = 9.8$ and 5.6 K for Pr_2CuSi_3 and Nd_2CuSi_3, respectively) where $d\chi_{ZFC}(T)/dT$ shows the largest value, indicating some kind of magnetic phase transition near this temperature. In this paper, T_C is defined as the magnetic phase transition temperature. The temperature dependences of specific heat and electrical resistivity of Pr_2CuSi_3 and Nd_2CuSi_3 are illustrated in figures 1(c)–(f). The

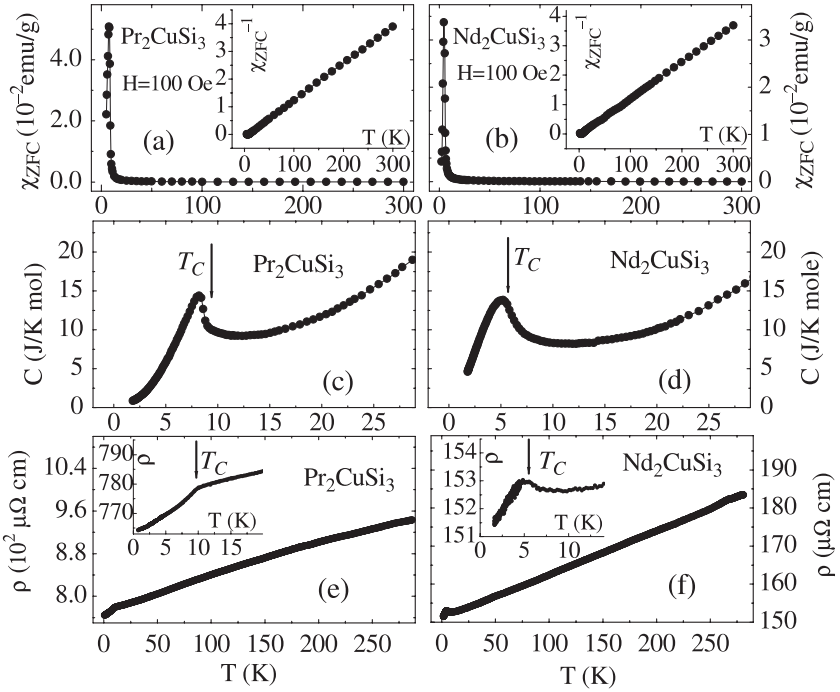

Figure 1. Temperature dependences of dc susceptibility ((a), (b)), specific heat ((c), (d)), and electrical resistivity((e), (f)) of Pr_2CuSi_3 and Nd_2CuSi_3. The insets of (a) and (b) show the Curie–Weiss behaviors of the reciprocal dc susceptibility of Pr_2CuSi_3 and Nd_2CuSi_3, respectively. The insets in (e) and (f) highlight the electrical resistivity around magnetic phase transition temperature for Pr_2CuSi_3 and Nd_2CuSi_3, respectively. The units of χ^{-1}_{ZFC} and ρ in the insets of (a), (b) and (e), (f) are 10^4 g emu^{-1} and $\mu\Omega$ cm^{-1}, respectively.

important observations are that a large peak in $C(T)$ and an evident kink in the $\rho(T)$ curves appear at the temperature (T_{sf} and T_ρ, respectively) near T_C for both samples, suggesting the existence of long-range magnetic ordering below T_C, in agreement with the susceptibility measurements (figures 1(a) and (b)).

Tien *et al* had reported similar properties, with a detailed discussion on the specific heat and electrical resistivity behaviors [23, 24]. In the literature, magnetic specific heat of R_2CuSi_3 (R = Pr and Nd) was defined as $C_m(T) = C(R_2CuSi_3) - C(La_2CuSi_3)$, and the large γ values of 505 mJ mol^{-1} K^{-2} for Pr_2CuSi_3 and 753 mJ mol^{-1} K^{-2} for Nd_2CuSi_3 were determined from the C_m/T–T^2 plots using the data between 20 and 40 K. For Pr_2CuSi_3, we have performed a similar analysis using our specific heat data between 2 and 4 K, and obtained the γ value to be 342 mJ mol^{-1} K^{-2} (171 mJ (mol-Pr)$^{-1}$ K^{-2}). Since specific heat $C(T) = C_p(T) + C_e(T) + C_m(T)$ contains contributions from vibrational (C_p), electronic (C_e), and magnetic (C_m) parts, based on our experimental data it is impossible to accurately separate the electronic part and magnetic part. Firstly, the temperatures of our measurements are not low enough relative to T_C, thus the magnetic contribution (including the possible influence of low-lying crystal levels and/or SG-like effect) should enhance the γ value. Secondly, considering that the large γ values have been determined for many 2:1:3 f-electronic systems even for U_2RuSi_3, the paramagnetic compound with ordered arrangement of all atoms and no SG behavior [4], we cannot rule out the contribution from the heavy fermion mechanism, although no evident heavy fermion behavior was found in $\rho(T)$ measurements [23]. These mechanisms are also applicable for Nd_2CuSi_3, although our $C(T)$ data below T_C cannot be used to estimate the γ value due to its much lower magnetic transition temperature.

In figure 2 we compare the FC and ZFC susceptibilities measured in different magnetic fields for the Pr_2CuSi_3 and Nd_2CuSi_3 samples. It is clear from this figure that there is no difference between the FC and ZFC curves in the paramagnetic state, and the magnetic transition peak can be observed only in the $\chi_{ZFC}(T)$ curve at a strongly field dependent temperature $T_m(H)$. Moreover, irreversible magnetism manifesting itself as the bifurcation between the $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ curves appears at low temperatures. With increasing H, the peak in $\chi_{ZFC}(T)$ becomes broader and its height decreases, the peak temperature T_m shifts toward lower temperatures, while almost no change can be observed for T_C. This irreversible magnetism indicates the metastable feature of the ground state of Pr_2CuSi_3 and Nd_2CuSi_3, and is similar to the character usually observed in some magnetic materials with long-range magnetic order or in SG systems. Above 2 kOe, $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ coincide with each other, and no peak can be observed even in the $\chi_{ZFC}(T)$ curve for either sample.

The distinction between FC and ZFC dc susceptibilities described above indicates the nonequilibrium character of the low-temperature magnetic states in Pr_2CuSi_3 and Nd_2CuSi_3. Thermodynamically, such nonequilibrium states directly relate to slow dynamics. In figure 3, we present the magnetic relaxation behavior of Pr_2CuSi_3 and Nd_2CuSi_3 in magnetic field $H = 500$ and 0 Oe by plotting the data of $M(t)/M(0)$ as a function of time t. The sample was first cooled in zero field

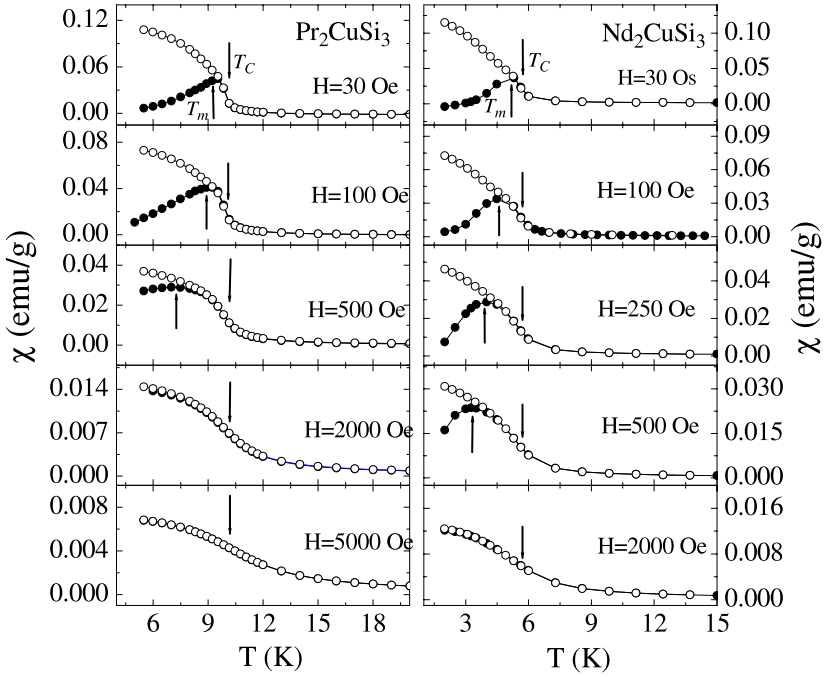

Figure 2. Temperature dependences of field-cooled (○) and zero-field-cooled (●) dc susceptibility ($\chi = M/H$) of Pr_2CuSi_3 and Nd_2CuSi_3 in various applied fields. The down arrows indicate the temperatures where χ shows the maximum temperature rate of change, the upward arrows indicate the peak temperatures in $\chi_{ZFC}(T)$ curves.

from a temperature far above T_C to the desired temperature. Then a field of 500 Oe was applied and $M(t)$ was measured in this field for about 2 h for Pr_2CuSi_3 (figure 3(a)) and about 1 h for Nd_2CuSi_3 (figure 3(b)). Next, the magnetic field was switched off and $M(t)$ was recorded again in zero field (see the insets of figure 3). For Pr_2CuSi_3 the decay of $M(t)$ is remarkably slow, nonsaturation magnetization in 500 Oe and nonzero remanence in zero field can be observed even after waiting for 2 h. Similar long-time magnetic relaxation behavior is also evident for Nd_2CuSi_3, as illustrated in figure 3(b). Using a logarithmic function, $M(t) = M_0 - S\ln(t+t_0)$, the obtained relaxation behaviors shown in figure 3 can been fitted very well over the full time range studied with three H- and T-dependent fitting parameters: initial zero-field magnetization M_0, magnetic viscosity S, and characteristic time t_0. The best fitting results obtained by using the least-squares method are shown by the solid lines in figure 3 with positive and negative S values in zero field and 500 Oe, respectively.

It is interesting to note that the characteristic phenomenon of irreversible magnetism and magnetic relaxation on a macroscopic timescale can be observed for ferromagnets with high magnetic anisotropy [29] below their Curie temperatures and for all spin glasses below their spin freezing temperatures [27–30]. Also, the logarithmic function could be used to reproduce the time dependence of magnetization for either the SG system or the ferromagnetic material subject to hysteresis. In order to explore the possible SG effect, we have performed ac susceptibility measurements in the frequency range 0.1 Hz $\leqslant \omega/2\pi \leqslant$ 1000 Hz on the Pr_2CuSi_3 and Nd_2CuSi_3 samples. The data of the real component, $\chi'_{ac}(T)$, of the ac susceptibility are illustrated in figure 4. A

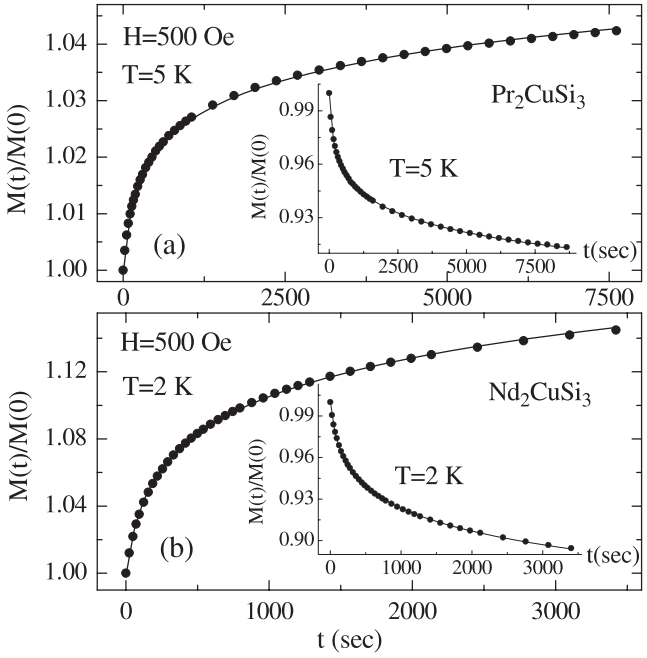

Figure 3. Magnetic relaxation behavior measured in an applied field of 500 Oe at 5 K for Pr_2CuSi_3 (a) and at 2 K for Nd_2CuSi_3 (b), plotted as $M(t)/M(0)$ versus t. The insets in (a) and (b) display the time dependence of the remanent magnetization at 5 and 2 K for Pr_2CuSi_3 and Nd_2CuSi_3, respectively. The solid lines represent least-squares fits using the equation.

pronounced maximum is observed in the $\chi'_{ac}(T)$ curve around a characteristic temperature $T_{ac}(\omega)$ for both samples. The T_{ac} value is determined to be 9.79 and 5.57 K at $\omega/2\pi$ =

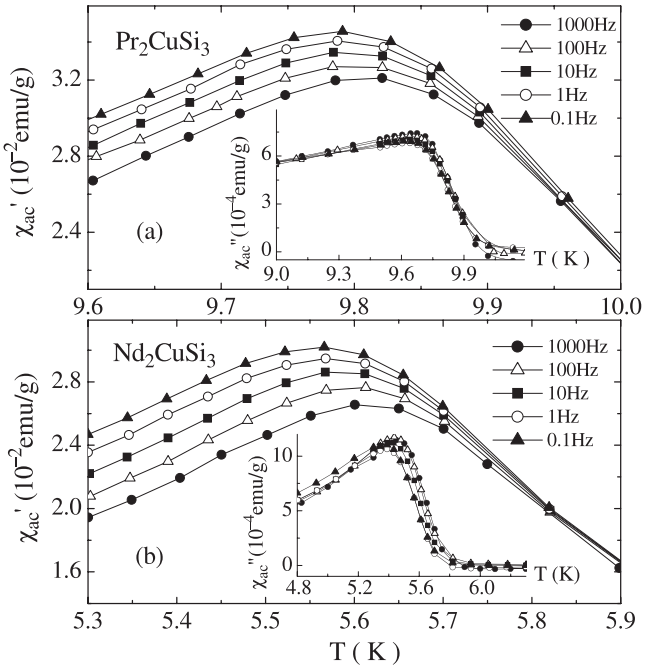

Figure 4. Temperature dependences of real and imaginary (inset) components of the ac susceptibility for Pr_2CuSi_3 (a) and Nd_2CuSi_3 (b) at various frequencies.

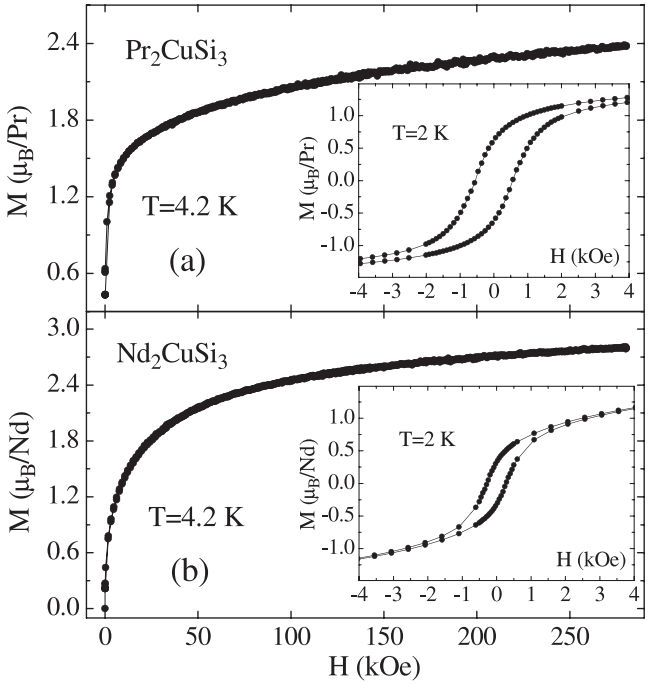

Figure 5. High-field magnetization $M(H)$ up to 280 kOe for Pr_2CuSi_3 (a) and Nd_2CuSi_3 (b) measured at 4.2 K. The insets illustrate the low-field data of the hysteresis loops measured at 2 K using a SQUID magnetometer.

0.1 Hz (in good agreement with the T_C values shown in figure 2), which shifts to 9.82 and 5.61 K at $\omega/2\pi = 1000$ Hz for Pr_2CuSi_3 and Nd_2CuSi_3, respectively. The upward-shift of the peak position in the $\chi'_{ac}(T)$ curve with increasing ω could be considered as important evidence for the existence of the random spin freezing effect in Pr_2CuSi_3 and Nd_2CuSi_3. However, the frequency shift rate of T_{ac} in both samples is very small. Using the expression $\delta T_{ac} = \Delta T_{ac}/(T_{ac}\Delta \log \omega)$ (it is often used to distinguish an SG material from an SG-like system), the frequency shift rate is determined to be $\delta T_{ac} = 0.001$ for Pr_2CuSi_3 and $\delta T_{ac} = 0.002$ for Nd_2CuSi_3. These values are roughly one order of magnitude smaller than δT_f (the frequency shift rate of the spin freezing temperature) reported for the cluster glass compound Ce_2CuSi_3 ($\delta T_f = 0.013$ [21]), and other typical NMAD SG systems ($\delta T_f \sim$ several percent [4, 5, 8–11]). In addition, the $T_f(\omega)$ data of Ce_2CuSi_3 and other NMAD SG systems can be fitted to the standard expression of critical slowing down $\tau_{max} = \tau_0[(T_f - T_s)/T_s]^{-z\nu}$ [31], but this expression cannot describe the $T_{ac}(\omega)$ behavior of the Pr_2CuSi_3 and Nd_2CuSi_3 samples. These results strongly suggest that the influence of random spin freezing in our Pr_2CuSi_3 and Nd_2CuSi_3 samples is very weak. Both Pr_2CuSi_3 and Nd_2CuSi_3 should be considered as long-range magnetic exchange interaction dominated ferromagnets with weak SG-like effect. The observed irreversible magnetism and long-time magnetic relaxation behavior seem to have their main origin in the metastable ferromagnetic ground state [28].

On the other hand, in [24] the ZFC susceptibility peak of Nd_2CuSi_3 near 5 K is considered to be of antiferromagnetic origin. For our Nd_2CuSi_3 sample (annealed at 950 °C × 480 h), although the real component $\chi'_{ac}(T)$ of the ac susceptibility shows a similar peak at ∼5.6 K (figure 4(b)) indicating a magnetic phase transition near this temperature, the imaginary component $\chi''_{ac}(T)$, however, shows an evident peak just below this temperature (inset of figure 4(b)) suggesting the ferromagnetic character of this phase transition as in the case of Pr_2CuSi_3 (inset of figure 4(a)). In addition, the ferromagnetic features of the magnetic phase transition of Nd_2CuSi_3 near 5.6 K are also manifested as a rapid increase in both $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ curves as T decreases near to T_C (figure 1) and the monotonic increase in the $\chi_{FC}(T)$ curve even when the temperature is decreased down to 1.8 K (figure 2). In fact, the observation of no downturn in the $\chi_{FC}(T)$ curves down to 1.8 K completely rules out the possibility of a simple antiferromagnetic phase transition at low temperatures [32] in both Nd_2CuSi_3 and Pr_2CuSi_3. Moreover, the experimental results of high-field magnetization provide more evidence for the ferromagnetic ground state of Pr_2CuSi_3 and Nd_2CuSi_3. Figures 5(a) and (b) show the M–H curves measured at 4.2 K ($<T_C$) up to 280 kOe for Pr_2CuSi_3 and Nd_2CuSi_3, respectively. Though complete saturation ($M_S = 3.2\ \mu_B$/Pr for Pr_2CuSi_3 and $M_S = 3.27\ \mu_B$/Nd for Nd_2CuSi_3) is not achieved in the field range of the measurement (may be due to the existence of magnetic anisotropy as usually observed in some ferromagnets), a sharp rise of $M(H)$ can be observed at low fields in the magnetically ordered state and there is a tendency to attain the full moment value at high fields. With increasing H, M reaches a value of 2.4 μ_B/Pr and 2.8 μ_B/Nd at 280 kOe and when H is returned from 280 kOe to zero a remanent magnetization of about 0.6 μ_B/Pr and 0.3 μ_B/Nd is detected for the Pr_2CuSi_3 and the Nd_2CuSi_3 sample, respectively. Further proof of the ferromagnetic nature can be obtained from the complete hysteresis loop measured at

2 K using a SQUID magnetometer in the field range between −50 and 50 kOe. The low-field data are shown in the insets of figure 5 in an expanded form. As expected, one observes an open loop with remanent magnetization and coercive field of about 0.63 μ_B/Pr and 559 Oe for Pr_2CuSi_3, and 0.34 μ_B/Nd and 273 Oe for Nd_2CuSi_3 at 2 K.

It may be of great interest to compare the magnetic properties of Pr_2CuSi_3 and Nd_2CuSi_3 with those reported earlier for typical SG material U_2PdSi_3 [4] and ferromagnet Nd_2PtSi_3 [33]. The former, U_2PdSi_3, shows the defining properties of an SG material. They are (i) the presence of a frequency dependent peak in the ac susceptibility at spin freezing temperature T_f with a relatively large δT_f value and the critical slowing down behavior of $T_f(\omega)$, and (ii) lack of periodic long-range magnetic order manifesting itself as no anomaly in either resistivity $\rho(T)$ or specific heat $C(T)$ curves at temperature T_f. These characteristic features cannot be observed for our Pr_2CuSi_3 and Nd_2CuSi_3 samples. In contrast, the Pr_2CuSi_3 and Nd_2CuSi_3 samples behave in a very similar manner to the metastable ferromagnetic compound Nd_2PtSi_3. In particular, the main metastable ferromagnetic characteristics displayed by Nd_2PtSi_3, e.g. (i) the rapid increase of $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ as T decreased near T_C followed by a sharp peak in the $\chi_{ZFC}(T)$ curve just below T_C, and the monotonic increase in $\chi_{FC}(T)$ below T_C, (ii) the sudden drop in the $\rho(T)$ curve and the large peak in the $C(T)$ curve near T_C, (iii) the sharp rise in initial magnetization $M(H)$, (iv) the very small δT_{ac} (frequency shift rate of the peak position in ac susceptibility) value, and (v) the irreversible magnetism and the long-time magnetic relaxation effect, are the same as those observed for Pr_2CuSi_3 and Nd_2CuSi_3 in this work. Thus it is much better to classify our Pr_2CuSi_3 and Nd_2CuSi_3 samples as ferromagnetically ordered materials with a very weak SG-like effect.

It has been commonly accepted that disorder and frustration are the necessary conditions of formation of an SG state. Since the electron diffraction patterns, however, indicate the ordered distribution of Cu and Si atoms in the Pr_2CuSi_3 and Nd_2CuSi_3 samples as stated above, a natural question to ask is why SG-like states in such magnetically ordered systems can be formed (despite its weak effect)? Although it is impossible to give a clear explanation at this stage, we can attempt to understand this behavior as follows. For an NMAD system, the disorder of nonmagnetic atoms could destroy the long-range magnetic correlation and result in the formation of finite-size granules with net magnetic moments (magnetic clusters). At low temperatures these randomly distributed clusters could interact with each other causing the formation of frustrated magnetic moments similar to what happens in amorphous or diluted metallic SG materials. In different NMAD systems, the magnetic cluster could exist with different geometric size depending on the degree of randomness and/or relative strength of magnetic interaction. For a system with completely disordered nonmagnetic atoms, the clusters could be so small that they could behave like individual spins and thus the system would show simple SG features such as the case of U_2PdSi_3 with almost completely disordered Pd and Si atoms [3, 4]. With gradual increase of the orderly arranged atoms in the magnetic systems, the size of the magnetic cluster could become larger and larger, while the magnetic properties of the systems would change gradually from simple SG to cluster glass behaviors such as the case of U_2RhSi_3 with partially disordered Rh and Si atoms [3]. Further, for a system with perfectly ordered atomic structure (such as the cases of U_2FeSi_3 [7] and U_2RuSi_3 [3]) or with sufficiently large magnetic clusters (such as U_2PdGa_3, U_2PtGa_3 [34], and Nd_2PtSi_3 [33]) the SG effect would disappear or very weak.

Table 1. Characteristic parameters of Pr_2CuSi_3 and Nd_2CuSi_3. T_{sf}: the peak temperature in the $C(T)$ curve; T_ρ: the kink point of the $\rho(T)$ curve; T_{dc}: the peak temperature in the $\chi_{ZFC}(T)$ curve at $H = 30$ Oe; T_{ac}: the peak temperature in the $\chi_{ac}(T)$ curve at $\omega/2\pi = 0.1$ Hz; T_C: the defined Curie temperature, where $d\chi_{ZFC}(T)/dT$ shows the largest value; δT_{ac}: the frequency shift rate of T_{ac}; M_0: the value of magnetization at $H = 280$ kOe and $T = 4.2$ K; M_r and M_C: the remanent magnetization and coercive field, respectively, at $T = 2$ K.

Compound	T_{sf} (K)	T_ρ (K)	T_{ZFC} (K)	T_{ac} (K)	T_C (K)	δT_{ac}	M_0[a]	M_r[a]	M_C (Oe)
Pr_2CuSi_3	8.2	9.5	9.5	9.79	9.8	0.001	2.4	0.63	559
Nd_2CuSi_3	5.0	4.9	5.2	5.57	5.6	0.002	2.8	0.34	273

[a] The unit is μ_B/Pr for Pr_2CuSi_3 and μ_B/Nd for Nd_2CuSi_3.

Based on these analyses, the observed low-temperature ferromagnetic nature for Pr_2CuSi_3 and Nd_2CuSi_3 can be explained as originating from the formation of large ferromagnetic clusters in the samples below T_C due to the existence of a few randomly distributed Cu and Si atoms, while the very weak SG-like effect could be understood to result from the random exchange interactions between the clusters. Thus ferromagnetic ordering coexists with a weak SG-like effect in the investigated compounds below T_C. In addition, the disorderly arranged atoms are so small that the electron diffraction technique could not detect their presence, and sufficiently large clusters could be formed, resulting in macroscopic ferromagnetic behavior. Note that the observed irreversible magnetism, manifesting itself as the bifurcation between $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ curves, appears at a field dependent temperature that, in fact, is approaching T_C in a very low applied field. On the other hand, the specific heat peak appears at a temperature slightly lower than T_C. This is also a common feature among magnetic materials with cluster effect. For convenience of comparison, the peak temperature T_{sf} in $C(T)$, T_m in $\chi_{ZFC}(T)$, and T_{ac} in $\chi_{ac}(T)$, the kink point T_ρ in $\rho(T)$, as well as some characteristic parameters of Pr_2CuSi_3 and Nd_2CuSi_3 are listed in table 1.

In earlier papers, we have explained the SG-like behavior observed in some other 2:1:3 NMAD compounds based on the assumption of formation of ferro- or antiferromagnetic magnetic clusters [11, 35]. A similar magnetic glass state seems to be easier to form in a magnet with relatively low magnetic moment such as in Ce or U compounds. Recently, the existence of ferromagnetic order and the cluster glass state was confirmed by Marcano *et al* in some compounds of the $CeNi_{1-x}Cu_x$ series with even lower magnetic moment [36]. Based on small angle neutron scattering measurements, the average size of the magnetic

clusters was determined to be $\xi = 27$ Å for $CeNi_{0.4}Cu_{0.6}$ and a much smaller value for $CeNi_{0.8}Cu_{0.2}$ due to the highly reduced magnetic moment in this composition. Marcano *et al* explained the unusual magnetic features obtained in $CeNi_{1-x}Cu_x$ by using a phenomenological magnetic cluster model. In their opinion, this model represents a more general situation than the particular case of $CeNi_{1-x}Cu_x$; it can be used to understand the unusual magnetic properties observed in other alloyed compounds with small magnetic moments and intrinsic disorder effects [36]. Indeed, ferro- or antiferromagnetic behaviors with magnetic cluster effects have also been observed in U_2PdGa_3 and U_2PtGa_3 ($\xi \sim$ 120–150 Å) [34], Ce_2PdSi_3 ($\xi \sim 100$ Å) [19], and many colossal magnetoresistive oxides [37–39]. Returning to the original topic, to provide the decisive evidence for the formation of ferromagnetic clusters in Pr_2CuSi_3 and Nd_2CuSi_3, neutron diffraction measurements are necessary, although it is impossible for us to do this at this stage.

In conclusion, we have studied the magnetic properties of Pr_2CuSi_3 and Nd_2CuSi_3, which exhibit an almost long-range magnetic order at $T_C = 9.8$ and 5.6 K, respectively, with clear ferromagnetic characteristics near and below T_C. For both samples the dc susceptibility reveals the irreversible magnetism below T_C, while the ac susceptibility show a small shift of the peak position to high temperatures with increasing frequency, suggesting a weak SG-like effect. These characteristic features are evidently different from the results reported for typical 2:1:3 NMAD SG materials, but very similar to those found for ferromagnetic Nd_2PtSi_3. The obtained results in this work can be understood based on the magnetic cluster mechanism, and thus suggest the formation of ferromagnetic clusters in the Pr_2CuSi_3 and Nd_2CuSi_3 samples with very large geometric sizes probably due to the relatively highly ordered atomic arrangement.

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