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Magnetic ordering in ternary germanide Nd_2CuGe_6

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Abstract

We have performed a systematic investigation on a well-annealed polycrystalline Nd_2CuGe_6 sample by measuring its AC and DC susceptibility $\chi(T)$, magnetization $M(H)$, magnetic relaxation $M(t)$, electrical resistivity $\rho(T)$ and specific heat $C(T)$. The sharp peak observed at about $T_N = 9.4$ K in $\chi_{AC}(T)$, $\chi_{DC}(T)$ and $C(T)$ curves, respectively, indicates the occurrence of an antiferromagnetic order, which is further confirmed by the sudden decrease in $\rho(T)$ at the same temperature. In the magnetically ordered state, $M(H)$ shows an evident metamagnetic transition. Moreover, the $\chi_{DC}(T)$ and $M(t)$ measurements reveal evident irreversible magnetism and long-time magnetic relaxation effect below T_N indicating the metastable characters of the magnetically ordered state. The formation of the metastable magnetic state cannot be explained as glass freezing of the neodymium magnetic moments in the Ce_2CuGe_6-type orthorhombic Nd_2CuGe_6 sample.

Keywords: Nd_2CuGe_6; Susceptibility; Magnetic relaxation; Irreversible magnetism; Metamagnetism

1. Introduction

Rare earth germanides R_2CuGe_6 (R = rare earth metal), crystallizing in the orthorhombic structure with space group *Amm*2 [1], form a new family in ternary intermetallic compounds with composition 2:1:6. In this family, magnetic properties of the compounds with R = Ce and Pr were first measured by Sologub et al. and later measured by Yamamoto et al. They classified them as either the antiferromagnets [1] or the ferrimagnets [2]. As for magnetic and transport behavior of Nd_2CuGe_6, up to date only the AC susceptibility in the range 4.5–100 K (AC field 10 Oe, 133.3 Hz) [1] and the electrical resistivity in the range 78–380 K [3] were measured. The former shows an "antiferromagnetic-like" anomaly at 9 K [1].

In order to gain a completely physical picture of the ground state of Nd_2CuGe_6, we have performed a systematic investigation on a well-annealed polycrystalline sample by measuring its DC susceptibility [4] (under different applied fields), AC susceptibility (at different frequencies), magnetization, magnetic relaxation, electrical resistivity and specific heat. In this paper, we present the experimental results, which reveal that Nd_2CuGe_6 is not a simple antiferromagnet, metamagnetic transition and irreversible magnetism exist in its magnetically ordered state.

2. Experimental

Polycrystalline sample of Nd_2CuGe_6 was prepared by arc melting appropriate amounts of high-purity starting elements (Nd: 3N; Cu: 4N; Ge: 5N) in a titanium-gettered argon atmosphere and subsequent annealing in vacuum at 850 °C for 2 weeks. X-ray powder diffraction was performed at room temperature with Cu Kα radiation to check the quality of the sample, which showed that the specimen is a single-phased compound of the orthorhombic Ce_2CuGe_6-type structure with the *Amm*2 space group. The determined room-temperature lattice constants are $a = 4.188$ Å, $b = 4.057$ Å and $c = 21.413$ Å.

The DC and AC susceptibilities, low field magnetization and magnetic relaxation were measured in the temperature

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range 1.8–300 K and in applied magnetic fields up to 70 kOe using a quantum design superconducting quantum interference device (SQUID) magnetometer. Using a hybrid magnet, the high-field magnetization experiment was performed at 4.2 K by means of a sample extraction method up to 270 kOe, and the absolute value of the magnetization was calibrated using the data measured by a 7T-SQUID. The adiabatic heat pulse method was employed for specific heat measurements in the temperature range 2–20 K. Electrical resistivity measurement was carried out between 0.5 and 290 K with a conventional four-terminal DC method.

3. Results and discussion

The temperature dependence of DC susceptibility $\chi(T)$ [4] of Nd_2CuGe_6 was measured in different applied magnetic fields employing both the zero-field cooling (ZFC) and field cooling (FC) conditions. In Fig. 1, we present the χ_{ZFC} and χ_{ZFC}^{-1} data up to 300 K measured in an applied field $H = 100$ Oe. At low temperatures, a very sharp peak appears similar to that usually observed in an antiferromagnetic (AF) material, suggesting the occurrence of an AF ordering at this temperature in the Nd_2CuGe_6 sample. The peak temperature is well consistent with the Néel temperature, $T_N = 9.4$ K, obtained from the specific heat and electrical resistivity data described below. Above about 30 K, χ_{ZFC}^{-1} curve follows the Curie–Weiss law, $\chi(T) = C/(T - \theta_p)$ (dashed line in Fig. 1), with the effective magnetic moment $\mu_{eff} = (C/8)^{1/2} = 3.65\ \mu_B$/Nd and the paramagnetic Curie temperature $\theta_p = 0.8$ K. The experimental value of μ_{eff} is close to the theoretical one ($\mu_{eff} = 3.62\ \mu_B$) expected for free-ion Nd^{3+} in the $J = 9/2$ Hund's rule ground state indicating 4f electrons are almost localized within the Nd atoms. On the other hand, our measurements also reveal that Nd_2CuGe_6 seems not to be a simple AF system. The large value of χ_{ZFC} at the peak temperature T_N and the very small and positive value of θ_P suggest the strong influence of ferromagnetic exchange interaction in this compound. In fact, we have detected the negative χ_{ZFC} values below 4.5 K in a field of 100 Oe. Note that for low applied fields such a behavior is usually observed at low temperatures for ferromagnet with strong magnetic anisotropy, if the superconducting magnet in SQUID magnetometer is not completely reset and thus a "net negative field" gives rise to a negative magnetization after cooling the sample under this condition [5]. In this sense, the observation of low temperature negative magnetization reflects the remarkable influence of ferromagnetic interaction in the Nd_2CuGe_6 sample even in its AF state.

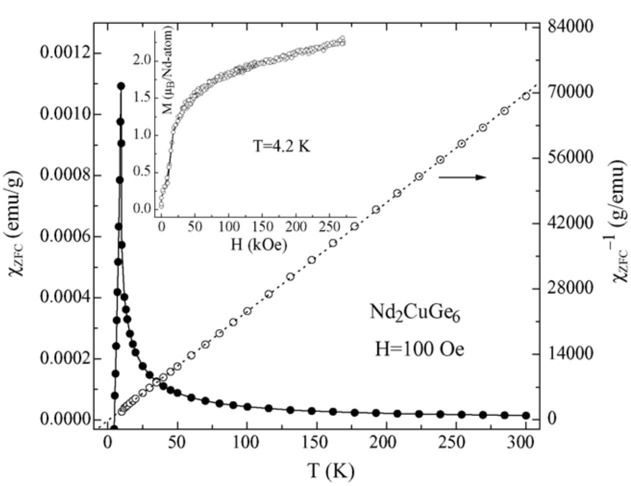

Fig. 1. DC susceptibility ($\chi_{ZFC} = M_{ZFC}/H$) and reciprocal susceptibility (χ_{ZFC}^{-1}) as a function of temperature for Nd_2CuGe_6 in a magnetic field of 100 Oe. The dashed line represents the fitting result using the Curie–Weiss law. The inset shows the field dependence of magnetization of Nd_2CuGe_6 up to 270 kOe at 4.2 K.

The presence of low temperature AF ordering in Nd_2CuGe_6 is further confirmed by the field dependence of magnetization $M(H)$. As shown in the inset of Fig. 1, $M(H)$ measured at 4.2 K shows a metamagnetic transition starting at $H_m \sim 10.5$ kOe followed by a rapid increase up to about 20 kOe. Similar metamagnetism is also observed in isostructural compounds Ce_2CuGe_6 and Pr_2CuGe_6 [2] at 4.2 K with the H_m values of about 11 and 13 kOe, respectively. Above 20 kOe, $M(H)$ increases monotonically with H up to 270 kOe, where M reaches a value of 2.3 μ_B per Nd atom much smaller than the theoretical saturation value ($M_S = 3.27\ \mu_B$/Nd-atom). The reduction of high-field neodymium magnetic moment with respect to its free ion value can be mainly ascribed to the crystalline electric field effect. At 2 K, the metamagnetic transition can be observed much more clearly at $H_m \sim 20$ kOe with a tiny hysteresis appearing at low field side and a small remanent magnetization of about 0.05 μ_B per Nd atom (not show here). These features further prove that Nd_2CuGe_6 is not a simple AF system, net magnetic moment seems to exist at zero field in the magnetically ordered state.

The inset (a) of Fig. 2 displays the variation of specific heat $C(T)$ of Nd_2CuGe_6 as a function of temperature. $C(T)$ shows a large and sharp peak at the temperature where a distinct peak is also observed in DC susceptibility (see Fig. 1) corresponding to the AF phase transition. The Néel temperature defined as the peak point is $T_N = 9.4$ K. At low temperatures, the C/T versus T^2 plot yields for $T \rightarrow 0$ K a γ-value (the specific heat coefficient of T-linear term) of about 25 mJ (mol Nd)$^{-1}$ K^{-2} for Nd_2CuGe_6. This value is much smaller than 170 and 1100 mJ mol^{-1} K^{-2} obtained for Ce_2CuGe_6 and Pr_2CuGe_6 [2], respectively.

The temperature dependence of electrical resistivity $\rho(T)$ of Nd_2CuGe_6 between 0.5 and 290 K is illustrated in Fig. 2. Firstly, $\rho(T)$ shows metallic conductivity with small negative curvature between about 80 and 200 K, This behavior is similar to that observed for Pr_2CuGe_6 above T_N but different from the $\rho(T)$ behavior of Ce_2CuGe_6 that shows a large upward convex in $\rho(T)$ curve around 100 K [2]. Secondly, as clearly shown in the inset (b) of Fig. 2 in an expanded scale, $\rho(T)$ curve manifests a sudden bend at $T_N = 9.4$ K. The rapid decrease of ρ below T_N resulted from the decrease of spin dis-

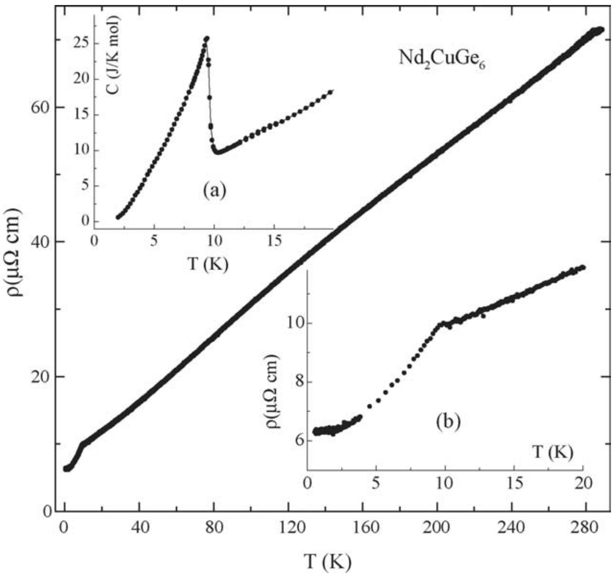

Fig. 2. The temperature dependence of electrical resistivity of Nd_2CuGe_6. The inset (a) presents the specific heat of Nd_2CuGe_6 between 2 and 20 K, and the inset (b) shows the low temperature part of electrical resistivity in an expanded scale.

order scattering due to AF ordering. Finally, a smaller residual resistivity $RR = \rho(T = 0.5\,K) = 6.3\ \mu\Omega cm$ was detected at 0.5 K, which results in the larger residual resistivity ratio $RRR = \rho(T = 290\,K)/\rho(T = 0.5\,K) = 11.5$ and suggests the relatively high quality for this Nd_2CuGe_6 sample.

A finding of emphasis here is the metastable magnetic ground state of Nd_2CuGe_6. In Fig. 3, we compare the temperature variations of the FC and ZFC DC susceptibilities measured in 10, 100 and 2000 Oe, respectively. There is no difference between $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ at the temperatures above T_N. As T is decreased near to T_N, both $\chi_{FC}(T)$ and $\chi_{ZFC}(T)$ increase rapidly signalling the onset of AF ordering. At T_N, $\chi_{ZFC}(T)$ shows an evident peak and no maximum appears in the low field FC curve (Fig. 3a and b). Below T_N, $\chi_{ZFC}(T)$ is time dependent, in contrast, $\chi_{FC}(T)$ is reversible, independent of the time of the measurement and bifurcates from $\chi_{ZFC}(T)$. This observation is very significant, because it means that the irreversible magnetism originated in the antiferromagnetically ordered state. With increasing the applied field, no evident change was found for the peak position in $\chi_{ZFC}(T)$ up to 10 kOe (not shown), but a cusp-like maximum is also observed in the $\chi_{FC}(T)$ curve as H is increased above 2 kOe (see Fig. 3c).

Further evidence for the metastable magnetic ground state of Nd_2CuGe_6 is offered by the magnetic relaxation measurement. To study the relaxation effect, magnetizations $M(t)$ in applied magnetic fields and $M(t)$ in zero field (remanent magnetization) were measured as a function of time t at 5 K, respectively. For the former, the sample was first cooled in zero field from 30 to 5 K, then a desired magnetic field was applied and the recording started immediately just as the field was stabilized ($t = 0$). For the latter, the sample was first cooled in a

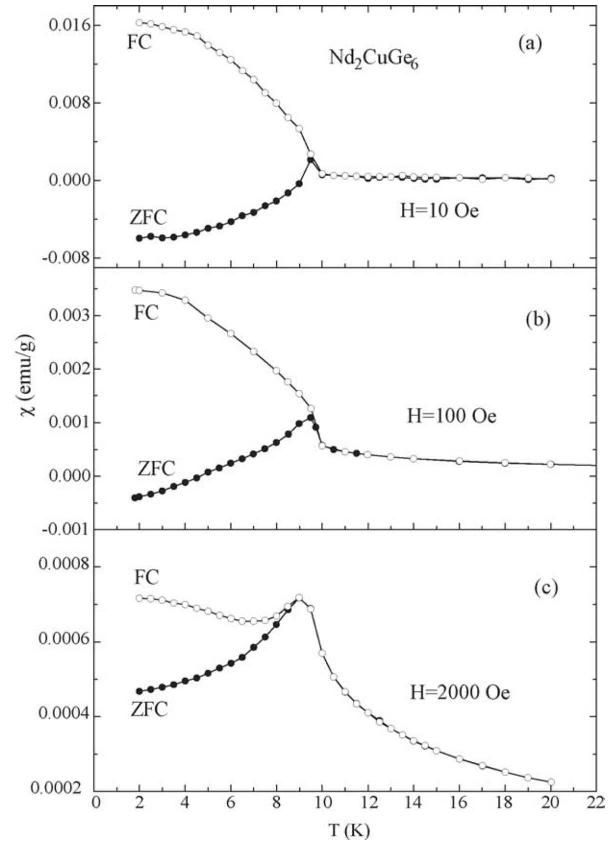

Fig. 3. Difference between field-cooled (◯) and zero-field-cooled (●) DC susceptibility of Nd_2CuGe_6 in applied fields of 10, 100 and 2000 Oe, respectively.

field of 100 Oe from 30 K, then the field was switched off as the temperature was stabilized at 5 K and $M(t)$ was measured immediately. As seen from Fig. 4, in both cases, the decay of $M(t)$ is remarkably slow, after waiting for 1 h, $M(t)$ is still far from saturation. Such long-time magnetic relaxation behaviors are characteristic of non-equilibrium magnetic state. Using a logarithmic function, $M(t) = M_0 + S\ln(t + t_0)$, the obtained relaxation behavior of Nd_2CuGe_6 can be 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 as shown by the solid lines in Fig. 4. Where, parameter t_0 reflects that the initial relaxation behavior (at short time about $t < 220$ s) is not consistent with a simple logarithm law due to the relatively rapid relaxation. In fact, at long time ($t > 220$ s) a simple logarithm function can give better representation for our relaxation data as usually observed for a ferromagnet with domain-wall pinning effect.

It is interesting to note that metastable magnetic behavior and long time magnetic relaxation effect are also the characteristic features of spin-glass materials [6] (explained as the existence of highly degenerate ground state), ferromagnets with strong magnetic anisotropy [5,7] (explained as the domain-wall pinning effect) and some long-range AF ordered systems [8,9] (may be originated from different mechanism

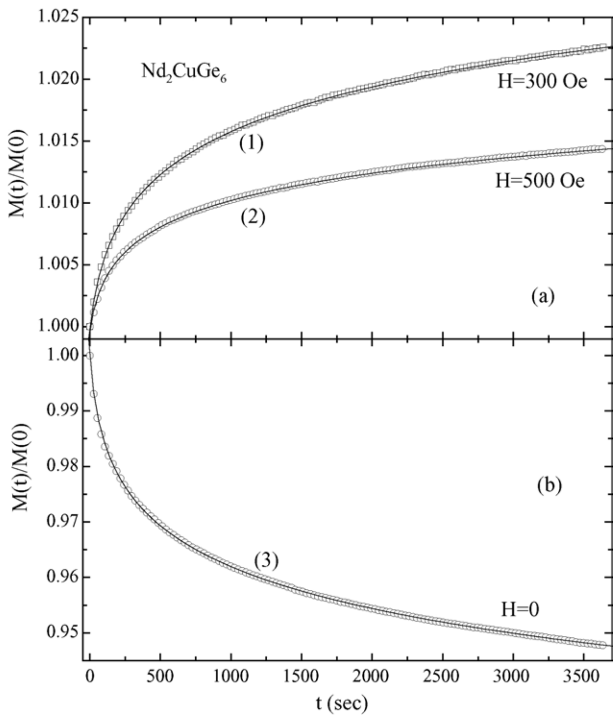

Fig. 4. Magnetic relaxation behavior of Nd_2CuGe_6 plotted as $M(t)/M(0)$ vs. t in different magnetic fields. The solid lines represent least-squares fits using equation $M(t) = M_0 + S\ln(t + t_0)$ with the fitting parameters $M_0 = 0.171$, 0.292 and 0.237 emu/g, $S = -0.946 \times 10^{-3}$, -0.971×10^{-3} and 2.551×10^{-3} emu/g, and $t_0 = 57.4$, 43.0 and 35.9 s for curve (1), (2) and (3), respectively.

for different material, e.g., for some antiferromagnets with frustrated magnetic moments, spin frustration may be one of the possible origin resemblance to a spin glass). In order to explore the possible spin-glass effect, AC susceptibility measurement on the Nd_2CuGe_6 sample was also performed at different frequencies. Fig. 5 shows the in-phase $\chi'_{AC}(T, \omega)$

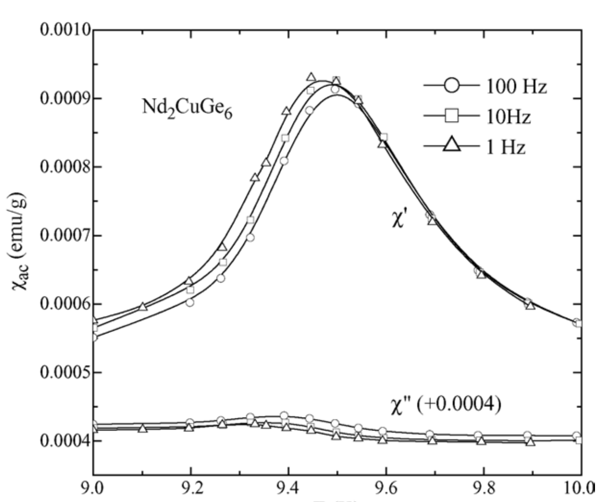

Fig. 5. Real (χ'_{AC}) and imaginary (χ''_{AC}) components of the AC susceptibility of Nd_2CuGe_6 vs. temperature at frequencies of 1, 10 and 100 Hz, respectively.

as well as the out-of-phase $\chi''_{AC}(T, \omega)$ components of the AC susceptibility versus temperature for Nd_2CuGe_6 taken at 1, 10 and 100 Hz. Clearly, χ'_{AC} exhibits a pronounced maximum at a temperature T_m (near T_N), which shifts to high temperature with increasing the frequency like that usually observed for a spin glass. However, it is well known that the initial frequency shift of the peak position in $\chi'_{AC}(T, \omega)$ calculated as $\delta T_m = \Delta T_m/(T_m \Delta\log\omega)$ is usually used to distinguish a spin glass from a spin-glass-like material. In the present case, $\delta T_m = 0.001$ is estimated for the Nd_2CuGe_6 sample. This value is much smaller than δT_f (the frequency shift of freezing temperature) reported for the typical metallic spin-glass systems [6,10]. Thus, spin-glass effect, if it exists, is very weak in Nd_2CuGe_6. On the other hand, a peak, although it is relatively small, is also detected in the χ''_{AC} curve near T_N indicating again the presence of ferromagnetic interaction in the magnetically ordered state, which consists with the consequence, i.e., Nd_2CuGe_6 is not a simple antiferromagnet, obtained from the DC susceptibility measurements.

In conclusion, we have investigated the magnetic, transport and thermal properties of ternary intermetallic germanide Nd_2CuGe_6 by AC susceptibility, DC magnetization, magnetic relaxation, specific heat and electrical resistivity measurements. This compound exists an AF ordering below the Néel temperature $T_N = 9.4$ K, where a sharp peak in magnetic susceptibility and specific heat and a sudden bent in electric resistivity are observed. In the magnetically ordered state, the field dependence of magnetization shows a metamagnetic transition and a weak hysteretic effect. An important feature found in this work for Nd_2CuGe_6 is the metastable behavior of the magnetically ordered state mainly behaving as (i) the magnetic irreversibility, e.g., the difference between FC and ZFC DC susceptibilities and (ii) the remanence and magnetic relaxation on macroscopic time scales below T_N. Since one of the necessary conditions, random structure, for the formation of spin glass state is impossible in an ideal orthorhombic Ce_2CuGe_6-type compound and also only a very small frequency shift of the AC susceptibility peak position was detected, the observed non-equilibrium magnetic state in Nd_2CuGe_6 can not be ascribed to spin-glass effect. Although a possible origin may be described as the domain-wall pinning like effect due to the existence of ferromagnetic exchange interaction, we cannot give further explanation on the metastable behavior of the magnetically ordered state of Nd_2CuGe_6 based on the present data. Detailed analysis in conjunction with crystal structure characters and further experimental works, particularly on single crystals once they become available, are necessary.

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