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The magnetic glass state in the magnetocaloric material Gd_5Ge_4

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Abstract: The metastable property of glasslike dynamics at low temperature of Gd_5Ge_4 was presented in contrast to the stable frozen spin glass state in cobaltite $La_{0.88}Sr_{0.12}CoO_3$ (LSCO). Through investigating the effect of temperature cycle on magnetization at the low temperature region after the zero field cooled procedure of Gd_5Ge_4 and $La_{0.88}Sr_{0.12}CoO_3$ respectively, it was found that the magnetization continues to increase with increasing the temperature cycle in Gd_5Ge_4, while there was hardly any effect on magnetization in $La_{0.88}Sr_{0.12}CoO_3$. The dc magnetization and ac susceptibility were also measured on Gd_5Ge_4 and $La_{0.88}Sr_{0.12}CoO_3$. The peaks of ac susceptibility in Gd_5Ge_4 did not move to the higher temperature region with increasing frequency, which were different from the phenomena of $La_{0.88}Sr_{0.12}CoO_3$. This kind of magnetic glass state in Gd_5Ge_4 is quite different from conventional spin glass.

Key words: magnetic glass sate; spin glass; magnetocaloric material

磁制冷材料 Gd_5Ge_4 中的磁玻璃态

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摘要:Gd_5Ge_4 低温时具有玻璃态的不稳定性,与钴氧化物 $La_{0.88}Sr_{0.12}CoO_3$ 的冻结的自旋玻璃态不同. 通过分别研究经过零场冷过程后 Gd_5Ge_4 和 $La_{0.88}Sr_{0.12}CoO_3$ 在低温区域的温度循环对磁化强度的影响,发现在 Gd_5Ge_4 样品中磁化强度随着温度循环的增加而不断增大,但是在 $La_{0.88}Sr_{0.12}CoO_3$ 样品中温度循环对其磁化强度几乎没有影响. Gd_5Ge_4 和 $La_{0.88}Sr_{0.12}CoO_3$ 的直流磁化强度和交流磁化率也进行了测量. Gd_5Ge_4 的交流磁化率的峰并不随着频率的增加而向高温区移动,这个现象不同于 $La_{0.88}Sr_{0.12}CoO_3$ 样品的. 通过不同物理参数的测量,证明了 Gd_5Ge_4 的这种磁玻璃态不同于传统的自旋玻璃态.

关键词:磁玻璃态;自旋玻璃;磁热材料
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0 Introduction

Gd_5Ge_4 is a parent compound of the $Gd_5(Si_xGe_{1-x})_4$ family, which shows a large magnetocaloric effect[1], giant magnetoresistance[2], and large magnetostriction[3]. It has been accepted that the order of Gd_5Ge_4 is antiferromagnetic (AFM) below 128 K in zero and low applied magnetic fields[4]. And this AFM state is the low-T metallic state in zero magnetic field[5]. Recently, a magnetic glasslike (MG) behaviour has been observed in Gd_5Ge_4[6-7]. Instead the AFM ground state, the low-T

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and low-H magnetic state attains a configuration consisting of transformed equilibrium ferromagnetic (FM) phase in an untransformed nonequilibrium AFM matrix[6]. In this state, the frozen FM and AFM ordering arrange randomly in polycrystalline samples of Gd_5Ge_4[6]. By varying both the magnetic field and temperature the process of devitrification of this MG state took place[4,7-8]. Recently in other alloys, such as $Pr_{0.2}La_{0.8}Fe_{11.4}Al_{1.6}$, similar magnetic structural transitions take place, and the mixture of AFM state and FM state has been revealed[14-15]. Further, in $Pr_{0.2}La_{0.8}Fe_{11.4}Al_{1.6}$, the ferromagnetic clusters appear randomly in the antiferromagnetic matrix, rather than a spin glass[11].

The MG state of Gd_5Ge_4 is distinctly different from the conventional spin glass state. In SG state, a random mixed-interacting system was indicated by a random, yet cooperative, freezing of spins at a well-defined temperature T_f[12]. Below T_f, a highly irreversible metastable frozen state occurs without the usual long-range spatial magnetic order. As reported previously, the SG state exists in the perovskite cobaltites and manganite etc[13-16]. In this work, MG dynamics at low temperature of Gd_5Ge_4 was studied and compared with that of $La_{0.88}Sr_{0.12}CoO_3$ which displayed a typical SG behaviour at low temperature[13].

1 Experiment

Polycrystalline Gd_5Ge_4 alloy was prepared by arc melting a stoichiometric mixture of the constituent elements using Gd (x = 99.9%, purity) and Ge (~ x = 99.99%, purity) under an argon gas atmosphere. The alloy was arc melted five times, with the button being turned over each time to ensure alloy homogeneity. Polycrystals of $La_{0.88}Sr_{0.12}CoO_3$ were fabricated from La_2O_3 (99.99%), $SrCO_3$ (99%), and Co_2O_3 (99%) starting materials by standard solid-state reaction method. The powders were thoroughly ground and calcined twice at 800 and 950 ℃ for 24 h. The reacted powders were then cold pressed under 14 MPa into pellets and sintered at 1 100 and 1 150 ℃ for 24 h respectively. No impurity phases were detected by x-ray powder diffraction. The magnetization and ac susceptibility measurements were performed by a physical property measurement system (PPMS-9). The temperature dependence of the magnetization was measured with using different experimental procedures: zero-field cooling (ZFC), field-cooled cooling (FCC), and field-cooled warming (FCW). In the ZFC mode the sample is cooled to 3 K before the measuring H is switched on and the measurement is made while warming up the sample. The applied H is switched on while cooling the sample from room temperature across T_N in the FCC mode and the measurement is made. On reaching 3 K, the data are taken again in the presence of the same H while warming up. This is the FCW mode. T was varied with a sweep rate of 0.5 K/min in the T cycling procedure and 1.5 K/min in the others procedures.

2 Results and discussion

Figure 1 shows the temperature dependence of the magnetization of Gd_5Ge_4. The magnetization was measured in H = 8 000 Oe with different procedures: ZFC, FCC and FCW. In both the FCC and FCW curves, the $M_{FCC}(T)$ saturates below 10 K and overlaps the $M_{FCW}(T)$ in the region of 2 K < T < 10 K. There is a distinct thermal hysteresis between the $M_{FCC}(T)$ and $M_{FCW}(T)$ branches above 10 K, which is dependent on the direction of the temperature change. And it is a typical characteristic of first order phase transition. The $M_{ZFC}(T)$ and $M_{FCW}(T)$ branches diverge below 17 K, and overlap above 17 K. It can be seen from the saturation of the $M_{FCW}(T)$ value in Figure 1 that the magnetic component doesn't change in Gd_5Ge_4 at T < 17 K, which indicates a frozen state existing in this process. However, the value of $M_{FCC}(T)$ does not saturate at 10 K < T < 17 K. The low temperature state of Gd_5Ge_4 in the ZFC and FC procedures becomes unstable with increasing temperature. The similar features in Gd_5Ge_4 had been observed in various applied H[6-7]. Concluding from the field (H)-temperature (T) phase diagram of Gd_5Ge_4[6], in the ZFC and the low field cooling path, the sample at 2 K < T < 10 K is deeply inside the nonergodic MG state, and at 10 K < T < 20 K, the incomplete frozen magnetic state is a mixture of the MG and AFM. Our experimental results correspond to this phase picture. In order to compare the MG state in Gd_5Ge_4 and the SG state, the properties of $La_{0.88}Sr_{0.12}CoO_3$ was investigated. The characteristic of M-T curves of $La_{0.88}Sr_{0.12}CoO_3$ have the divarication between the $M_{ZFC}(T)$ and $M_{FC}(T)$ branches which is a key property of SG state.

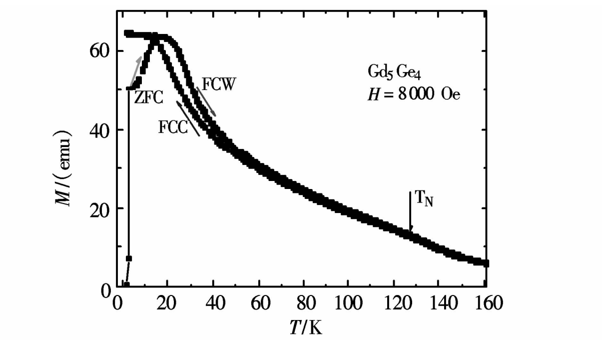

Fig. 1 Temperature dependence of magnetization for Gd_5Ge_4 in ZFC, FCC, FCW modes in an applied field of 8 000 Oe. TN is the temperature of the transition from paramagnet to AFM in Gd_5Ge_4

The effects of T cycle on $M(T)$ after the ZFC procedure in 500 Oe for Gd_5Ge_4 are presented in Figure 2(a). In the ZFC procedure, instead of increasing T unidirectionally, after reaching $T_0 = 2$ K, T is then raised to T_M and then reduced back to T_0. In the first cycle, T_M is 4 K, then $T_M = 6$, 8, 10, 12, 14 and 18 K respectively in the subsequent cycles. M_0 at T_0 clearly increases discontinuously with increasing T_M in each T cycle. It is similar to the results reported by ROY S B et al[4]. This reflects that highly metastable nature of the underlying magnetic state exists in Gd_5Ge_4, which embodies the glasslike dynamics in the low temperature region. In the T cycle progress, the frozen metastable AFM matrix may be gradually converted into equilibrium FM state due to the energy fluctuation. On the other hand, switching H on will further stimulate spin alignment into the FM state[4]. So these may result in the increase of $M_0(T_0)$.

For comparison, the effect of T cycle on M after the ZFC procedure of $La_{0.88}Sr_{0.12}CoO_3$ are presented in Figure 2(b). The whole T cycle process of measurement is same to that of Gd_5Ge_4. When the temperature increases from T_0 to T_M in the first cycle, there is a step in M. However, after the step of M, there is hardly any effect of T cycle on M. It can be concluded that the SG state in $La_{0.88}Sr_{0.12}CoO_3$ is a stable state at the low temperature, which is different from the state of Gd_5Ge_4.

Disorder and frustration are the key parameters to classify the magnetism[6]. Ac susceptibility is an important method to express the disorder and frustration state. The temperature dependence of ac susceptibility of $La_{0.88}Sr_{0.12}$

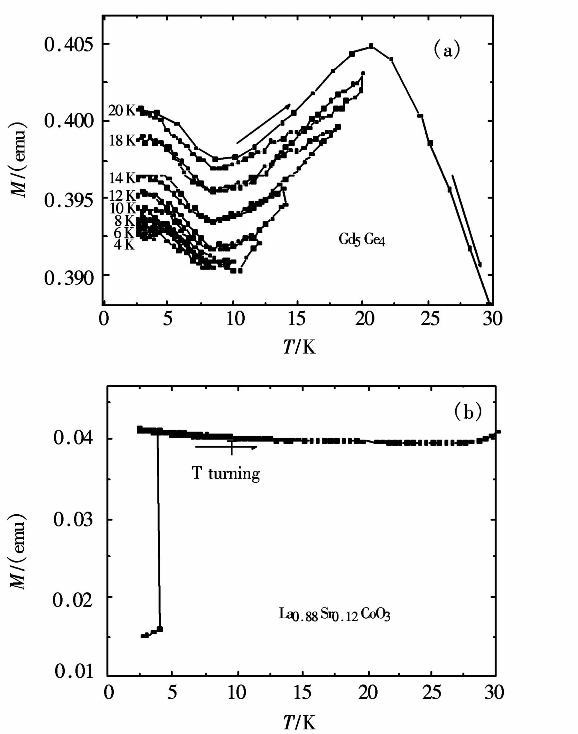

Fig. 2 The effects of T cycling on $M(T)$ after the ZFC procedure in an applied field of 500 Oe of (a) Gd_5Ge_4 and (b) $La_{0.88}Sr_{0.12}CoO_3$

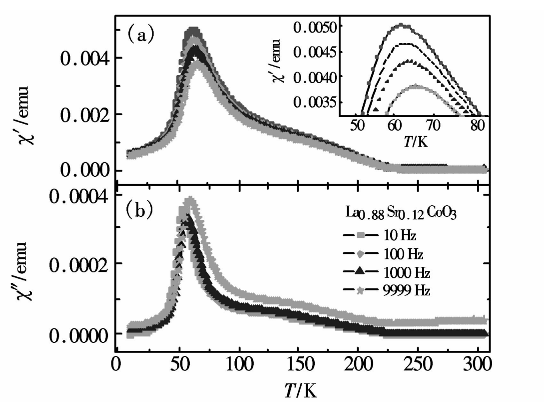

Fig. 3 Temperature dependence of in-phase (a) and out-of-phase (b) components of the ac susceptibility for $La_{0.88}Sr_{0.12}CoO_3$ The inset is a magnifying graph of the peaks of χ' curves of $La_{0.88}Sr_{0.12}CoO_3$.

CoO_3 is shown in Figure 3. Both χ' and χ'' were measured at 10, 100, 1 000 and 9 999 Hz. From Figure 3(a) we can see that χ' show frequency-dependent peaks. The maximum value of peak decreases with increasing frequency, and moves to the higher temperature region. The frequency dependence is depicted more clearly in the insert of Figure 3(a), which is a direct indication of spin dynamics. As reported[6-7], the peak corresponds to the SG freezing temperature T_f which ascends monotonically with increasing frequency. In this sample, the SG phase is achieved due to the frustration between the AFM superexchange interaction (between Co^{3+}—Co^{3+} and Co^{4+}—Co^{4+}) and the FM double exchange interaction (Co^{3+}—Co^{4+})[7]. The peaks of χ'' are also dependent on frequency, which are displayed at the vicinity of T_f where the ferromagnetic clusters freeze.

The temperature dependence of ac susceptibility in Gd_5Ge_4 is shown in Figure 4. Both χ' and χ'' are measured at 33, 331 and 1 000 Hz. With the decrease of temperature, χ' in the three different frequencies increase and achieve the maximum value at about 42 K. The peaks of three different frequencies are identical in both the shape and the value at this point. Close examination of χ', and the $M_{ZFC}(T)$, $M_{FC}(T)$ (in Figure 1) reveals that the peaks in χ' correspond to the T_C extracted from dc M-T curves. In Figure 1 the FOPT to FM in FC procedures took place over a wide T region. At T_C the rate of the FOPT is the fastest. The peaks of χ' at $T < T_C$ are expressed more clearly in the insert of Figure 4 (a). At about 16 K, another peaks show frequency dependence, the maximum value of which decrease with increasing frequency. They correspond to the temperature where the MG state exists. However, they don't move to the higher temperature region, which are different from the phenomena of $La_{0.88}Sr_{0.12}CoO_3$ discussed above. SG in $La_{0.88}Sr_{0.12}CoO_3$ is random in either position of the spins or neighboring interactions which causes 'frustration'. The disorder and frustration of SG are expressed in experiment by the peaks' movement in the curves of ac susceptibility. So we conclude that the MG state in Gd_5Ge_4 is not a random mixed-interacting system which is characterized by a highly irreversible metastable frozen state without the usual long-range spatial magnetic order. It might be MG state that a frozen-in-time magnetic phase configuration consists of a small number of transformed equilibrium FM islands and a metastable AFM matrix.

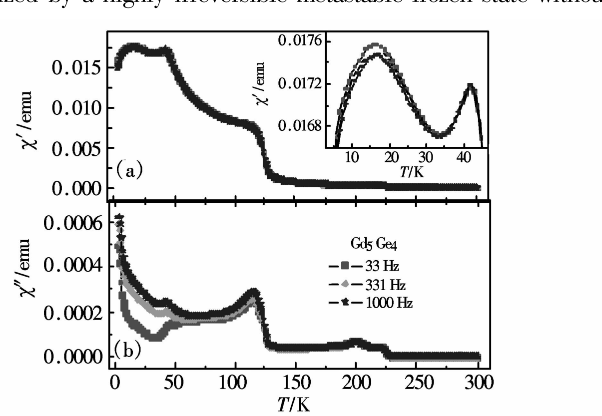

Fig.4 Temperature dependence of in-phase (a) and out-of-phase (b) components of the ac susceptibility for Gd_5Ge_4
The inset is a magnifying graph of the peaks of χ' curves of Gd_5Ge_4

3 Conclusion

In conclusion, the metastable property of MG state in Gd_5Ge_4 was discussed in contrast to the stable frozen SG state in $La_{0.88}Sr_{0.12}CoO_3$. The magnetization continues to increase with increasing T cycle in Gd_5Ge_4, however there is hardly any effect of T cycle on magnetization in $La_{0.88}Sr_{0.12}CoO_3$. In T cycle process, the frozen metastable AFM matrix may be gradually converted to equilibrium FM state due to the energy fluctuation in Gd_5Ge_4. The peaks of ac susceptibility in Gd_5Ge_4 do not move to the higher temperature region with increasing frequency, which are different from the phenomena of $La_{0.88}Sr_{0.12}CoO_3$. This kind of magnetic glasslike state in Gd_5Ge_4 is quite different from conventional spin glasses where the spin configuration is frozen at random on a microscopic scale.

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