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Frustration-Induced Relaxation in Polycrystalline $Nd_{1-x}Sr_xCoO_3$ (x=0.10, 0.15, 0.20)

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This paper attempts to examine the details on the magnetic relaxation and aging effect of cobaltite $Nd_{1-x}Sr_xCoO_3$ (x=0.10, 0.15, 0.20). To this end, a series of polycrystalline $Nd_{1-x}Sr_xCoO_3$ samples were prepared in the traditional way, and their properties were investigated from the DC magnetization, relaxation and aging effect. The field-cooled and zero-field-cooled test curves were in obvious mirror symmetry, an evidence of the disorder and frustration in the system. This situation obeys the extended exponential relationship at low temperature for $Nd_{1-x}Sr_xCoO_3$. Based on the relaxation rate W (t), the author confirmed that the spin glass state is the coexistence of the spin glass and the ferromagnetic cluster. In other words, the system is spontaneously separated into the ferromagnetic cluster, the spin glass and the non-magnetic base. In addition, the relaxation and aging effect were inherent properties of the system, and the results of the interaction of ferromagnetic clusters and spin glass at the low temperature. Therefore, in $Nd_{1-x}Sr_xCoO_3$ system, the spin glass behavior was determined by ferromagnetic interaction and spin glass phase; the magnetic relaxation and aging effect of $Nd_{1-x}Sr_xCoO_3$ system originate from the magnetic structure of the system.

1. Introduction

In recent years, perovskite cobaltites have set off a new wave of research, because of the rich magnetic phenomena in doped cobaltite system. The exchange bias and magnetic relaxation of cobaltite were explored in great details, leading to the discovery of spin glass in cobaltite system. Some scholars suggested that magnetic phase separation is an obvious trend in perovskite cobaltite system, and presented a rich phase diagram of cobaltite system (Wu and Leighton, 2003; Luo et al., 2006; Yang, 2014; Kundu, et al., 2006). In particular, the cobaltite $La_{1-x}Sr_xCoO_3$ (LSCO) has been a research hotspot, due to the competition between spin glass/cluster glass and the ferromagnetic cluster (Huang et al., 2016; Mukherjee et al., 1996). For example, Tang and Sun concluded that the LSCO does not have long-range ferromagnetic order because of its magnetic exchange bias (Tang et al., 2006). Thus, the LSCO system consists of ferromagnetic cluster and spin glass order, i.e. short-range ferromagnetic cluster embedded in non-magnetic region. Nam et al. obtained the spin glass dynamics according to the critical slowing down formula (Nam et al., 2000), and confirmed that spin glass exists in cobaltite $La_{0.95}Sr_{0.05}CoO_3$ after probing into the magnetic relaxation and aging effects. In these studies, a lot of magnetic properties of samples have been obtained through characterization methods, but there are still differences in the details (Paraskevopoulos et al., 2001; Yoshii et al., 2001; Stauffer and Leighton, 2004; Nam et al., 1999). This calls for further research into the properties of perovskite cobaltite.

In light of the above, this paper attempts to examine the details on the magnetic relaxation and aging effect of cobaltite $Nd_{1-x}Sr_xCoO_3$ (NSCO) samples. The research results show that the magnetic relaxation and aging of the system are not induced by external conditions, but the inherent properties of the system.

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2. Experiments

2.1 Materials

High-purity raw materials Nd_2O_3, Co_2O_3 and $SrCO_3$ were prepared for the experiments. Prior to sample preparation, the differential thermal analysis was conducted at the air temperature of 20 °C ~1,000 °C to remove the moisture from the rare earth oxide Nd_2O_3.

2.2 Synthesis of samples

The perovskite cobaltite NSCO (x=0.10, 0.15, 0.20) samples were obtained by the traditional solid-state reaction method. First, the high-purity Nd_2O_3 powder was burned for 4 h at 800 °C; second, the $SrCO_3$, Co_2O_3 and Nd_2O_3 powders were mixed with alcohol at the ideal ratios; third, the mixtures were ground into powders and then pressed into pellets at the air temperature of 1,000 °C for 48 h; fourth, the pellets were reground and sintered again at 1,100 °C; finally, the sintered objects were slowly cooled to room temperature to complete the sample preparation.

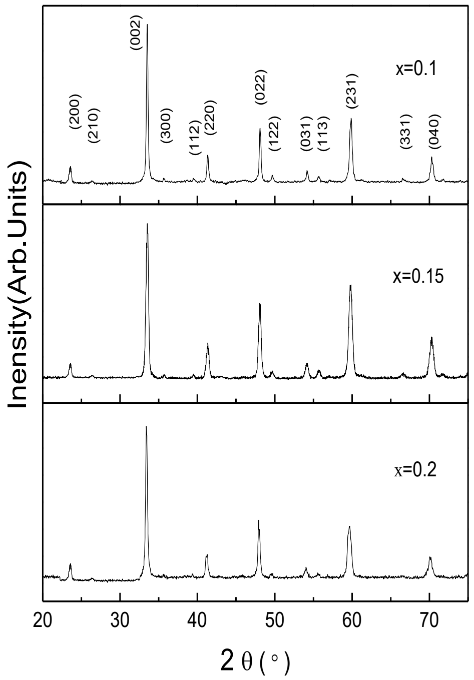

Figure 1: The room temperature X-ray diffraction pattern of $Nd_{1-x}Sr_xCoO_3$ (x=0.10, 0.15, 0.20)

2.3 Characterization techniques

The test of powder X-ray diffraction (XRD) is based on a D[1] X ray diffractometer produced by Bede. The instrument uses the Cu Kα radiation. The measurements of aging effect, dc magnetization and relaxation effects are based on the physical properties measurement system designed by Quantum Company.

3. Results and discussion

3.1 Dc magnetization

According to the XRD pattern of room temperature (Figure 1), the samples are of single phase and orthorhombic perovskite structure.

Figure 2 shows the M (T) curve of the NSCO (x=0.10, 0.15 and 0.20) polycrystalline samples with field cooled (FC) and zero field cooled (ZFC) thermal magnetic curve. It can be seen from the figure that the FC and ZFC curves separated from each other at low temperature, forming an obvious bifurcation (i.e. irreversible behavior). With the reduction of temperature, the FC curve gradually increased, while the ZFC curve first increased to the peak value and then decreased. The width of the peak slowly widened with the increase in doping ratio. In short, the FC and ZFC curves are bifurcated, and the peak of the ZFC curve is commonplace in the spin glass system (Fondado et al., 2000; Zobel et al., 2002; Wu et al., 2015; Yang, 2017).

x=0.1 samples showed different behaviour compared with other samples, and the magnetization decreased sharply in value compared with other doping ratio. In particular, its magnetization declined at a much faster rate than the samples of the other doping ratios. The magnetization intensified with the temperature, but at a rather slow rate, and peaked at low temperature. This trend echoes with the low doping $La_{1-x}M_xCoO_3$ (M=Sr, Ca and Ba) in Reference (Kriener et al., 2004). This indicates when the number of Co^{4+} is less, that the double exchange function is weak. With a weak ferromagnetism, the samples exhibited little ferromagnetic behaviour in magnetization curve. The ZFC peak of x=0.10, 0.15 sample is produced by spin freezing effect. This effect means the magnetic spin in the spin-glass system cannot rotate freely at low temperature. According to the microstructure of the test systems, there were significant differences in the environment of magnetic moments. Hence, the magnetic spins in the systems froze in different directions.

The ZFC peak of x=0.20 sample is attributable to the competition between the unidirectional and anisotropic local field and the external magnetic field (Gruyters, 2005). Because of the gradual increase of the ferromagnetic cluster in the nonmagnetic base, the cluster randomly arranged to form a local anisotropic field similar to the $La_{0.5}Sr_{0.5}CoO_3$ system (Nam et al., 1999). While ZFC curve peak of x=0.15 sample appeared near T_{f}=35 K, the ZFC peak of x=0.20 sample emerged near T_{f}=47 K. This behaviour agrees well with that of the LSCO system, that is, the behaviour of spin glass/cluster glass (Tang et al., 2006). The ZFC peak of spin glass is often observed at freezing temperature.

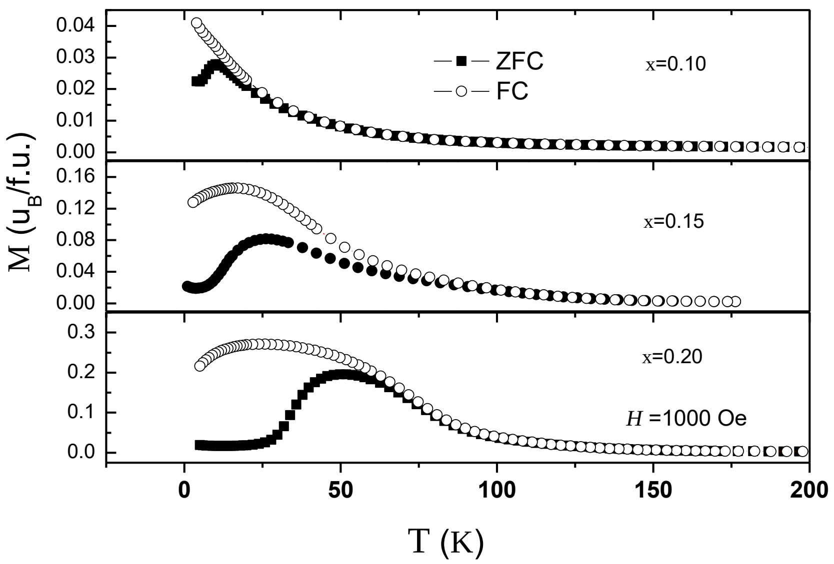

Figure 2: Field cooled and zero field cooled magnetization of $Nd_{1-x}Sr_xCoO_3$ (x=0.10, 0.15, and 0.20)

3.2 Magnetic relaxation and aging effects

The spins of perovskite cobaltites are disorder, producing setbacks to the system. In other words, the spin glass system is frustrated. The frustrated system does not have a lowest energy state. Instead, there is countless metastable state at low temperature. Any change of test state will lead to the variation in the free energy of the system, which in turn alters the spin state. Of course, the spin state does not change immediately, due to the barrier in the phase space. Under a constant temperature, the barrier is positively correlated with the distribution of relaxation time. Thus, the magnetic relaxation is another prominent feature of spin glass system (Caiuffo et al., 1999; Yamaura et al., 1999; Saron et al., 2016; Li et al., 2016). To detect the spin glass properties of the object, the author conducted a relaxation phenomenon test, seeking to gain more insights into the system. Figure 3 presents the FC and ZFC residual magnetization of the NSCO at different measuring times under 10 K for x=0.15.

It can be seen from Figure 3 that the magnetization varied with the measuring time. With the increase of measuring time, the residual magnetization gradually reduced under the FC condition, and increased under the ZFC condition. There is an obvious mirror symmetry between FC and ZFC curves, that is, the two curves were exactly opposite in this system under the same test field, temperature and wait time (DeFotis et al., 1998).

The test results show that relaxation and aging, as the intrinsic properties of the system, solely rely on the magnetic structure of the system. A lot of spin glass system also have characteristics of relaxation phenomenon which are the characteristic of spin glass system. (Tang et al., 2006). Hence, the relaxation and aging of the NSCO are not caused by external factors, but the magnetic structure of spin glass. The change of the test conditions are only different research means. Double exchange coupling in ferromagnetic clusters are very obvious, relaxation and aging is due to exist frustration and result in slow growth of the ferromagnetic clusters in the system. In essence, the aging effect demonstrates the disorder and frustration of the system.

The relaxation effects are due to the disorder and frustration in the NSCO system. The NSCO is frustrated system, resulting in slow growth ferromagnetic clusters.

In the spin glass system, the relaxation phenomenon usually obeys the stretched exponential relationship equation (DeFotis et al., 1998):

$$M(t) = M_2 \exp[-(\frac{t}{t_p})^{1-n}] \quad (1)$$

where M_2 is the contribution of spin glass; t_p is the constant time. M_2, t_p and n are undetermined parameters. The former two parameters are associated with temperature and waiting time, and the last parameter only depends on the temperature.

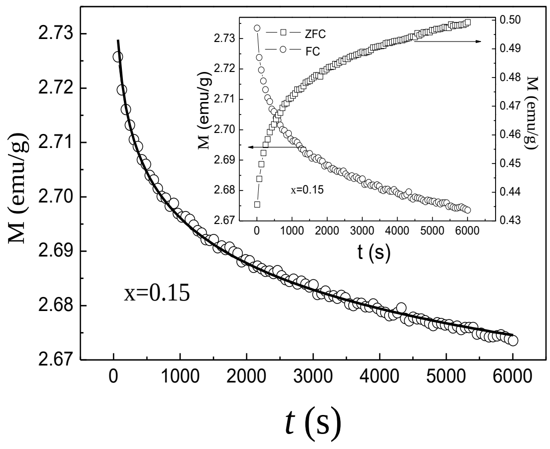

Figure 3: The remanent magnetization of $Nd_{1-x}Sr_xCoO_3$(x=0.15). The solid line is the best fits Eq. 1

Using the equation (1) fit the experimental data in the FC conditions. According to the fitted results, the relaxation data is in line with the stretched exponential relationship. Experimental fitting parameters of x = 0.10 and x = 0.15 samples are displayed in table 1. The results was similar to the behavior observed in the spin glass system by DeFotis (DeFotis et al., 1998).

Table 1: The experimental fitted parameters of Eq. 1 for x = 0.10 and x = 0.15

stretched exponential form	M_2(emu/g)	t_p(s)	n
x=0.10	0.13(1)	$5.2(1)\times10^5$	0.62(5)
x=0.15	7.27(8)	$4.7(2)\times10^3$	0.97(2)

To sum up, the relaxation and aging effects confirm the spin glass properties of the NSCO (x=0.10, 0.15, 0.20) system. In fact, the two effects are determined by the magnetic features of spin glass, rather than the external influence. The Magnetic relaxation phenomenon of cobaltite system is inherent in the system.

To further explore the magnetic relaxation phenomenon, the relaxation rate W (t) was introduced to analyse the magnetic phenomenon under the FC. Ulrich et al. using Monte Carlo relationship of ferromagnetic particles system (Ulrich et al., 2003), found that for all the different grain density, system of relaxation rate W (t) according to the exponential decay.

$$W(t) = At^{-n} \quad (2)$$

where n is the particle density; A is the leading factor related to temperature.

The relaxation rate W (t) can be expressed as:

$$W(t) = -(d/dt)\ln M(t) \quad (3)$$

Here, the relaxation rate W (t) is discussed based on the residual magnetic moment. Figure 4 presents the attenuation of the relaxation rate at 10 K (solid line: the data fitted by equation (2)).
From Figure 4, it is clear that the test data are in accordance with the relationship in equation (2). The n value was close to 1, an indicator of the strong interaction between clusters. Thus, it is confirmed that the system was spontaneously separated into the ferromagnetic cluster, the non-magnetic base and the spin glass. This is similar to the case of $La_{0.82}Sr_{0.18}CoO_3$ system (Huang et al., 2008). When the ferromagnetic clusters are embedded in the non-magnetic substrate or the magnetic cluster size is small enough, a spin disordered interface layer or surface layer forms, resulting in the formation of the spin glass phase. The magnetic behaviour of spin glass in cobaltite is not like manganese compound, only consider the interaction between clusters. In the cobaltite system, the interaction of ferromagnetic cluster and spin glass phase resulted in the behaviour of spin glass. The above tests and analyses on magnetization and relaxation provide valuable insights on the magnetic interaction of the NSCO series.

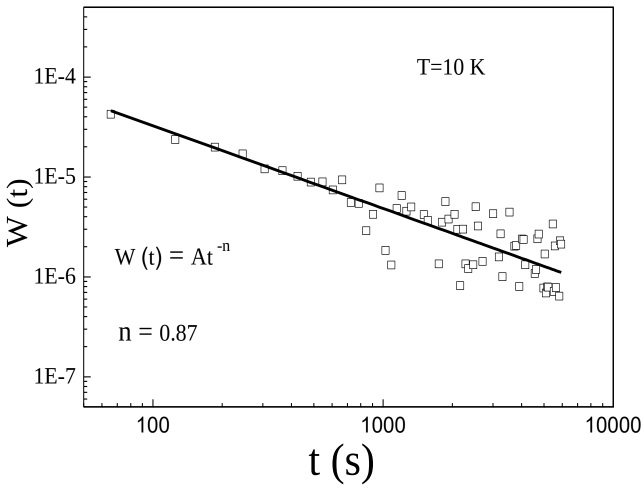

Figure 4: W vs $log_{10}t$ for x=0.15. The solid line is the best fits Eq. 2

4. Conclusions

This paper digs deep into the DC magnetization and magnetic relaxation of polycrystalline NSCO (x=0.10, 0.15, 0.20) samples. Several tests were performed to determine the DC magnetization and magnetic relaxation of the object. The DC magnetization data indicate that x=0.10 and x=0.15 samples are in the spin glass phase, while the x=0.20 sample is in the cluster glass phase. The test results on relaxation shows the system exhibited glassy magnetic behaviour in low doping. From the relaxation rate W (t), the author confirmed that the spin glass state is coexistence of the spin glass and the ferromagnetic cluster, and the system is spontaneously separated into the ferromagnetic cluster, the spin glass and the non-magnetic base. The FC and ZFC curves show a good mirror relationship, indicating the disorder and frustration in NSCO (x=0.10, 0.15, 0.20) system. The magnetic relaxation and aging effect of NSCO system are determined by the magnetic structure of the system, and the relaxation and aging phenomenon are the characteristics of the spin glass system.

Acknowledgments

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