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Investigation of the Ferrimagnetic Transition in Doped Cobaltite $Nd_{1-x}Sr_xCoO_3$ ($0.1 \leq x \leq 0.5$)

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In the present study, the ferrimagnetic transition of doped cobaltite $Nd_{1-x}Sr_xCoO_3$ ($0.1 \leq x \leq 0.5$) was investigated in detail. The samples were successfully synthesized through solid state reaction method while the mixtures were ground and sintered. X-ray diffraction power patterns showed that all the samples were crystallized in the single perovskite structure with orthorhombic. Dc magnetization and ac susceptibility of samples were performed from 300 K to 5 K in the magnetic field. The results of dc magnetization measures suggest that $Nd_{1-x}Sr_xCoO_3$ is ferrimagnetic phase below 60 K. The lower doping samples are well shown by a fit to the critical slowing down of the spin class. Moreover, the study shows that magnetic interaction appears between Co spins and Nd spins. Therefore, the investigation suggests that the Nd and Co anti-parallel, $Nd_{1-x}Sr_xCoO_3$ ferrimagnetic transition exists at low temperature. Furthermore, in the paper we summarized the phase diagram obtains from the magnetic studies which presented the system is divided into ferromagnetic and spin-glass-like regions.

1. Introduction

In recent years, doped cobaltite $Nd_{1-x}Sr_xCoO_3$ (NSCO), have attracted wide spread attention due to the spin-glass behavior which is inherent characteristics of phase separation system. Moreover, in order to study the properties of the doped compound, a lot of good research methods were adopted, which is successfully research in the areas. (Fondado et al., 2001; Ghoshray et al., 2004; Yang and Sui, 2010; Krimmel et al., 2001). Apart from this, Stauffer has reported the magnetic interaction of NSCO (Stauffer and Leighton, 2004), in which NSCO with $x \leq 0.18$ was reported as spin glass phase. At $x=0.18$ there exist an obvious change of the magnetization and the $x>0.18$ region was ferromagnetic behavior. A remarkable feature of the system is that its magnetic behavior changes with x in the spin-glass (SG) region which is very similar to that seen in the $La_{1-x}Sr_xCoO_3$ samples (Nam et al., 1999; Joseph et al., 2005; Señarís-Rodríguez et al., 1999). For $La_{1-x}Sr_xCoO_3$ system, a lot of investigations on magnetic behavior for the lower doping samples have been systematically reported (Mao et al., 2013; Huang et al., 2008), especially, for exchange bias phenomenon of the $La_{1-x}Sr_xCoO_3$ ($0.12 \leq x \leq 0.3$) samples which was recently confirmed (Tang et al., 2006), but less study has been done about this phenomenon of $Nd_{1-x}Sr_xCoO_3$ system. Thus, further study about $Nd_{1-x}Sr_xCoO_3$ is very important in order to explore this system more clearly. In general, the research in this aspect is helpful to the development of magnetic electronics which is a general consensus now (Saron et al., 2016; Shirinova et al., 2016; Wu et al., 2015).
In this thesis, we study the dc magnetization and ac susceptibility of doped cobaltite $Nd_{1-x}Sr_xCoO_3$. Dc and ac magnetic properties data show region was named ferrimagnetic phase.

2. Experiments

2.1 Materials

The high purity Nd_2O_3, $SrCO_3$ and Co_2O_3 powders were prepared. In order to remove the moisture in the rare earth oxide Nd_2O_3, before prepared samples, we made thermogravimetric-differential thermal analysis (TG-DTA) tests. TG-DTA tests were collected by the TG-DSC2960 instrument in the temperature range 20 °C-1000 °C in the air. The test results (not shown here) show in the 280 °C and 420 °C appears obvious peak.

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And after 800 °C, the qualities of Nd_2O_3 remain unchanged. As a result, the Nd_2O_3 were precalcined at 800 °C in the air.

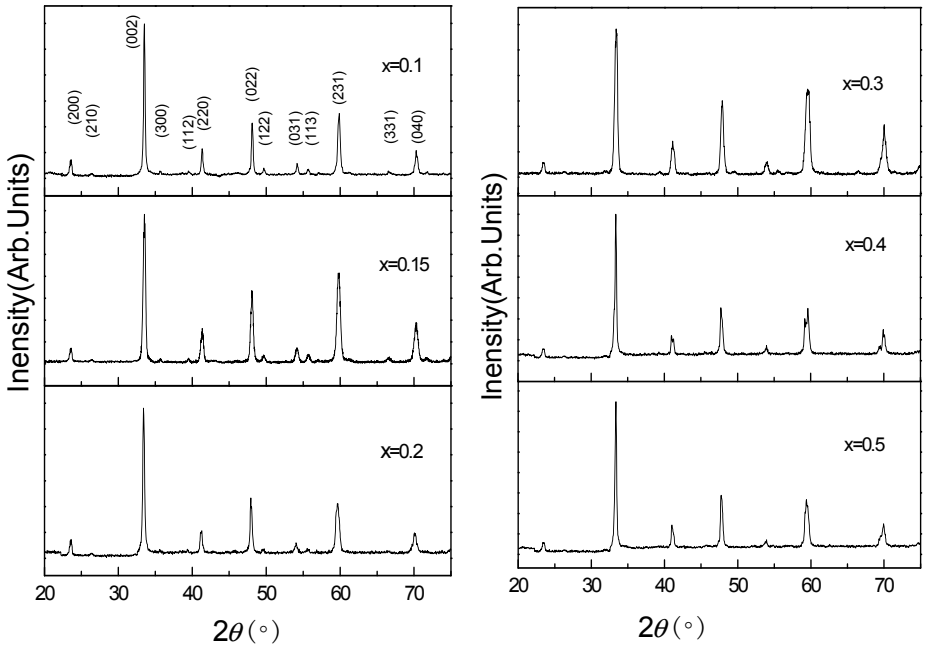

Figure 1: The room temperature X-ray diffraction pattern of $Nd_{1-x}Sr_xCoO_3$ ($0.1 \le x \le 0.5$)

2.2 Synthesis of $Nd_{1-x}Sr_xCoO_3$ samples

The doped cobaltite NSCO samples were synthesized by solid state reaction method. First, a certain proportion of Nd_2O_3, Co_2O_3 and $SrCO_3$ were ground and sintered at 1000 °C. After that, the mixture was reground and pressed into pellets in 8 Mpa pressure and fired at 1100 °C and 1200 °C for 24h, respectively. The last, along with the furnace cooling to room temperature, complete the preparation of the samples.

2.3 Characterization techniques

X-ray diffraction (XRD) power patterns were measured through the Bede D^1 XRD spectrometer. The magnetization testing was made by the physical properties measurement system (PPMS) in field cooled process (FC) and in a larger temperature range. Ac susceptibility measurements were collected in the frequency range 10 Hz<f<10 kHz and the same temperature range as dc measurement.

3. Results and discussion

3.1 Dc magnetization

X-ray diffraction power patterns in Figure 1 present the absence of impurity phases, which was indicated that the samples were crystallized in the single perovskite structure with orthorhombic.

In Figure 2 are the dc magnetization measured in a static field after FC. With increasing x, dc magnetization increase in magnitude. It can be seen clearly from the figure that the samples increase in the magnetization below Curie temperature T_C. This means when field cooled the cluster align, leading to the onset of large ferromagnetic-type magnetization. These results are consistent with those described in $La_{1-x}Sr_xCoO_3$ samples (Nam et al., 1999; Joseph et al., 2005). In the FM region, the T_C monotonously increases with x.

A maximum of magnetization for $Nd_{0.90}Sr_{0.10}CoO_3$ sample was obtained at low temperature, but not visible for else samples. Kriener el at pointed out this feature in $La_{1-x}Sr_xCoO_3$ (Kriener et al., 2004). Such as $x \ge 0.15$, due to the effect of Nd^{3+} spins, magnetization decrease in low temperature as shown in the figure. Krimmel observed this phenomenon in $Nd_{0.67}Sr_{0.33}CoO_3$ cobaltite (Krimmel et al., 2001). Because of $Co^{3+}/Co^{4+}$and Nd^{3+} magnetic moment in reverse order, which cause the ferrimagnetic transition. The Nd ions are induced via the Co moments, but the Nd moments are aligned anti-parallel to the field created by the Co moments and some Nd-Co magnetic interaction must be invoked. The ferrimagnetic transition appears only at low temperature, because of the weak interaction between Co^{3+}/Co^{4+} and Nd^{3+} magnetic moment. Moreover, ferrimagnetic

temperature (T_{Ferri}) of the samples increase with x, due to the strong coupling of Nd and Co spin as a result of increase of the number of ferromagnetic clusters.

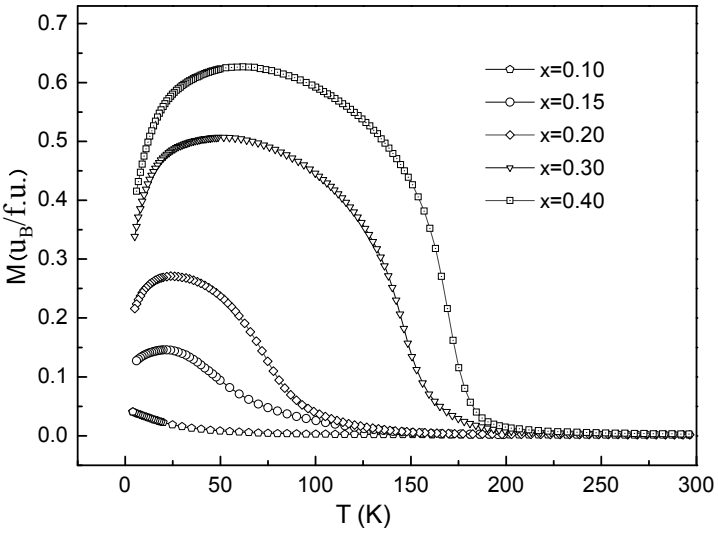

Figure 2: Field cooled magnetization of $Nd_{1-x}Sr_xCoO_3$ (0.1≤x≤0.4), measured in the field 1000 Oe

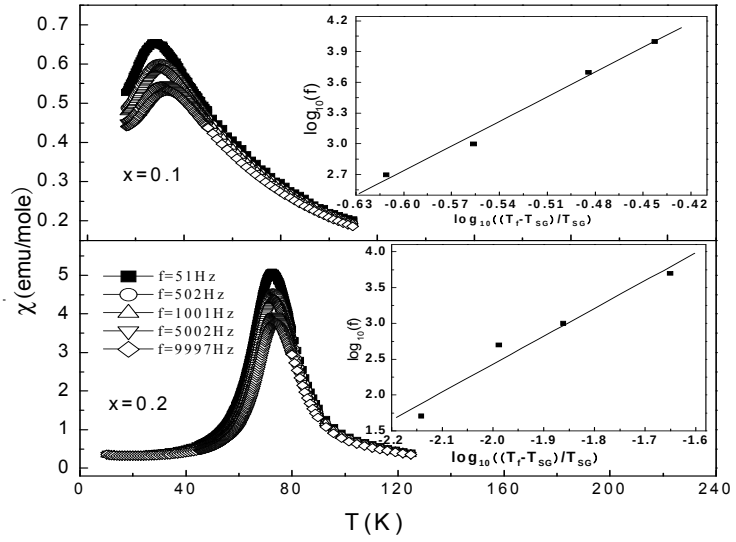

Figure 3: The ac susceptibility of x=0.1, 0.2 sample. Inset fit of ac susceptibility with the critical slowing down

3.2 Ac susceptibility

In order to understand the magnetization further, ac susceptibility was collected at difference frequencies. Due to the magnetic moments were frozen at frozen temperature T_f, ac susceptibility curve peaks change with frequency. In Figure 3 presents respectively the ac susceptibility of x=0.1, 0.2 and 0.4. The x=0.1, 0.2 are spin glass (SG), however, from the χ' (T) curve we concluded that x=0.4 is the FM behavior (Nam et al., 1999; Krimmel et al., 2001).

In Figure 3 the ac susceptibility peaks change significantly with frequency of x=0.1 which appears at T_f. As we known that this behavior is the important feature of SG phase (Bianco et al., Yang, 2014; 2004; Gruyters, 2005; Caiuffo et al., 1999; Passamani, et al., 2006). Different with the x=0.1 sample, then, for x=0.20 simple present some weak frequency dependent peaks. This frequency-dependent for x=0.10 and x=0.20 is similar qualitatively to that describe for $La_{1-x}Sr_xCoO_3$ and $Gd_{1-x}Sr_xCoO_3$ (Señarís-Rodríguez et al., 1999; Rey-Cabezudo, et al., 2002; Luo, et al., 2006; Li, et al., 2016). We assume the x=0.2 sample is cluster glass (CG) due to present a small dc magnetization and the weak frequency dependent peaks. The presence of the

typical features of spin-glass state in NSCO was well revealed by ac susceptibility. The ac susceptibility of x=0.4 sample is a decrease with decreasing of temperature which shows frequency independent peak. The peak, not changed with frequency at Curie temperature, marks the beginning of the ferromagnetic order. The difference of the χ' (T) between x=0.20 and x=0.4 sample indicated that the number of ferromagnetic clusters increase in higher doped sample. In general, the tests of ac susceptibility make us understand internal mechanism of the freezing dynamics.

The ac susceptibility data of the lower doping samples are well shown by a fit to the critical slowing down of the spin class. These properties are performed with the following equation:

$$\tau = \tau_0[(T_f - T_{SG})/T_{SG}]^{-ZV} \quad (1)$$

Table 1: The fitted parameters of Eq. 1 while fitted with ac susceptibility

Slowing down model	τ_0 (s)	ZV	T_{SG} (K)
x=0.1	$3.1(6)\times10^{-10}$	9.3(9)	12.3(1)
x=0.15	$1.6(9)\times10^{-12}$	10.8(5)	35.1(5)
x=0.2	$6.0(6)\times10^{-11}$	4.0(2)	72.0(6)

The best fit, for example x=0.1 and 0.2 sample, which are displayed in inset of Figure 3.

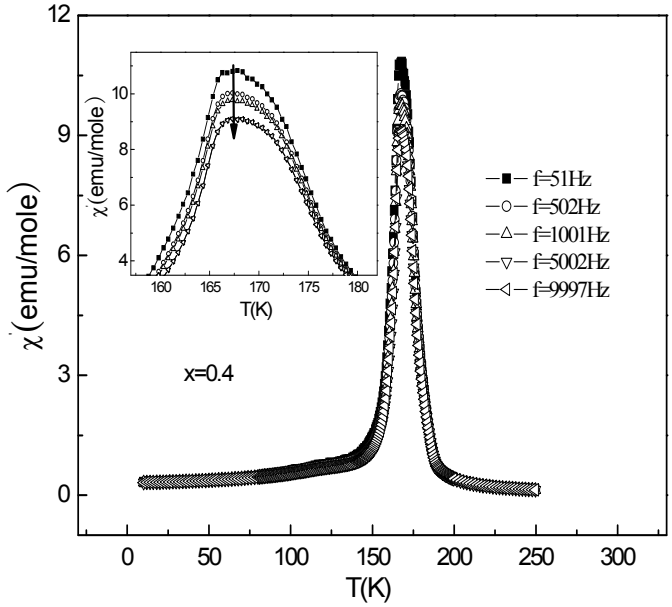

Figure 4: Temperature dependence of the real part of the ac susceptibility of x=0.4 sample

3.3 Phase diagram

Chapter 2 From what has been discussed above, in Figure 5 we summarized the phase diagram obtain from the magnetic studies. The phase diagram presented here is divided into two regions. As is shown, below x≤0.2 the magnetic properties are dominated by the spin glass or cluster glass. In this region, the dc and ac susceptibility show features which are typical spin glass/cluster glass behavior and the frozen temperature T_f strongly increases with x. We emphasized that additional anomalous feature in ac susceptibility curves for 0.2, which has been observed in polycrystalline $Gd_{1-x}Sr_xCoO_3$ system (Luo, et al., 2006), occur in our sample. Thus, we conclude that the x=0.2 sample is not spin glass but is cluster glass. Above x=0.2, the doped cobaltite system becomes ferromagnetic properties and presents ferrimagnetic properties below 60 K. Furthermore, the temperature of ferrimagnetic transition shows some remarkable characteristics. As is shown in the figure 5, the temperature of ferrimagnetic transition increases with x and tends to saturate around 60 K for larger x. Our results agree with that obtained by Neutron power diffraction in the literature (Krimmel et al., 2001; Paraskevopoulos, et al., 2001).

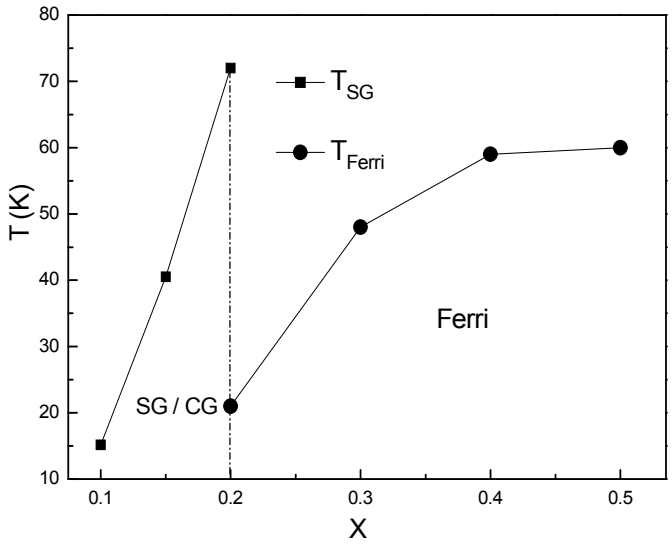

Figure 5: Ferrimagnetic (Ferri) and spin/cluster glass (SG/CG) phase diagram of $Nd_{1-x}Sr_xCoO_3$. The solid lines are to guide the eye

4. Conclusions

To conclude, we have measured and analyzed the magnetization data of NSCO over a wide range of doping. The detailed research was performed on the $Nd_{1-x}Sr_xCoO_3$ ($0.1 \leq x \leq 0.2$) which is typical spin or cluster-glass behavior. Moreover, for $x>0.2$ samples, the system become ferromagnetic and show ferrimagnetic properties below 60 K. The Curie temperature T_C increases with x up to 0.5. Thus, the investigation suggests that the magnetic moment of Nd and Co in reverse order, $Nd_{1-x}Sr_xCoO_3$ ferrimagnetic transition exists at the low temperature.

Acknowledgments

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