Vol 18 No 11, November 2009
1674-1056/2009/18(11)/5034-04

Chinese Physics B

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Fe-doping induced Griffiths-like phase in $La_{0.7}Ba_{0.3}CoO_3$*

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(Received 6 February 2009; revised manuscript received 4 May 2009)

The effect of Fe-doping on the magnetic properties of the ABO_3-type perovskite cobaltites $La_{0.7}Ba_{0.3}Co_{1-y}Fe_yO_3$ ($0 \leq y \leq 0.80$) is reported. With no apparent structural change in any doped sample, the Curie temperature (T_C) and the magnetization (M) are greatly suppressed for $y \leq 0.30$ samples, while a distinct increase in T_C for the $y = 0.40$ sample is observed. With the further increase of Fe concentration, T_C increases monotonically. Griffiths-like phases in $0.40 \leq y \leq 0.60$ samples are confirmed. The formation of the Griffiths-like phase is ascribed to B-site disordering induced isolation of ferromagnetic (FM) clusters above T_C.

Keywords: perovskite cobaltites, Fe doping, Griffiths phase

PACC: 7280G, 7530K, 7590

Nowadays materials with the colossal magnetoresistance (CMR) effect attract much attention because of their potential application in magnetoelectronic applications.[1−3] Intrinsic inhomogeneity, namely phase separation, is essential to the CMR effect in manganites and cobaltites.[4,5] An uncorrelated cluster state, named the Griffiths phase,[3,6] started to form at the Griffiths temperature T^* above T_C for low-doped phase-separated manganites where ferromagnetic (FM) clusters were formed out of antiferromagnetic (AFM) matrix. In high-doped manganites, the Griffiths phase was also observed by B-site doping.[7,8] As addressed by Griffiths dealing with the diluted Ising model,[9] the non-uniform distribution of interactions in the magnetic lattice is the key to the appearance of the Griffiths phase. In other words, quenched disorder ('dirt') is needed for the Griffiths phase to exist.[3,4] As for doped manganites, the Griffiths phase has usually been observed in low-doped regions.[10−14] With the increase of doping concentration, FM clusters start to interact with each other to form long-range order (LRO) FM state. For high-doped manganites, B-site doping can dilute the magnetic lattice and block the interactions between FM clusters, and the formation of an FM cluster state instead of the appearance of an LRO FM state is observed in a temperature range where non-B-site doping manganites exhibit the LRO FM state. Although it has been proved that the Griffiths phase universally exists in phase-separated manganites,[15] further work is needed to clarify the universality of this phenomenon in other phase-separated systems including phase-separated perovskite cobaltites. However, only a few studies have addressed this issue in cobaltites.[16−18] FM $La_{1-x}Sr_xCoO_3$ is a non-Griffiths phase, while a Griffiths phase is observed in single-layered $La_{2-x}Sr_xCoO_4$ and $Nd_{2-x}Sr_xCoO_4$. So far there has still been no such work on $La_{1-x}Ba_xCoO_3$ which has the same crystal structure as and similar magnetic properties to $La_{1-x}Sr_xCoO_3$.[19] The exchange bias-like effect in $La_{1-x}Ba_xCoO_3$ suggested that this system was also phase-separated.[20] By simply analysing the inverse susceptibility in our present work, no Griffiths-like phase can be obtained in FM $La_{0.7}Ba_{0.3}CoO_3$. However, B-site doping can invoke quenched disorder and offer us a way to test the possibility of the existence of a Griffiths phase in this system. In this work, we choose Fe as a dopant because Fe atoms and Co atoms have almost identical radii and no apparent structural change will be induced.[21] We present the results of Fe doping into perovskite cobaltite $La_{0.7}Ba_{0.3}Co_{1-y}Fe_yO_3$ with y up to 0.80 and we find the formation of the Griffiths phase when $0.30 \leq y \leq 0.60$.

Bulk polycrystalline samples with nominal composition $La_{0.7}Ba_{0.3}Co_{1-y}Fe_yO_3$ (y = 0, 0.10, 0.20,

*Project supported by the National Basic Research Program of China (Grant No 2009CB929201) and the National Natural Science Foundation of China (Grant No 10774179).

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0.30, 0.40, 0.50, 0.60, 0.80) were prepared by the conventional solid-state reaction method. Phase analysis and lattice parameters were determined by powder x-ray diffraction (XRD) with Cu Kα radiation. The magnetization measurements were performed by a commercial superconducting quantum interference device (SQUID) magnetometer.

XRD data indicate that all samples are of single phase with $R\bar{3}c$ rhombohedreal symmetry even when y is 0.80, which can be seen from Fig.1. Refinements were done by the Rietveld method implemented in the program Rietica.[22] The obtained structural parameters were listed in Table 1. As we can see from Table 1, the lattice constants a and c increase as Fe concentration increases. There is no structural change induced by Fe-doping through the whole doping concentration.

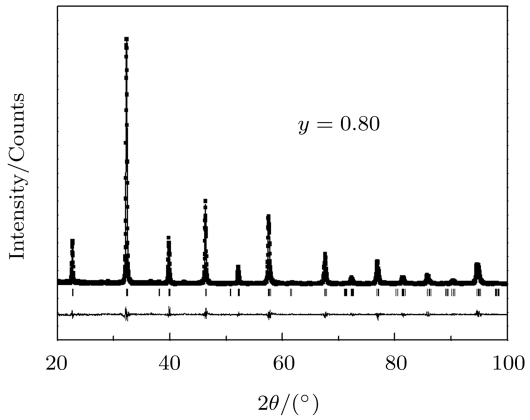


Fig.1. Representative Rietveld refined powder x-ray diffraction pattern corresponding to $y = 0.80$ sample with $R\bar{3}c$ space group.

Table 1. Lattice constants a and c, inflection of Curie point T_C, and Curie temperature θ obtained by fitting to Curie–Weiss law for all samples studied.

y	a/Å	c/Å	T_C/K	θ/K
0	5.4731	13.3662	201	213.4
0.10	5.4777	13.3738	164	166.5
0.20	5.4829	13.3905	109	146.7
0.30	5.4894	13.4046	88	92.8
0.40	5.4975	13.4209	133	53.7
0.50	5.5077	13.4424	183	–3.2
0.60	5.5195	13.4670	235	–9.9
0.80	5.5490	13.5406	> 300	

To investigate the doping effects on magnetic properties of ferromagnetic $La_{0.7}Ba_{0.3}CoO_3$, the temperature dependence of the magnetization (M–T) was measured at 500 Oe (1 Oe = 79.5775 A/m) for all samples after cooling in the same magnetic field, and the results are shown in Fig.2. From Fig.2, the undoped sample shows a sharp paramagnetic–ferromagnetic phase transition at $T_C \sim 201$ K, a typical characteristic of a ferromagnet. Here, T_C is defined as the temperature corresponding to the peak of dM/dT in the M–T curve. For doped samples, it can be seen that Fe doping not only weakens the magnetization but also drives the Curie temperature T_C to lower temperatures. For the $y = 0.20$ sample we note that there is a significant decrease of M after M has reached its peak and then a plateau is formed with the decrease of the temperature below T_C, indicating the occurrence of a rather sophisticated phase instead of a simple ferromagnet or antiferromagnet. This may originate from the competition between FM interaction and AFM interaction. Similar behaviour with a smaller amplitude of decrease was also observed for the $y = 0.30$ sample. However, what we are interested in most is a slight increase of M and a significant increase of T_C as the doping concentration further increases to $y = 0.40$, just opposite to what we expected. With the further increase of Fe doping concentration, M decreases again while T_C increases monotonically. T_C of the $y = 0.80$ sample exceeds our measuring range, namely 300 K. To gain a better understanding, we have calculated T_C for all samples and the results are listed in Table 1. As can be seen, when y increases from 0.30 to 0.40, T_C increases about 45 K, which is too large to be explained by the usual doping theories. Because slight Fe doping usually destroys the FM interactions in such a kind of compound, resulting in a decrease of T_C,[23] this anomaly may suggest the appearance of a new phase.

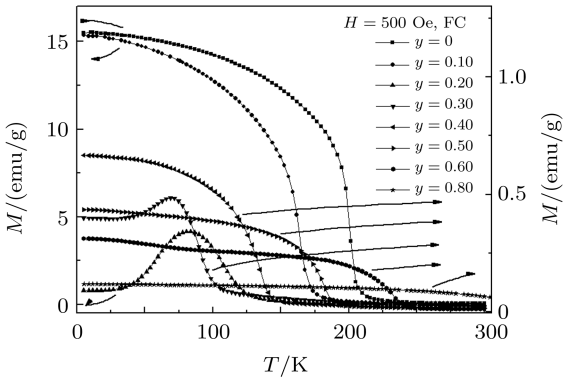


Fig.2. Temperature dependences of magnetization measured in 500 Oe after cooling in the same magnetic fields for all samples.

To gain an insight into the underlying physics, the temperature dependences of inverse magnetization ($1/M$–T) for all samples are shown in Fig.3. At high

temperatures, the $1/M$–T curve is best fitted to the Curie–Weiss law $\chi = C/(T-\theta)$ and the corresponding θ is obtained and listed in Table 1. A reduction in θ is observed with the value of y increasing even up to 0.40, which is opposite to the trend of $T_{\rm C}$ for the $y = 0.40$ sample. As can be seen from Fig.3, for the $y \leq 0.20$ samples, the inverse susceptibility can be well fitted to the Curie–Weiss law above their $T_{\rm C}$. However, a downturn deviation from the Curie–Weiss law above $T_{\rm C}$ for the $y = 0.30$ sample is observed. The deviation is more obvious for the $y = 0.40$ sample. To our knowledge, this anomaly takes the form of the characteristics of the Griffiths phase with a Griffiths temperature $T^* \sim 174$ K, above which the $1/M$–T curve follows the Curie–Weiss law. Griffiths-like phases are also observed in samples with $y = 0.50$ and 0.60, with their Griffiths temperatures being 230 and 270 K, respectively.

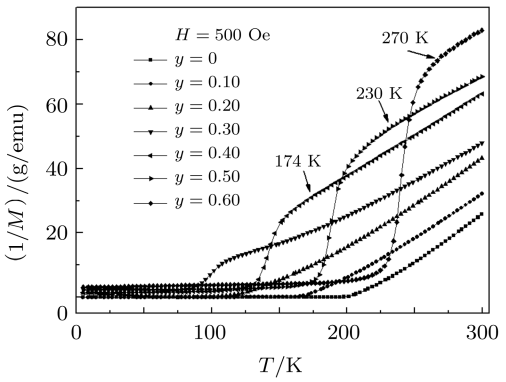


Fig.3. Temperature dependences of the inverse magnetization for all samples except for the sample with $y = 0.80$ corresponding to Fig.2.

According to many other studies on the Griffiths phase in the past,[7,9,17] several characteristics are essential to identify Griffiths phases: (i) the susceptibility deviates from the Curie–Weiss law as $T \to T_{\rm C}$ from above (at) $T_{\rm G}$, (ii) the deviation takes the form of a downturn in the $1/\chi$ - T curve, (iii) this deviation is suppressed in large magnetic field (H) due to polarization of spins outside the clusters. To further confirm the Griffiths like phase in Fe-doped perovskite cobaltites, we selectively study the field dependence of $1/\chi - T$ curve of the $y = 0.40$ sample and the collected data are shown in Fig.4. A sharper downturn is observed in a small field of 50 Oe than in a field of 500 Oe. The downturn is greatly suppressed as magnetic field increases. When the field reaches 5 T, the downturn completely disappears and the susceptibility follows the Curie–Weiss law above $T_{\rm C} \sim 133$ K, which is consistent with the behaviour of the Griffiths phase in other compounds. Similar behaviour can be expected to occur in the samples with $y = 0.50$ and 0.60 separately.

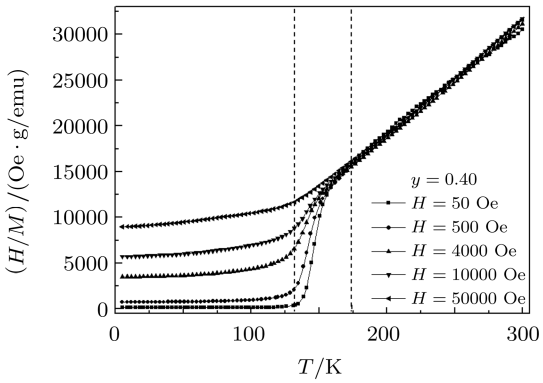


Fig.4. Field dependences of inverse susceptibility $1/\chi - T$ curve for $y = 0.40$ sample.

The concept of Griffiths phase was proposed a few decades ago by Griffiths who wanted to deal with the diluted magnetic system. He found the resulting disorder by diluting to suppress the long-range ferromagnetic ordering to form a temperature region in which the ferromagnetic clusters were dispersed in a paramagnetic matrix. As a phase-separated system composed of FM clusters and non-FM matrix, $La_{1-x}Ba_xCoO_3$ does have non-uniform interactions in the lattice. However, the thermomagnetization of $La_{0.7}Ba_{0.3}CoO_3$ takes the form of a typical ferromagnet. A Griffiths-like phase is observed by B-site doping with 30%∼60% Fe substitution for Co. According to Table 1, there is no apparent structural change for our studied samples. We notice that the undoped sample $La_{0.7}Ba_{0.3}CoO_3$ exhibits a long-range FM state.[19] However, because of the different chemical potentials of the two kinds of ions, Fe doping into the B site can break the FM interactions between Co ions. With the increase of B-site doping concentration, long-range FM state is blocked and FM Co clusters are formed by the separation of Fe atoms. That is to say, the quenched disorder induced by B-site doping dramatically suppresses the spin/orbital coupling and induces an inhomogeneous magnetic distribution. With little effect of structural change on the magnetic properties as mentioned above, we can conclude that B-site disordering induced by Fe doping should be the reason for the appearance of the Griffiths-like phase in this system.

It is noteworthy that with the variation of Fe doping concentration, the Griffiths temperature changes

too. In the original work by Robert, a constant temperature scale T^* is expected in a random Ising ferromagnet with the probability p of occupancy of a given site ranging from 0 to 1.[9] However, in extensively studied manganites, the Griffiths temperature only exists and remains constant at a small range of A-site doping concentrations.[10,11] In B-site doped compounds, it is another story. B-site substitution reduces the magnetic ions in the lattice if nonmagnetic ions are doped, thereby resulting in a variation of Griffiths temperature with change of doping concentrations.[8] This can happen even with magnetic ions doped into the B-site.[24] In our studied samples, B-site doping induced disorder together with cluster-glass characteristics can result in a behaviour similar to that in other B-site doped compounds.

In summary, we have studied the effect of Fe doping on the magnetic properties of $La_{0.7}Ba_{0.3}CoO_3$. With Fe doping concentration increasing to $y = 0.30$, M and T_C are observed to be suppressed while a significant increase of T_C appears for the $y = 0.40$ sample, which suggests the appearance of a Griffiths-like phase. The Griffiths-like phase is confirmed by the field dependence of the $1/\chi - T$ curve. The Griffiths-like phase is also observed in the samples with $y = 0.50$ and 0.60. B-site disordering induced by Fe doping is attributed to the existence of the Griffiths-like phase in this compound.

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