Short-range ferromagnetic correlations in the spin-chain compound Ca_3CoMnO_6

Z. W. Ouyang,* N. M. Xia, Y. Y. Wu, S. S. Sheng, J. Chen, Z. C. Xia, and L. Li
Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China

G. H. Rao
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 10080, People's Republic of China

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Unusual short-range ferromagnetic (FM) correlations, which can be understood in terms of a Griffiths-like singularity, have been illustrated in the spin-chain compound Ca_3CoMnO_6 by systematic magnetization measurements. First, these FM correlations can be dramatically suppressed by a small stoichiometric mismatch of Co/Mn atoms. Second, these FM correlations develop at $T_G = \sim 125$ K, a temperature much higher than the ordering temperature of $T_N = \sim 13$ K, and survive in magnetic fields of more than 2 T, indicating their robustness. This feature is quite different from the general case—a Griffiths-like anomaly was usually observed in very low magnetic fields and, in many cases, was suppressed in a field of several kilo-oersted.

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I. INTRODUCTION

In 1969, Griffiths predicted theoretically a particular short-range ferromagnetic (FM) correlation in randomly diluted Ising ferromagnets, which was later termed a Griffiths phase.[1] This particular magnetic state is characterized by completely random and competing magnetic interactions between T_C^{rand}, the critical temperature for random FM clusters, and T_G, a temperature for the onset of a conventional paramagnetic (PM) state. Bray[2] extended this scenario to magnetic systems containing any bond distribution in which the magnetization fails to be an analytical function of a magnetic field between T_C^{rand} and T_G when the magnetic field approaches zero. The Griffiths-like phase is closely related to quenched disorder and competing interactions and, to date, was found in a diluted quasi–two-dimensional magnet,[3] manganites,[4,5] a dilute magnetic semiconductor,[6] rare earth intermetallic compounds,[7–11] and so on.

The spin-chain compounds with formula $Ca_3(Co, T)_2O_6$ (T = 3d transition metals) belong to systems exhibiting complicated competing magnetic interactions. The parent compound $Ca_3Co_2O_6$ crystallizes in a K_4CdCl_6-type structure with space group R-3c.[12] Below $T_C = 24$ K, the compound is composed of Ising spin chains along the c-axis with the intrachain FM interaction being much larger than the interchain antiferromagnetic (AFM) interaction.[12–14] The dominant intrachain FM interaction can be strongly diluted by element substitution for Co sites.[15–20] Thus, the Griffiths-like phase is expected to exist in $Ca_3(Co, T)_2O_6$. Recent μSR and Mössbauer experiments evidenced the existences of FM fluctuation and incipient one-dimensional magnetic order below a characteristic temperature in the PM matrix for the Rh- and Ir-doped compounds,[21–23] indicating that the PM state of $Ca_3(Co,T)_2O_6$ is far from the conventional one. For $Ca_3Co_{2-x}Mn_xO_6$, intensive investigations were focused on the compounds, with x close to 1.0 because of a wealth of physical properties. Particularly interesting among them are ferroelectricity, which is much investigated from both experiment and theory,[15,24,25] and the "order-by-disorder" phenomenon.[26] For the latter, the up-up-down-down (↑↑↓↓) long-range order in the Co-Mn-Co-Mn spin chain is abruptly lost in a narrow vicinity of $x = 1.0$, with almost perfect Co/Mn ionic order. This lost long-range magnetic order may imply an existence of short-range FM correlations as x approaches 1.0. Recent μSR experiments confirmed the existence of dynamic spin fluctuation for $x = 0.95$.[27] The inverse susceptibilities of the ab-plane and c-axis for $x = 0.96$ show a small positive and negative deviation, respectively, below ~150 K.[28] Although explained as spin-state crossover,[28] this does not rule out a magnetic correlation effect. A similar feature existed for samples with $x = 0.5$ (Ref. 20) and 1.0,[29,30] but the details were left without discussion in the literature. In this paper, we demonstrate the presence of unusual short-range FM correlations in Ca_3CoMnO_6 by systematic magnetization measurements.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $Ca_3Co_{1+\delta}Mn_{1-\delta}O_6$ ($\delta = 0, 0.04$, and 0.08) were prepared using the citrate-gel method (ethanol and citric acid) by mixing stoichiometric amounts of high-purity $Ca(NO_3)_2{\cdot}4H_2O$, $Mn(NO_3)_2$, and $Co(NO_3)_2{\cdot}6H_2O$. This mixture was then heated at 170 °C. The resultant precursor was milled and incinerated at 850 °C for 24 hours. The x-ray diffraction patterns (Fig. 1) show that all samples are single phase (space group R-3c) with $a = 9.001$ Å and $c = 10.413$ Å for Ca_3CoMnO_6. No significant changes in lattice constant are found for the other two samples. The morphology and chemical composition were checked by a scanning electron microscopy (SEM) and an energy-dispersive x-ray spectroscope (EDS). The magnetization was measured by using a superconducting quantum interference device magnetometer. The magnetic relaxation measurements were performed by zero-field-cooled (zfc) heating and field-cooled (fc) cooling of the sample in a 0.005 T field to 50 K and measuring the magnetization as a function of time at constant temperature and field.

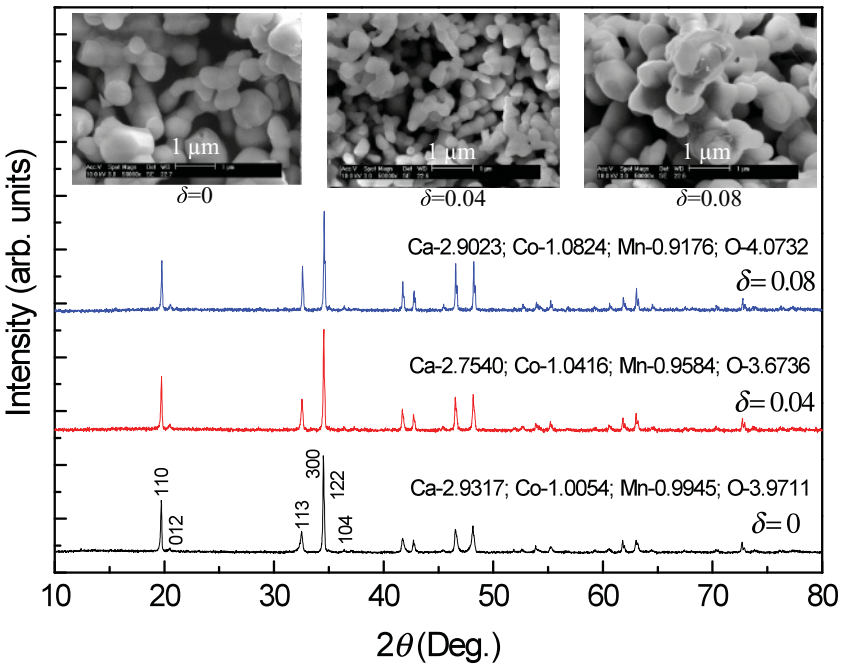

FIG. 1. (Color online) X-ray diffraction pattern of $Ca_3Co_{1+\delta}Mn_{1-\delta}O_6$. Miller indices of reflections below 40° are shown. The inset shows the SEM images. The EDS data normalized to two Mn/Co atoms are also shown.

III. RESULTS AND DISCUSSION

We performed the $M(T)$ measurements of Ca_3CoMnO_6 in fields of 0.001∼2.0 T, two representatives of which are shown in Fig. 2. Like the earlier report,[29] the 1 T $M(T)$ curves present a cusp around $T_N = \sim 13$ K because of the AFM-PM transition. Below T_N, the fc cooling $M(T)$ curve branches from the zfc heating curve and further exhibits an upturn below ∼5 K, probably because of FM correlations. In the PM region above T_N, both magnetization curves overlap each other. As the magnetic field reduces, an anomaly starts to emerge around $T_G = \sim 125$ K accompanied by a significant divergence of the fc cooling $M(T)$ curve from the zfc heating curve. For the 0.005 T $M(T)$ curve, magnetization between T_N and T_G is unusually large so that both the zfc and fc curves mimic an FM-like transition around T_G. The magnetic relaxation data measured at 50 K ($<T_G$) (inset, Fig. 2) show that both zfc heating and fc cooling $M(t)$ curves are not exponential functions of time. Therefore, the magnetization decay/enhancement appears to be unrelated to any thermally activated process. The unusual magnetization and dynamic behavior of the $M(T)$ curves below T_G imply considerable ambiguity in defining the true temperature region for the PM state.

To clarify the magnetic state, we performed the $M(H)$ measurements at temperatures below and above T_N, as shown in the inset of Fig. 2. The 2 K $M(H)$ curve is nearly linear, albeit with a weak curvature below ∼3 T, again characterizing the AFM ground state. Increasing the magnetic field gives rise to a metamagnetic-like transition. The transition is broadened so that the magnetization is not saturated in 6.5 T. The hysteretic $M(H)$ curves indicate the first-order character of the transition. At 50 K, the $M(H)$ curves evolve almost linearly (but a close scrutiny still reveals the presence of a weak curvature in low fields), and no hysteresis is present, showing practically a PM behavior. These observations are basically consistent with those reported by Rayaprol *et al.*[30] Thus, the large zfc-fc hysteresis and the anomaly below $T_G = \sim 125$ K observed in the low-field $M(T)$ curves (Fig. 2) point to the presence of short-range FM correlations in the PM matrix, which apparently sits at a much higher temperature than T_N and extends into the low-temperature AFM regime.

The presence of FM correlations in the PM region is accordingly manifested in the inverse magnetic susceptibility (H/M), as shown in Fig. 3(a) for the fc cooling H/M curves. It can be seen that all the H/M curves follow Curie–Weiss law above $T_G = \sim 125$ K, with an effective magnetic moment of $p_{eff} = 6.10\,\mu_B$/f.u. and a PM Curie temperature of $\theta_p = -50$ K, indicating strong intrachain AFM coupling in the compound. Both values are a little larger than previous reports of θ_p ranging from about −35 to −45 K, with $p_{eff} = 5.8\sim6.0\,\mu_B$/f.u.[20,29] All the H/M curves more or less exhibit a downturn below

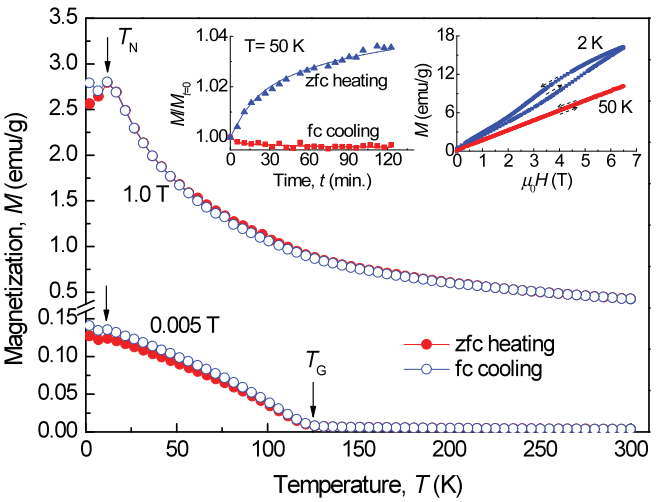

FIG. 2. (Color online) The zfc heating and fc cooling $M(T)$ curves measured at 0.005 T and 1 T. The insets show the $M(H)$ curves measured at 2 K and 50 K and the time evolution of the magnetization measured in a 0.005 T field after zfc heating and fc cooling the sample to 50 K.

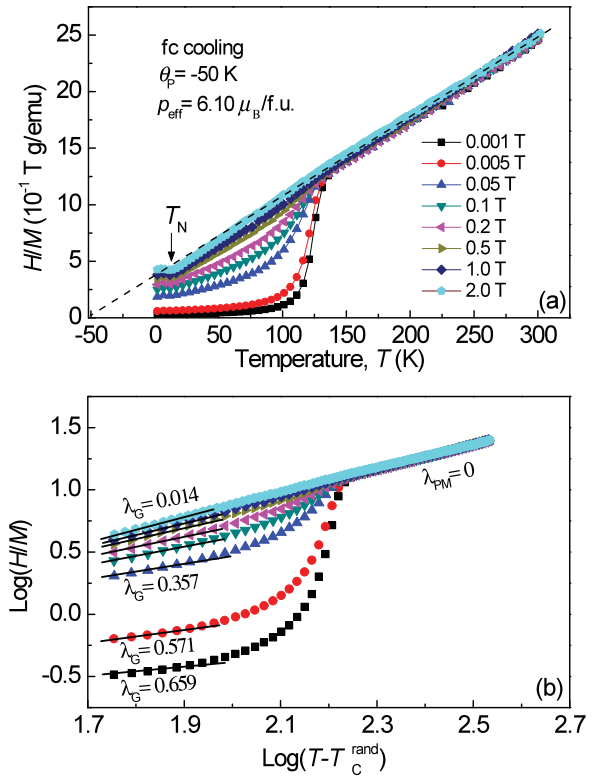

FIG. 3. (Color online) (a) The fc cooling H/M curves measured in magnetic fields ranging from 0.001 to 2.0 T. The dashed line represents the Curie–Weiss fit. (b) The fc cooling log(H/M) vs log($T - T_C^{rand}$) curves. Solid lines are linear fits of the curves to establish λ in $H/M \propto (T - T_C^{rand})^{1-\lambda}$.

T_G, indicative of nonanalytical behavior of magnetization. The lower the field, the larger the negative deviation from the conventional PM behavior. Thus, unlike the high-field PM state, in which the magnetization of the PM matrix prevails over that of the FM clusters because of a linear increase of the former with the field, the low-field magnetization is now dominated by the FM clusters embedded in the PM matrix. Obviously, the negative downturn of the H/M curves and its hardening with a progressive decrease in the magnetic field

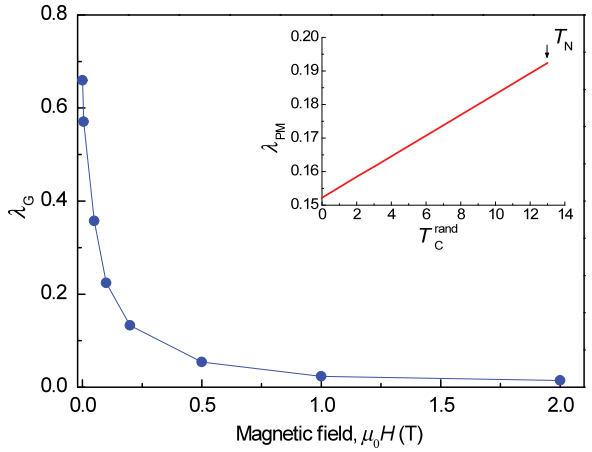

FIG. 4. (Color online) The magnetic field dependence of λ_G. The inset is the λ_{PM} vs T_C^{rand} curve.

are typical signatures of the Griffiths phase, which was also observed in variety of other systems.[4,6,7,11]

To further confirm whether the short-range FM correlations in the PM state can be ascribed to the Griffiths phase, we analyze the magnetic susceptibility with the following equation describing the Griffiths singularity,

$$\frac{H}{M} = \left(T - T_C^{rand}\right)^{1-\lambda}, \quad (1)$$

where $0 \leqslant \lambda < 1$.[31] Note that T_C^{rand} can be set as θ_p, T_C, T_N, or some values higher than T_C,[5,9,11,32] showing a subtlety of T_C^{rand}. Apparently any choice of T_C^{rand} should ensure $\lambda_{PM} = 0$ in the conventional PM regime above T_G [in this case, Eq. (1) is the exact Curie–Weiss law]. For Ca_3CoMnO_6, the λ_{PM} vs T_C^{rand} curve plotted in the inset of Fig. 4 shows that λ_{PM} is nonzero for any positive values of T_C^{rand}, varying from 0 to T_N. Recall that in our reports on the Griffiths-like phase of the antiferromagnet Gd_5Ge_4,[9,32] T_C^{rand} was set as θ_p, which is positive because of strong intralayer FM coupling. Analogously, we here take T_C^{rand} as θ_p for Ca_3CoMnO_6, which is now negative because of strong AFM coupling. The negative value of θ_p is now considered only a fitting parameter to guarantee $\lambda_{PM} = 0$ above T_G. Figure 3(b) shows the logarithm of H/M curves along with corresponding values of λ. The field dependence of λ_G as plotted in Fig. 4 shows that λ_G decreases rapidly below ~0.5 T and then tends toward saturation. Extrapolating λ_G to zero yields $\mu_0 H_c =$ ~4 T, a field for complete suppression of short-range FM correlations.

So far, we have illustrated the signatures of short-range FM correlations (i.e., Griffiths-like phase) in the spin-chain compound Ca_3CoMnO_6. This is quite unusual because a Griffiths-like phase was not observed in previous investigations of $Ca_3Co_{2-x}Mn_xO_6$ (x is close to 1.0),[26,28] or the feature was quite small and ignored by the authors.[29,30] This may be caused by small differences in Co/Mn concentration. For the samples in Refs. 29 and 30, the exact Co/Mn ratio is not clear

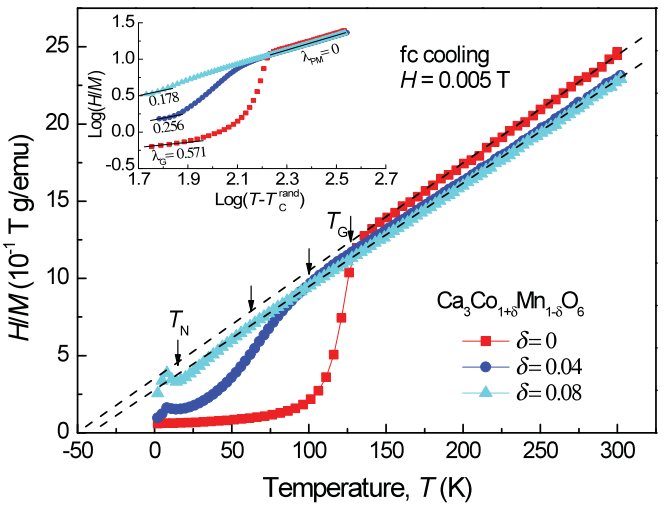

FIG. 5. (Color online) The fc cooling H/M curves of $Ca_3Co_{1+\delta}Mn_{1-\delta}O_6$ measured in 0.005 T. The dashed lines represent Curie–Weiss fits. The inset shows the log(H/M) vs log($T - T_C^{rand}$) curves. Solid lines are linear fits of the curves to establish λ in $H/M \propto (T - T_C^{rand})^{1-\lambda}$.

and is difficult to discuss here. For the samples in Ref. 26, it was confirmed by neutron diffraction that the nominal sample with $x = 1.0$ owns a perfect ionic order with Co and Mn occupying the trigonal and octahedral sites, respectively. Surprisingly, this sample exhibits a much less ordered magnetic state compared with those with ionic disorder ($x < 1.0$). This, referred to as "order-by-disorder," reflects that the magnetism of Ca_3CoMnO_6 is very sensitive to the difference in Co/Mn concentration. Inspired by this, we examine the Co/Mn ratio and magnetization of compounds with stoichiometric mismatch, $Ca_3Co_{1+\delta}Mn_{1-\delta}O_6$ ($\delta = 0 \sim 0.08$). The SEM images (see inset of Fig. 1) show that grain sizes (typically smaller than 1 μm) were not changed dramatically except for a small reduction for $\delta = 0.04$. Significant defects in the nonmagnetic elements, especially the O atoms, exist in these samples ($\delta = 0.04$ is more prominent). Importantly, the EDS data (Fig. 1) show that the true Mn/Co atom ratio is very close to the nominal ratio for all samples, including $x = 1.0$. Figure 5 shows the fc cooling *H*/*M* curves and logarithm plots measured in 0.005 T. Surprisingly, a small deviation of the Co/Mn ratio from 1:1, $\delta = 0.04$, dramatically modifies the H/M curves, decreasing the values of T_G and λ_G. As the deviation is increased to $\delta = 0.08$, the downturn of the *H*/*M* curve from the Curie–Weiss law is much suppressed. Thus, the short-range FM correlations are rather sensitive to the stoichiometric proportion of Co/Mn atoms. A Co/Mn ratio of 1:1 is optimal for observation of a Griffiths-like anomaly. This finding is compatible with the fact that long-range magnetic order disappears rapidly as x approaches 1.0.[26]

We now discuss the origin of a Griffiths-like anomaly for Ca_3CoMnO_6. We note that a similar Griffiths-like feature was observed in another spin-chain compound, Sr_3CuRhO_6, crystallizing in a K_4CdCl_6-derived monoclinic structure,[33] and the role of the Jahn–Teller effect of Cu ions was proposed. For Ca_3CoMnO_6, no or less structural distortion exists, suggesting that the origin of a Griffiths-like phase in this compound is somewhat different. On the basis of the symmetric superexchange constructed using an Ising spin chain with competing nearest neighbor FM (J_{FM}) and next-nearest-neighbor AFM (J_{AFM}) interactions,[15] the ground magnetic structure is of the ↑↑↓↓ type for $|J_{AFM}/J_{FM}| > 1/2$. If magnetic ions are arranged alternately along the chain, electric polarization can be induced through symmetric exchange striction. Recent neutron diffraction experiments[15,20] confirmed that $Ca_3Co_{2-x}Mn_xO_6$ ($x \sim 1.0$) own ↑↑↓↓-type magnetic order. Hence, competing Mn-Co nearest neighbor FM interaction and Mn-Mn (or Co-Co) next-nearest-neighbor AFM interaction within the spin chain, probably also including the longer range interchain superexchange interaction,[26] play an important role in achieving a Griffiths-like phase in Ca_3CoMnO_6.

Finally, it should be pointed out that the FM correlations in Ca_3CoMnO_6 are unusually strong compared with other systems exhibiting the same features. First, T_G (∼125 K) is much larger than T_N (∼13 K). Defining the range of the Griffiths-like phase as $GP = [(T_G - T_{C,N})/T_{C,N}]$,[5] one obtains $GP = 8.61$, which is much larger than those of reported Griffiths-like phases,[4–11] with GP being usually less than ∼2.0. Second, a close scrutiny of Fig. 3(a) reveals that the negative deviation of H/M below T_G is still seen, even in a high field of 2 T. Accordingly, Figs. 3(b) and 4 show that the value of λ_G is much large in a very low field and will completely reach zero in a field of ∼4 T. These are quite different from other systems, in which the negative deviation in H/M was generally observed in very low magnetic fields and, in many cases, was suppressed in magnetic fields of several kilo-oersted.[5,6,9,11]

IV. CONCLUSIONS

We have demonstrated the presence of short-range FM correlations in the spin-chain compound Ca_3CoMnO_6 by revealing a negative deviation of *H*/*M* curves from the conventional Curie–Weiss behavior below $T_G = \sim 125$ K, a temperature much above the ordering temperature, $T_N = \sim 13$ K. The Griffiths-like FM clusters are distributed over a large temperature range, and they are not suppressed in a magnetic field of 2 T, showing that the short-range FM correlations in this system are rather robust. The occurrence of FM correlations is associated with competing AFM and FM interactions because of the ↑↑↓↓-type magnetic order, and it can be dramatically suppressed by a small deviation of the Co/Mn ratio from 1:1. The optimal observation of a Griffiths-like anomaly, along with the lost long-range magnetic order reported previously, makes Ca_3CoMnO_6 an extremely interesting magnetic system.

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*zwouyang@mail.hust.edu.cn

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