Anomalous ferromagnetic behavior and large magnetoresistance induced by orbital fluctuation in heavily doped $Nd_{1-x}Sr_xMnO_3$ ($0.57 \leqslant x \leqslant 0.75$)

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We have elaborately investigated heavily doped $Nd_{1-x}Sr_xMnO_3$ with $x=0.57-0.75$. $3z^2-r^2$ and x^2-y^2 orbital orders strongly compete with each other at $x=0.625$. The competition causes spatial orbital fluctuation on nanometer scale below the orbital ordering temperature ($T_{OO} \sim 500$ K), which is evidenced by the observation of tweed structure using transmission electron microscopy. The orbital fluctuation, which persists down to lowest temperatures, gives rise to anomalous ferromagnetic behavior and concomitant large magnetoresistance well below the Néel temperature ($T_N=220$ K).

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I. INTRODUCTION

Perovskite manganites, $Ln_{1-x}Ae_xMnO_3$ (Ln=rare earth and Ae=alkaline earth elements), have been attracting considerable interest because of the colossal magnetoresistance (CMR) effect, i.e., a huge drop in resistivity by applying external magnetic fields, which is one of the main issues of strongly correlated electron physics.[1,2] It is widely accepted that the phase competition between a ferromagnetic metal and charge or orbital-ordered (CO/OO) insulator is essential for the CMR effect. The CMR effect is classified mainly into two types:[3] (1) the CMR effect observed at low temperatures near the phase boundary between the ferromagnetic metallic (FM) and CO/OO insulating states, and (2) the prototypical CMR effect observed immediately above the FM transition temperature (T_C). The former CMR effect results from a field-induced phase transition from the CO/OO to FM states, while the latter is attributed to large phase fluctuation between the FM and CO/OO states.

The electronic phases of the perovskite manganites are strongly affected by the orbital degree of freedom, which plays an important role not only in the CMR manganites but also in many other strongly correlated electron materials.[4] In half-doped manganites such as $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$, the $3x^2-r^2/3y^2-r^2$ orbital and Mn^{3+}/Mn^{4+} charge ordering concomitantly occur, and the CE-type antiferromagnetic (AF) state appears as the ground state.[5–7] Electron doping or application of external magnetic fields often destroys the CO/OO insulating state into the orbital-disordered FM state. In intermediate bandwidth manganites such as $Nd_{1-x}Sr_xMnO_3$ (NSMO), on the other hand, there exist two types of orbital orders exhibiting highly anisotropic magnetic and transport properties without charge order in the heavily doped region.[8] One is the x^2-y^2 (planar-type) OO state located in $0.52 \leqslant x < 0.63$, accompanying the *A*-type AF order in which the x^2-y^2 electrons are conducting within the ferromagnetic (F) plane.[9] The other is the $3z^2-r^2$ (rod-type) OO state located in $0.63 \leqslant x \leqslant 0.80$, accompanying the *C*-type AF order in which charge dynamics shows one-dimensional-like behavior along the F chain.[10] It should be noted that the orbital-ordering temperature (T_{OO} =400–600 K) is much higher than that of the AF ordering temperature (T_N=200–250 K). These two OO states meet in a bicritical manner around $x=0.63$. Near the phase boundary, a weak ferromagnetic (WF) phase emerges at low temperatures,[8] the origin of which still remains an unsettled question. A detailed investigation of such a phase boundary is expected to provide a further understanding of the CMR physics, whereas much attention has not been paid to the heavily doped manganites so far compared with the moderately doped manganites which often show the CMR. In this paper, we demonstrate that orbital fluctuation arising from the competition between the $3z^2-r^2$ and x^2-y^2 orbital orders gives rise to F fluctuation and concomitant large magnetoresistance (MR) using heavily doped NSMO crystals.

II. EXPERIMENT

NSMO crystals with $x=0.57-0.75$ were prepared using the floating zone method.[11] We confirmed that all synthesized crystals are of single phase by the powder x-ray diffraction method. Magnetic and transport properties were measured using a Quantum Design physical property measuring system (PPMS). We randomly cut the synthesized crystals with the size larger than twin-domain size for measurements of magnetic and transport properties. We confirmed that the size of them is large enough to average the magnetic and transport anisotropies. Transmission electron microscopy (TEM) experiments were performed with a Hitachi HF-3000L operating at 300 kV in the temperature range of 18–750 K.

III. RESULTS AND DISCUSSION

First, we show in Fig. 1(a) the temperature (T) dependence of the magnetization (M) of $x=0.72$, 0.66, 0.64, and 0.625. The M of $x=0.72$ shows a slight anomaly around 280 K due to the second-order *C*-type AF transition [inset of Fig. 1(a)]. The *C*-type AF transition temperature ($T_{C\text{-AF}}$) gradually shifts to lower temperatures with decreasing x, finally reaching 220 K at $x=0.625$. On the other hand, at low temperatures well below $T_{C\text{-AF}}$, the M of $x=0.72$ shows a slight upturn, i.e., F correlation, indicating the appearance of the WF phase. With a decrease in x, the F correlation is abruptly evolving, and the WF transition temperature (T_{WF})

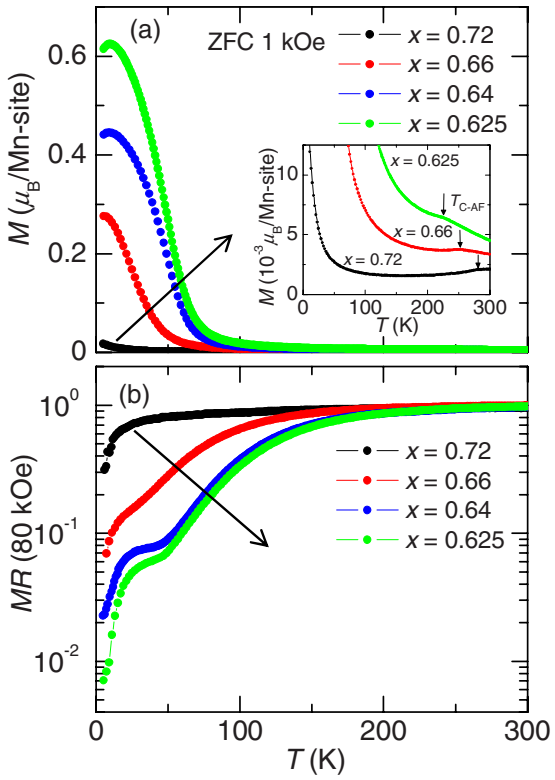

FIG. 1. (Color online) Temperature (T) dependence of (a) magnetization (M) and (b) magnetoresistance [MR(80 kOe)] of $Nd_{1-x}Sr_xMnO_3$ (NSMO) with x=0.72, 0.66, 0.64, and 0.625. ZFC represents zero field cooling process. MR(80 kOe) is defined as MR(80 kOe) $\equiv \rho$(80 kOe)/ρ(0 Oe), where ρ(0 Oe) and ρ(80 kOe) are resistivities measured in H=0 and 80 kOe, respectively. $T_{C\text{-AF}}$ denotes the C-type antiferromagnetic (AF) transition temperature. The inset shows enlargement of Fig. 1(a).

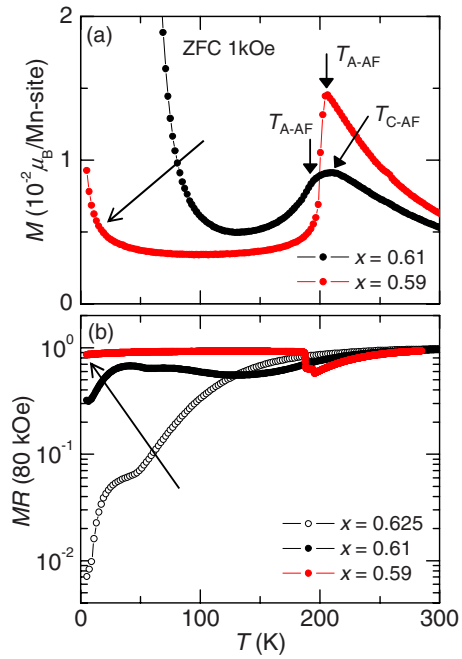

FIG. 2. (Color online) T dependence of (a) M and (b) MR(80 kOe) of NSMO with x=0.61, and 0.59. $T_{A\text{-AF}}$ denotes the A-type AF transition temperature. The MR(80 kOe) of x=0.625 is also displayed in Fig. 2(b) for comparison.

shifts to higher temperatures in contrast to $T_{C\text{-AF}}$. The F correlation is most enhanced at x=0.625, while the M remains unsaturated even at H=80 kOe, taking a much smaller value of $\sim 0.8\mu_B$ than expected ($\sim 3.4\mu_B$). Figure 1(b) shows the T dependence of the MR [MR(80 kOe)] of x=0.72, 0.66, 0.64, and 0.625. Here MR(80 kOe) is defined as MR(80 kOe) $\equiv \rho$(80 kOe)/ρ(0 Oe), where ρ(0 Oe) and ρ(80 kOe) are resistivities measured in H=0 Oe and 80 kOe, respectively. In x=0.72, with decreasing T, the MR(80 kOe) decreases from 1 down to 0.3; that is, the negative MR is observed at low temperatures where the F correlation is seen. As clearly seen from Fig. 1, the MR and the F correlation are simultaneously evolving with a reduction in x and are most enhanced at x =0.625, where the resistivity at 5 K drops more than two orders of magnitude by applying a magnetic field of H =80 kOe. From these results, it is evident that the F correlation is strongly coupled with charge dynamics.

Then, we exhibit the T dependence of the M of x=0.61 and 0.59 in Fig. 2(a). In x=0.59, an abrupt drop in the M is clearly seen at 200 K, which corresponds to the first-order A-type AF transition accompanying the planar-type (x^2-y^2) orbital order. As x decreases from 0.59 to 0.57, the A-type AF transition temperature ($T_{A\text{-AF}}$) is rising up to 230 K. In contrast to the $3z^2-r^2$ OO state with the C-type AF order ($0.625 \leqslant x \leqslant 0.75$), the F correlation is not observed at low temperatures in $0.57 \leqslant x \leqslant 0.59$. In $0.60 \leqslant x \leqslant 0.62$, on the other hand, the M shows somewhat complicated behavior due to the coexistence of the C-type AF ($3z^2-r^2$ OO) and A-type AF (x^2-y^2 OO) phases on micrometer scale at low temperatures.[8,12] As shown in Fig. 2(a), in x=0.61, two anomalies are discerned around 190 and 210 K, which are attributed to the A-type and C-type AF transitions, respectively. The T profiles of the MR(80 kOe) of x=0.625, 0.61, and 0.59 are shown in Fig. 2(b). With decreasing x from 0.625, the MR at low temperatures is steeply suppressed and is almost negligible at x=0.59. It is obvious that the MR and WF behavior in the phase-separated region ($0.60 \leqslant x \leqslant 0.62$) arise mainly from the coexisting $3z^2-r^2$ OO phase with the C-type AF order. In x=0.57–0.59, the negative MR is observed around $T_{A\text{-AF}}$; it is beyond the scope of the present study.

We plot the M under H=2 kOe and MR(80 kOe) at 5 K as a function of x in Figs. 3(a) and 3(b), respectively. Figure 3(c) shows the detailed phase diagram of NSMO with x =0.57–0.75 obtained from the present work. As shown in Fig. 3(c), in x=0.625–0.75, the ground state shows the C-type antiferromagnetism with the $3z^2-r^2$ orbital order. The $3z^2-r^2$ orbital ordering occurs at T_{OO}=450–550 K, i.e., well above $T_{C\text{-AF}}$=220–280 K. In x=0.57–0.59, on the other hand, the A-type AF state with the x^2-y^2 orbital order appears below $T_{A\text{-AF}}$. It should be noted that in $x \sim 0.60$, the A-type AF structure has a propagation vector, τ =[1/2,1/2,0], in the $I112/m$ setting just like the magnetic structure of $Pr_{0.5}Sr_{0.5}MnO_3$,[8,13] indicating that the planar-type (x^2-y^2-type) orbital uniformly orders with Mn spins ferromagnetically polarized in the (110) plane. Above $T_{A\text{-AF}}$,

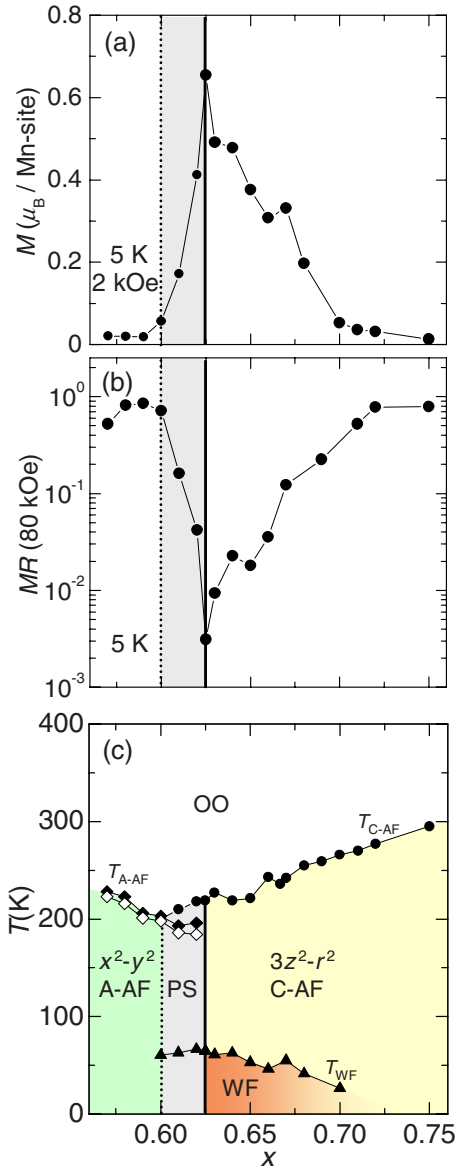

FIG. 3. (Color online) x dependence of (a) M under $H=2$ kOe at 5 K and (b) MR(80 kOe) at 5 K. (c) The electronic phase diagram of NSMO obtained in the present study. OO, $3z^2-r^2$, x^2-y^2, C-AF, A-AF, and WF denote orbital-ordered (OO), $3z^2-r^2$ OO, x^2-y^2 OO, C-type AF, A-type AF, and weak ferromagnetic phases, respectively. $T_{C\text{-AF}}$, $T_{A\text{-AF}}$, and T_{WF} represent the C-AF, A-AF, and WF transition temperatures, respectively. PS denotes the phase-separated regime between the C-type and A-type AF phases.

NSMO with $x=0.57-0.59$ have the tetragonal structure ($I4/mcm$ setting) with the lattice constants, $a<c/\sqrt{2}$, implying that the planar-type OO state turns into the rod-type OO state at $T_{A\text{-AF}}$. The phase separation in $0.60\leqslant x\leqslant 0.62$ is due to the competition between the $3z^2-r^2$ orbital (C-type AF) and x^2-y^2 orbital (A-type AF) orders. The MR accompanying the WF behavior is observed at low temperatures in $0.60\leqslant x\leqslant 0.72$. It is curious that the F correlation turns up in the heavily doped region far from the FM state ($0.3\leqslant x<0.5$). The F correlation and the MR are most enhanced at $x=0.625$ [Figs. 3(a) and 3(b)]. This suggests that the WF phase and the concomitant MR are closely related to the competition between the $3z^2-r^2$ and x^2-y^2 orbital orders.

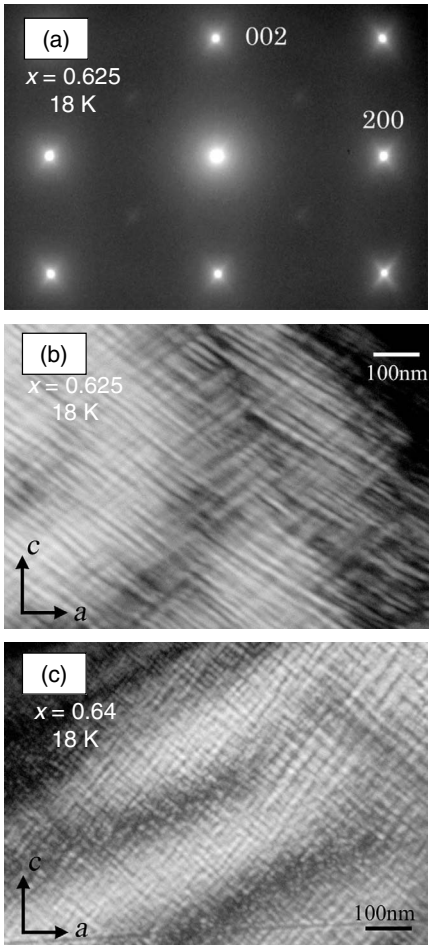

FIG. 4. (a) [010]-zone electron-diffraction pattern of $x=0.625$ at 18 K, and (b) corresponding dark-field image obtained using a 002 spot in the ac plane. (c) Dark-field image of $x=0.64$ obtained using a 002 spot in the ac plane.

For further investigation of the WF phase and the MR, we performed TEM experiments. Figure 4(a) shows the [010]-zone electron-diffraction pattern (EDP) of $x=0.625$ at 18 K. The striking feature of the EDP is that the streak is clearly discerned around fundamental spots. As shown in the corresponding dark-field image of $x=0.625$ at 18 K [Fig. 4(b)], tweed contrast is clearly seen running perpendicular to the streak direction; that is, the streak arises from the tweed structure. The tweed contrast spreads over the whole $x=0.625$ crystal without macroscopic phase separation. Tweed contrast usually appears as a precursor of a structural phase transition and is caused by local lattice mismatch (in the present case, mismatch between the $3z^2-r^2$ OO and its competing states) immediately before the phase transition. Therefore, the appearance of the tweed structure is strong evidence of phase competition. Here it should be noted that the tweed structure is different from the phase coexistence on micrometer scale observed in $x=0.60-0.62$. The most prominent feature of the present case is that the tweed contrast is observed in the wide temperature range of 18–470 K, totally disap-

pearing above T_{OO}=470 K. The matrix component of the tweed contrast has the tetragonal structure ($I4/mcm$) with the $3z^2-r^2$ orbital order. On the other hand, it is difficult to determine what is the embedded phase (that is, the competing phase) because the embedded phase does not grow into the long-range ordered phase even at lowest temperatures. The tweed contrast is observed only in the vicinity of the phase boundary (x=0.625 and 0.64 [Fig. 4(c)]), but not away from x=0.625. From these results, it is obvious that the tweed contrast arises from phase competition (fluctuation) related to the orbital order.

Let us discuss the origin of the WF phase and of the concomitant MR. As described above, the tweed structure [Figs. 4(b) and 4(c)] is observed near the phase boundary (x=0.625) between the rod-type ($3z^2-r^2$) and planar-type (x^2-y^2) OO states. With the slightest decrease in x from 0.625, the second phase, i.e., the x^2-y^2 OO state with the A-type AF order suddenly appears [see the phase diagram in Fig. 3(c)]. This phase-separation tendency strongly indicates that the tweed structure is observed as a precursor of the phase transition from the $3z^2-r^2$ OO to the x^2-y^2 OO states. Namely, strong competition between the $3z^2-r^2$ and x^2-y^2 OO phases gives rise to the tweed structure, i.e., spatial orbital fluctuation on nanometer scale. Obviously, the orbital fluctuation is closely related to the F correlation and MR because the tweed contrast is observed near the phase boundary where the F correlation and MR are most enhanced. Therefore, we conclude that the orbital fluctuation causes the F correlation and MR (probably, FM correlation) near the phase boundary in heavily doped NSMO. In perovskite manganites, it is generally accepted that orbital disordering (i.e., the mixed state of $3z^2-r^2$ and x^2-y^2 orbitals) stabilizes FM phases.[2] Furthermore, Maezono *et al.* theoretically demonstrate that a large orbital fluctuation plays a crucial role in the emergence of FM states.[14] Therefore, we are confident that our conclusion is reasonable.

Similar phase competition between the two OO states is also observed in $La_{1-x}Sr_xMnO_3$ (LSMO) around x=0.7.[15,16] In contrast to NSMO, however, heavily doped LSMO exhibits neither F correlation nor MR near the phase boundary. This result implies that Nd $4f$ spin is significant for the emergence of the F correlation. The abrupt drop in the MR(80 kOe) and slight decrease in the M of x=0.625 below ~20 K are probably due to Nd $4f$-spin ordering (Fig. 1). Otherwise, the difference between NSMO and LSMO could be attributed to the A-site cation mismatch effect defined as the variation of the A-site cations.[17,18] The A-site cation mismatch of NSMO is larger than that of LSMO, and such a mismatch might cause the orbital fluctuation near the phase boundary in heavily doped NSMO. To reveal the detailed mechanism of the F correlation, further study is needed. In any case, the most important point we would like to emphasize is that the orbital fluctuation is an essential ingredient for the F correlation and concomitant large MR observed in heavily doped NSMO, whether Nd $4f$ spin is essential or not.

The F correlation (the WF phase) near the phase boundary shows anomalous behavior: the specific heat measurement of x=0.625 does not show any anomaly around the onset temperature of the F correlation (T_{WF}). This suggests that the WF behavior is attributed to F fluctuation. Because of the F fluctuation, the resistivity, which is strongly coupled with spin dynamics, shows a large response to external magnetic fields, i.e., the large MR near the phase boundary. The MR observed in this study reminds us of the prototypical CMR arising from phase fluctuation between the F metal and CO/OO insulator, which is demonstrated by x-ray diffuse scattering experiments.[19–21] What is a significant difference between the two MR effects is that the present MR has no relation to the FM or CO/OO insulating phases because the FM and CO/OO states in NSMO are located in $0.3 \leqslant x \leqslant 0.5$, i.e., far from x=0.625. That is, only the orbital fluctuation produces the large MR accompanying the F fluctuation. The tweed contrast is observed above $T_{C\text{-AF}}$ as described above, indicating that the competition between the two orbital orders persists up to T_{OO}.

IV. SUMMARY

In summary, we have investigated heavily doped $Nd_{1-x}Sr_xMnO_3$ with x=0.57–0.75 in detail. Near the phase boundary (x=0.625) where the $3z^2-r^2$ and x^2-y^2 orbital orders strongly compete with each other, the spatial orbital fluctuation on nanometer scale is present in the wide temperature range of 18–470 K. Such an orbital fluctuation gives rise to the ferromagnetic fluctuation (i.e., the anomalous weak ferromagnetic phase) and the concomitant large magnetoresistance well below the Néel temperature (T_N =220 K).

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[1] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
[2] Y. Tokura, Rep. Prog. Phys. **69**, 797 (2006).
[3] H. Aliaga, D. Magnoux, A. Moreo, D. Poilblanc, S. Yunoki, and E. Dagotto, Phys. Rev. B **68**, 104405 (2003).
[4] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[5] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).
[6] P. G. Radaelli, D. E. Cox, M. Marezio, and S.-W. Cheong, Phys. Rev. B **55**, 3015 (1997).
[7] Z. Jirak, S. Krupicka, Z. Simsa, M. Dlouha, and S. Vratislav, J. Magn. Magn. Mater. **53**, 153 (1985).
[8] R. Kajimoto, H. Yoshizawa, H. Kawano, H. Kuwahara, Y. Tokura, K. Ohoyama, and M. Ohashi, Phys. Rev. B **60**, 9506 (1999).

[9] H. Kuwahara, T. Okuda, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. Lett. **82**, 4316 (1999).
[10] K. Tobe, T. Kimura, and Y. Tokura, Phys. Rev. B **67**, 140402(R) (2003).
[11] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science **270**, 961 (1995).
[12] We confirmed the phase coexistence in $x=0.62$ by powder x-ray diffraction experiments at low temperatures. Detailed results will be published elsewhere.
[13] H. Kawano, R. Kajimoto, H. Yoshizawa, Y. Tomioka, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **78**, 4253 (1997).
[14] R. Maezono, S. Ishihara, and N. Nagaosa, Phys. Rev. B **57**, R13993 (1998).
[15] J. Hemberger, A. Krimmel, T. Kurz, H.-A. Krug von Nidda, V. Yu. Ivanov, A. A. Mukhin, A. M. Balbashov, and A. Loidl, Phys. Rev. B **66**, 094410 (2002).
[16] O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, J. D. Jorgensen, and S. Short, Phys. Rev. B **67**, 094431 (2003).
[17] J. P. Attfield, Chem. Mater. **10**, 3239 (1998).
[18] L. M. Rodriguez-Martinez and J. P. Attfield, Phys. Rev. B **63**, 024424 (2000).
[19] S. Shimomura, N. Wakabayashi, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **83**, 4389 (1999).
[20] L. Vasiliu-Doloc, S. Rosenkranz, R. Osborn, S. K. Sinha, J. W. Lynn, J. Mesot, O. H. Seeck, G. Preosti, A. J. Fedro, and J. F. Mitchell, Phys. Rev. Lett. **83**, 4393 (1999).
[21] S. Shimomura, T. Tonegawa, K. Tajima, N. Wakabayashi, N. Ikeda, T. Shobu, Y. Noda, Y. Tomioka, and Y. Tokura, Phys. Rev. B **62**, 3875 (2000).