

Temperature dependent memory effects in the bilayer manganite (La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn₂O₇

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We report on the low-temperature resistance and magnetization of a single crystal of the bilayer manganite (La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn₂O₇. In zero field the sample is an insulator at all temperatures while at fields larger than 3 T a transition to a ferromagnetic metallic state is observed. Below 50 K the sample shows a pronounced memory effect, in which both resistivity and magnetization become dependent on the magnetic history and clearly demonstrate hysteretic behavior. At these low temperatures a difference in zero-field resistivity before and after magnetization of six orders of magnitude has been measured. The relaxation of the memory effect follows a stretched exponential function with a characteristic decay time of 5 hours at 10 K, which decreases to less than 1 ms above 40 K. These low-temperature properties can be related to magnetostriction data, indicating the presence of a field-induced change in the orbital occupancy of the e_g electrons of Mn³⁺.

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I. INTRODUCTION

Since the discovery of colossal negative magnetoresistance (CMR) in manganese perovskites of the type $R_{1-x}D_x\text{MnO}_3$, with R a trivalent rare earth and D a divalent ion, a considerable research effort has been devoted to the understanding of the properties of these compounds.¹ The partial substitution of the rare earth by the divalent element introduces a mixing of Mn³⁺ and Mn⁴⁺ ions, responsible for the observed electronic and magnetic properties. These cubic manganites are the $n=\infty$ members of the Ruddlesden-Popper series $(R,D)_{n+1}\text{Mn}_n\text{O}_{3n+1}$.² More recently, bilayer manganites with $n=2$ of the type $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ have been studied and compared to the $n=\infty$ case.³⁻⁵ In contrast with those of the cubic materials, the electronic and magnetic properties of the $n=2$ crystals are highly anisotropic. The charge transport within the ab plane generally is similar to that in the cubic manganites with a transition from a paramagnetic semiconducting state to a ferromagnetic metallic state at a reduced Curie temperature $T_C \approx 120$ K. The resistivity along the c axis ρ_c shows the same features, but is typically two orders of magnitude larger than the resistivity ρ_{ab} in the ab plane. This is due to the layered structure, which confines the charge carriers within the MnO₂ planes of the material. Furthermore, a close relation between the magnetotransport and the magnetoelastic properties has been observed for these compounds.^{4,6}

A magnetoresistive memory effect has been reported for several manganites, for which the resistivity depends not only on the applied magnetic field but also on the magnetic history of the sample.⁷⁻¹³ This occurs mainly in materials characterized by competing electronic ground states. In this paper we report on the magnetoresistive memory effect (MME) observed in a single crystal of the bilayer manganite (La_{1-z}Pr_z)_{1.2}Sr_{1.8}Mn₂O₇ with $z=0.6$. This material shows no spontaneous ferromagnetic ordering, and stays insulating

down to the lowest temperatures,^{14,15} in contrast to its parent compound La_{1.2}Sr_{1.8}Mn₂O₇ (LSMO) which becomes metallic below $T_C \approx 125$ K.^{3,5} This different behavior is caused by the substitution of Pr at the La site which modifies the lattice constants, suggesting a change in Jahn-Teller (JT) distortion.⁶ Both at room temperature and in the ground state, the lattice parameter ratio c/a increases with increasing z . This leads to a lowering of T_C and an enhancement of the CMR-effect due to a change in the orbital occupancy of the e_g states. In the undoped crystal ($z=0$) the planar $d_{x^2-y^2}$ orbitals of Mn³⁺, which are responsible for the long-range ferromagnetic (FM) ordering, are dominant.¹⁶ However by substituting the smaller Pr atom for La, the MnO₆ octahedra elongate along the c axis, modifying the crystal field and favoring the $d_{3z^2-r^2}$ orbitals of Mn³⁺, directed perpendicular to the MnO₂ planes.⁶ This reduces the transfer integral t of the e_g electrons and weakens the FM interaction, ultimately destroying the spontaneous phase transition around $z=0.5$. In a similar way, the character of the preferred e_g states can be altered by either changing the Sr content in LSMO,⁴ or by doping the system with other rare earths such as Nd instead of Pr.¹⁷

II. EXPERIMENTAL

Single crystals of (La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn₂O₇ were grown from sintered rods of the same nominal composition by the floating-zone technique, using a mirror furnace.¹⁴ A thin platelet shaped sample with a shiny surface was cleaved from one of these crystals after orientation by Laue x-ray diffraction. The flat side of the platelet corresponds to the ab plane and the c axis is perpendicular to its surface with a misorientation of approximately 5°. No cubic or other second phases were found in the x-ray powder pattern of part of the cleaved crystal. The dimensions of the sample were 5 × 4 mm² in the ab plane and 0.4 mm along the c axis. Six evaporated and annealed gold pads on the flat side served as

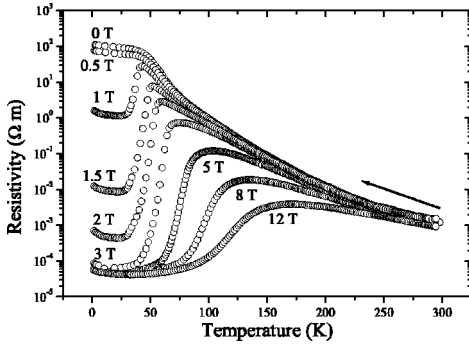


FIG. 1. Temperature-dependent resistivity within the ab plane of a $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ single crystal. All measurements were performed upon cooling in a magnetic field oriented parallel to the \vec{c} axis of the crystal.

low-resistive current- and voltage probes. Resistivity measurements were performed in a He4-flow cryostat with variable temperature insert by sending a pulsed and polarity-reversed current of 10 nA through the sample and measuring the induced voltage with a nanovoltmeter. A magnetic field up to 12 T could be applied parallel or perpendicular to the c -axis of the sample. Magnetization measurements were performed in a Quantum Design SQUID magnetometer operating between 5 and 300 K, with fields up to 5 T, again oriented either parallel or perpendicular to the c axis of the crystal.

III. RESULTS AND DISCUSSION

The resistivity ρ_{ab} of a single crystal of $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ (LSMO) is shown in Fig. 1 as a function of temperature, for different external magnetic fields in the geometry $\vec{B} \parallel \vec{c}$. The room temperature value $\rho_{ab} = 130 \text{ } \Omega\text{m}$ corresponds well to that reported for similar Pr-doped compounds.^{6,14} In zero field the sample is insulating down to the lowest temperatures, in contrast to the metallic behavior of the parent compound $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$, which has a Curie temperature $T_C = 125 \text{ K}$.⁵ On applying a magnetic field, the resistivity decreases very fast at low temperatures, and a transition to a quasimetallic state is observed for $B \geq 3 \text{ T}$. This transition is accompanied by a field-induced contraction of the c axis and an expansion of the ab plane.¹⁴ According to Moritomo *et al.*,¹⁷ this points to a field-induced change in orbital occupancy of the e_g electrons of Mn^{3+} , which favors the $3d_{x^2-y^2}$ states with respect to the $3d_{3z^2-r^2}$ states, leading to a long-range FM interaction. For fields above 3 T and temperatures below 50 K, a colossal negative magnetoresistance (CMR) with an amplitude of 6 orders of magnitude is observed. In undoped LSMO however, the maximum amplitude of the CMR effect around T_C is only 2 orders of magnitude.⁵ The field dependence of the magnetoresistivity at constant temperatures above 50 K can be described by a spin-dependent hopping model,¹⁸ in which ferromagnetic clusters (ferrons) are able to move in a paramagnetic or antiferromagnetic background.¹⁵ The complex magnetic behavior of $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ is discussed elsewhere.^{14,15} The system undergoes several ferro-

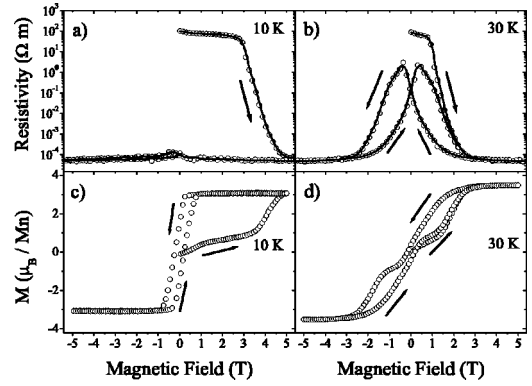


FIG. 2. Field-dependent resistivity of the $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ crystal at 10 K (a) and 30 K (b). The solid lines are a guide to the eye. (c) and (d) show the magnetic moment per Mn ion as a function of field for 10 and 30 K, respectively. For all measurements the sample was first heated to room temperature and then zero-field cooled. The magnetic field was always oriented along the \vec{c} axis.

magnetic and antiferromagnetic transitions, but a spontaneous long-range order is not established. Below 50 K, however, the sample goes from an antiferromagnetic ground state to a metastable ferromagnetic state in a field of several T. This is clearly related to the field-induced electronic and lattice transitions, and is caused by the increasing $d_{x^2-y^2}$ character of the occupied e_g states in high magnetic fields.

The enhanced CMR effect of six orders of magnitude and the field-induced ferromagnetic transition might be explained in terms of a competition between the ferromagnetic double exchange interaction and short-range charge/orbital ordering interactions at low temperatures. It has been suggested recently that in LSMO short-range charge and orbital ordering exist in the paramagnetic phase, but disappear below T_C .¹⁹ By doping the system with Pr, which changes the lattice constants and influences the orbital character of the e_g electrons, the short-range order might be enhanced and the double exchange mechanism suppressed. This would lead to a weakening of the spontaneous ferromagnetic transition, and consequently cause a larger CMR effect. The observed field-induced transition in $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ can in this scenario be interpreted as a melting of the ordered state.

In order to study the low-temperature properties in more detail, we have performed magnetoresistance measurements. Figures 2(a) and 2(b) show the field dependent resistivity at 10 and 30 K, respectively, with the field applied along the c axis. Before each measurement the sample was zero-field cooled from room temperature, while during the measurements the magnetic field was increased from 0 to +12 T, lowered to -12 T, and finally raised to +12 T again, at a sweep rate of 100 mT per minute. At these low temperatures we observe a difference in low-field resistivity before and after magnetization of the sample in a field of +12 T. This means that the resistivity becomes dependent on the magnetic history of the crystal. This is in accordance with several cubic manganites for which a similar magnetoresistive memory effect (MME) was reported.⁷⁻¹² The MME was also

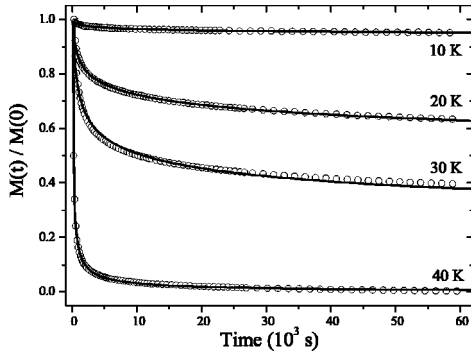


FIG. 3. Time-dependent magnetization $M(t)$ of the $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ crystal at several temperatures after magnetization in a field of 5 T with $\vec{B}\parallel\vec{c}$. The solid lines are fits of the stretched exponential function to the $M(t)$ data, as described in the text.

detected in a double layered thin film of LSMO.¹³ At 10 K the resistivity decreases by a factor of 10^6 on applying a field $B \geq 5$ T. Upon removing the field however, the resistivity does not rise to its original zero-field value but remains very low, giving an MME of 6 orders of magnitude. At 30 K the same qualitative behavior is observed, but the amplitude of the effect is already much smaller. Above 50 K it completely vanishes. A similar temperature-dependent hysteresis has been noted for the magnetostriction of the c -axis and the ab plane of $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$.¹⁴ This clearly indicates that the MME is related to the observed metastable magnetic ordering at low temperature, caused by a field-induced change in the orbital occupancy of the e_g electrons. After magnetizing the sample, the original state is recovered by heating the crystal above 50 K or by waiting for the spontaneous relaxation of the system, which is highly temperature sensitive.

Figures 2(c) and 2(d) show magnetization measurements at 10 and 30 K, respectively, showing also the memory effect. The crystal was always zero-field cooled before a magnetic field of 5 T was applied along the c axis. The virgin curve at 10 K shows a steep increase around 3.5 T, corresponding to a field-induced transition to a metastable ferromagnetic state. After magnetizing the sample in a field of 5 T, a narrow rectangular hysteresis loop with a coercive field of 0.2 T is obtained upon sweeping the field between +5 and -5 T. The virgin curve itself lies outside this loop. When the magnetic field is switched off, the magnetic moment drops from its saturated value, but does not go to zero immediately. Unless the sample is heated above 50 K, the magnetization relaxes very slowly to zero with a characteristic relaxation time of the order of several hours. At temperatures above 10 K [compare the curve at 30 K in Fig. 2(d)], the hysteresis loop becomes more and more slanted, and the virgin curve moves closer towards the loop. Above 50 K the whole effect vanishes and hysteresis can be no longer observed. These results closely resemble those for the low-temperature resistivity and magnetostriction,¹⁴ and are related to the MME effect. When the magnetic field is applied in the ab plane, the magnetization is smaller by typically 15%, even at 5 T, indicating that the c -axis is the easy magnetization axis. Fur-

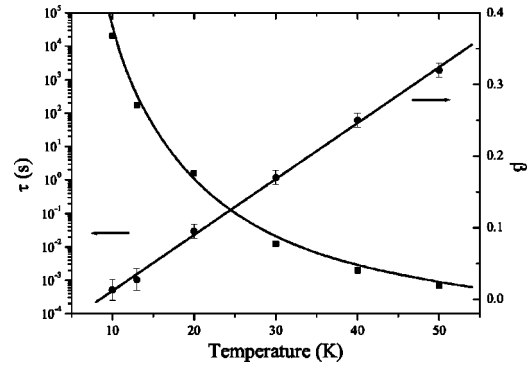


FIG. 4. Temperature dependence of the relaxation time τ (squares) and the parameter β (circles) as obtained from the fits in Fig. 3. The solid lines are fits of the data. τ is thermally activated with an activation energy $\Delta = 18.6$ meV, while β is linear in temperature.

thermore no remanent magnetization or sign of a memory effect is found even at 10 K.

In order to investigate the relaxation behavior of the memory effect, time-dependent magnetization measurements were performed at different temperatures below 50 K, as shown in Fig. 3. The crystal was always zero-field cooled before a field of 5 T was applied along the c axis. After removing this field, the magnetization $M(t)$ was measured as a function of time. During the field sweep to zero field, the magnetization drops at all measured temperatures from its maximum value at 5 T to a lower, nonzero value $M(0)$ before relaxing much slower to the ground state. The higher the temperature the larger this initial drop becomes, and at temperatures above 50 K, the magnetization relaxes almost instantaneously. This agrees well with the observed hysteresis behavior of magnetization, resistivity, and magnetostriction. The relaxation behavior can be described by the stretched exponential function $M(t) = M_0 \cdot \{1 - \exp[-(\tau t)^\beta]\}$, where τ is the characteristic decay time, and β a dispersion parameter between 0 and 1. The fits of the relaxation curves are presented as solid lines in Fig. 3. A similar relaxation behavior is common to many physical phenomena, including the relaxation of photoinduced conductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.²⁰ Several cubic manganites show a relaxation of their magnetic properties which can also be described by a stretched exponential function.^{21,22} The temperature dependence of the fit parameters τ and β is shown in Fig. 4. We find that τ decreases from approximately 5.5 hours at 10 K to less than 1 ms at $T > 40$ K. The temperature dependence of τ is thermally activated according to $\tau = \tau_0 \exp[\Delta/(k_B T)]$ with $\Delta = (18.6 \pm 0.2)$ meV. The dispersion parameter β can be fitted with the linear function $\beta(T) = -0.07 + T(\text{K})/128$. The fits are presented as solid lines in Fig. 4. These results agree well with those found for the cubic manganites $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ and $\text{La}_{2/8}\text{Pr}_{3/8}\text{Ca}_{3/8}\text{MnO}_3$.²² When the field is applied in the ab plane and then removed, the magnetization at all temperatures immediately drops to zero and no sign of a memory effect is observed. An understanding of the time scales of these relaxation effects requires detailed information about the orbital orientations in the nonmagnetized ground state and in the metastable conducting state. The

magnetostriction data on our compound¹⁴ were measured with the field parallel to the ab plane, i.e., in the direction where the magnetization decays instantaneously at all temperatures. Upon increasing the field, the ab plane expands while the c axis is compressed, meaning that the e_g orbitals become mainly directed parallel to the MnO_2 bilayers. The improved orbital overlap within the ab plane enhances the charge-transfer probability and mediates ferromagnetic interactions. In this sense, the ferromagnetic alignment is corroborated by the orbital structure itself. Since magnetization along the c axis results in identical ρ_{ab} values, we suppose to deal also here with a field-induced preferential in-plane orientation of the orbitals. The higher stability of the magnetization along the c axis compared to the ab plane points to a possible spin-orbit coupling. A situation with the spins standing perpendicular on the orbitals rather than pointing in the orbital plane seems to be energetically preferred.

IV. CONCLUSIONS AND SUMMARY

We have investigated the low-temperature resistivity and magnetization of a single crystal of the bilayer manganite $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. Although in zero field the crystal is insulating, an applied magnetic field induces a transition to a ferromagnetic metalliclike state. This is accompanied by a colossal negative magnetoresistance of six orders of magni-

tude at the lowest temperatures. Furthermore, a magnetoresistive memory effect is observed below 50 K where the resistivity, the magnetization and the magnetostriction of the sample become dependent on its magnetic history and show a large hysteresis. This effect is strongly temperature dependent, and is especially large around 10 K where the difference in zero-field resistivity before and after magnetization in a field of 12 T, is a factor of 10^6 . The original state is only regained by heating above 50 K, or by waiting for the sample to relax spontaneously. The relaxation of the memory effect was studied by time-dependent magnetization measurements. After a initial steep decrease, the magnetization follows a stretched exponential behavior with a thermally activated time constant τ . The low-temperature properties can possibly be explained in terms of a field-induced change in the orbital occupancy of the e_g electrons of Mn^{3+} at low temperatures, which favors the planar $d_{x^2-y^2}$ orbitals, leading to a metastable ferromagnetic state.

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- ¹R.M. Kusters, J. Singleton, D.A. Keen, R. McGreevy, and W. Hayes, *Physica B* **155**, 362 (1989); R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993).
- ²T. Kimura, and Y. Tokura, *Annu. Rev. Mater. Sci.* **30**, 451 (2000).
- ³Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, *Nature (London)* **380**, 141 (1996).
- ⁴T. Kimura, Y. Tomioka, A. Asamitsu, and Y. Tokura, *Phys. Rev. Lett.* **81**, 5920 (1998).
- ⁵W. Prellier, R. Suryanarayanan, G. Dhalenne, J. Berthon, J.-P. Renard, C. Dupas, and A. Revcolevschi, *Physica B* **259-261**, 833 (1999).
- ⁶H. Ogasawara, M. Matsukawa, S. Hatakeyama, M. Yoshizawa, M. Apostu, R. Suryanarayanan, G. Dhalenne, A. Revcolevschi, K. Itoh, and N. Kobayashi, *J. Phys. Soc. Jpn.* **69**, 1274 (2000).
- ⁷R. von Helmolt, J. Wecker, T. Lorenz, and K. Samwer, *Appl. Phys. Lett.* **67**, 2093 (1995).
- ⁸G.C. Xiong, Q. Li, H.L. Ju, S.M. Bhagat, S.E. Lofland, R.L. Greene, and T. Venkatesan, *Appl. Phys. Lett.* **67**, 3031 (1995).
- ⁹H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, *Phys. Rev. B* **52**, R13 145 (1995).
- ¹⁰J. Barratt, M.R. Less, G. Balakrishnan, and D. McK Paul, *Appl. Phys. Lett.* **68**, 424 (1996).
- ¹¹P. Wagner, V. Metlushko, M.J. Van Bael, R.J.M. Vullers, L. Trappeniers, A. Vantomme, J. Vanacken, G. Kido, V.V. Moshchalkov, and Y. Bruynseraede, *J. Phys. IV* **6**, C3-309 (1996).
- ¹²A. Anane, J.-P. Renard, L. Reversat, C. Dupas, P. Veillet, M. Viret, L. Pinsard, and A. Revcolevschi, *Phys. Rev. B* **59**, 77 (1999).
- ¹³Y. Konishi, T. Kimura, M. Izumi, M. Kawasaki, and Y. Tokura, *Appl. Phys. Lett.* **73**, 3004 (1998).
- ¹⁴M. Apostu, R. Suryanarayanan, A. Revcolevschi, H. Ogasawara, M. Matsukawa, M. Yoshizawa, and N. Kobayashi, *Phys. Rev. B* **64**, 012407 (2001).
- ¹⁵P. Wagner, I. Gordon, V.V. Moshchalkov, Y. Bruynseraede, M. Apostu, R. Suryanarayanan, and A. Revcolevschi, *Europhys. Lett.* (to be published).
- ¹⁶D.S. Dessau, T. Saitoh, C.-H. Park, Z.-X. Shen, P. Villeda, N. Hamada, Y. Moritomo, and Y. Tokura, *Phys. Rev. Lett.* **81**, 192 (1998).
- ¹⁷Y. Moritomo, Y. Maruyama, T. Akimoto, and A. Nakamura, *Phys. Rev. B* **56**, R7057 (1997).
- ¹⁸P. Wagner, I. Gordon, L. Trappeniers, J. Vanacken, F. Herlach, V.V. Moshchalkov, and Y. Bruynseraede, *Phys. Rev. Lett.* **81**, 3980 (1998); **84**, 4018 (2000).
- ¹⁹K. Yamamoto, T. Kimura, T. Ishikawa, T. Katsufuji, and Y. Tokura, *J. Phys. Soc. Jpn.* **68**, 2538 (1999); 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); D.B. Romero, Y. Moritomo, J.F. Mitchell, and H.D. Drew, *Phys. Rev. B* **63**, 132404 (2001).
- ²⁰V.I. Kudinov, I.L. Chaplygin, A.I. Kirilyuk, N.M. Kreines, R. Laiko, E. Lähderanta, and C. Ayache, *Phys. Rev. B* **47**, 9017 (1993).
- ²¹R.H. Heffner, L.P. Le, D.E. MacLaughlin, G.M. Luke, K. Kojima, B. Nachumi, Y.J. Uemura, G.J. Nieuwenhuys, and S.-W. Cheong, *Physica B* **230-232**, 759 (1997).
- ²²M. Uehara and S.-W. Cheong, *Europhys. Lett.* **52**, 674 (2000).