THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

2005, *109,* 15667−15670
Published on Web 08/02/2005

Direct Investigation of Orbital Ordering in a Colossal Magnetoresistance Manganite by Means of X-ray Linear Dichroism at the Mn *L* Edge

K. Kuepper,*,† F. Bondino,‡ K. C. Prince,‡,§ M. Zangrando,‡ M. Zacchigna,‡ A. F. Takács,† T. Crainic,† M. Matteucci,|| F. Parmigiani,‡,⊥ A. Winiarski,# V. R. Galakhov,⊗ Ya. M. Mukovskii,○ and M. Neumann†

Department of Physics, University of Osnabrück, Barbarastr. 7, D-49069 Osnabrück, Germany, Laboratorio TASC−INFM, Strada Statale 14, km 163.5, in Area Science Park, I-34012 Basovizza (Trieste), Italy, Sincrotrone Trieste, Strada Statale 14, km 163.5, in Area Science Park, I-34012 Basovizza (Trieste), Italy, ICGEB, in Area Science Park, Padriciano 99, I-34012 Trieste, Italy, Dipartimento di Matematica e Fisica, Università Cattolica del Sacro Cuore, Brescia, Italy, A. Chelkowski Inst. Phys., Silesian University, PL-40007 Katowice, Uniwersytecka 4, Poland, Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-170, Russia, and Moscow State Steel and Alloys Institute, 117936 Moscow, Russia

Received: May 25, 2005; In Final Form: July 5, 2005

We have investigated for the first time the orbital ordering in a three-dimensional colossal magnetoresistance manganite, namely $La_{7/8}Sr_{1/8}MnO_3$, by applying soft X-ray linear dichroism (XLD) to the Mn *L* edge. We found that the cooperative Jahn−Teller distorted orthorhombic phase, which is present at a temperature of 240 K, is probably accompanied by a predominantly cross type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering. This result is discussed in the light of different exchange interaction models.

1. Introduction

Transition metal oxides exhibit a remarkably rich variety of magnetic, structural, and electronic transport properties. Therefore, these materials have been attracting much attention in order to understand the complex interplay between the electronic structure, magnetic degrees of freedom, and the orbital degrees of freedom.[1−5] In 3d transition metal oxides, the Coulomb interaction between the d electrons as well as the charge transfer interaction between transition metal site and oxygen ligand are of importance for understanding fascinating properties such as high temperature superconductivity or colossal magnetoresistance. Among these compounds, systems showing an orbitally degenerate state have attracted much attention, since a preferential occupation of the d-orbitals may lead to long-range orbital occupancy, also called *orbital ordering*. This ordering strongly influences the bonding between the transition metal (TM) ions and the oxygen ligand in the compound, which determines both the magnetic interactions and electronic properties. The investigation of the orbital degree of freedom by both experimental and theoretical approaches is one of the most striking challenges in state-of-the-art condensed matter chemistry and physics.

$LaMnO_3$, an A-type antiferromagnetic insulator with a Neel temperature of 140 K, is of special interest as the parent compound of colossal magnetoresistance (CMR) compounds, which are the possible magnetic materials for applications in the next generation of magnetic data storage read heads.[1,3,6] Doping by a moderate number of holes by Sr between 10% and 20% leads to a very interesting temperature-dependent competition between ferromagnetism and a cooperative Jahn−Teller distorted phase in $La_{1-x}Sr_xMnO_3$ ($0.1 < x < 0.2$).[7−9] In particular, around a hole concentration of $x \approx 0.125$, $La_{1-x}Sr_xMnO_3$ is a rare example of a compound showing a fascinating combination of Jahn−Teller distortion, orbital ordering, and ferromagnetism.[10,11] $La_{7/8}Sr_{1/8}MnO_3$ undergoes a phase transition from a slightly orthorhombic distorted phase at high temperature into a cooperative Jahn−Teller distorted phase upon cooling at around 270 K, induced by a contraction of the *c*-cell parameter.[9,12] If T decreases through T_c around 180 K, the ferromagnetic order suppresses the cooperative Jahn−Teller distortion and the system undergoes another transition into a ferromagnetic phase. In a cubic crystal, the Jahn−Teller distortion leads to a lowering of the symmetry and thus a splitting of the e_g level. Its occupation, influenced by doping and the energetic position, strongly influences the hybridization between the Mn 3d and the O 2p states, which is crucial for the understanding of the underlying physics of the family of CMR manganites. In the case of $La_{7/8}Sr_{1/8}MnO_3$, the $(c/\sqrt{2})/a$ ratio is reduced from 0.993 to 0.986 in the cooperative orbital ordered phase. This contraction is accompanied by an elongation of the *b*-cell parameter, resulting in an orthorhombic Q_2-type Jahn−Teller interaction, which stabilizes in a certain superposition of

* Corresponding author: Karsten Kuepper. E-mail: karsten.kuepper@uos.de.
† University of Osnabrück.
‡ Laboratorio TASC−INFM.
§ Sincrotrone Trieste.
|| ICGEB.
⊥ Università Cattolica del Sacro Cuore
Silesian University.
⊗ Russian Academy of Sciences-Ural Division.
○ Moscow State Steel and Alloys Institute.

10.1021/jp052762s CCC: $30.25

TABLE 1: Type of Orbital Ordering of $La_{7/8}Sr_{1/8}MnO_3$ Revealed by Different Approaches and at Different Temperatures

ref	type of orbital ordering	technique
Endoh et al.[14]	hybridization of $d_{(x^2-z^2)-(y^2-z^2)}$ and $d_{(3x^2-r^2)-(3y^2-r^2)}$ in the low-temperature ferromagnetic phase (below 145 K), no orbital ordering in the cooperative Jahn−Teller distorted phase	RXS on the Mn *K* edge
Geck et al.[15]	$(3x^2 - r^2)/(3y^2 - r^2)$ orbital ordering in the cooperative Jahn−Teller distorted phase (probed at 220 K), other type of orbital ordering in the ferromagnetic phase (below 170 K)	RXS on the Mn *K* edge
present work	$(x^2 - z^2)/(y^2 - z^2)$ orbital ordering in the cooperative Jahn−Teller distorted phase (probed at 240 K)	XLD on the Mn *L* edge

$(3r^2 - z^2)$ and $(x^2 - y^2)$ orbitals.[13] Whereas the magnetic properties of CMR manganites, such as spin or charge ordering have been subject to intense studies, i.e., by means of electron or neutron diffraction analysis, the direct investigation of orbital ordering is known to be a difficult task. The orbital ordering in $La_{7/8}Sr_{1/8}MnO_3$ has been studied by resonant X-ray scattering (RXS) on the Mn *K* edge by Endoh et al.[14] and Geck et al.[15] There are some differences in detail (Table 1). Endoh et al. find evidence for a new type of orbital ordering, the hybridization of $d_{(x^2-z^2)-(y^2-z^2)}$ and $d_{(3x^2-r^2)-(3y^2-r^2)}$ in the low-temperature ferromagnetic phase (below 145 K), but do not find any indication for orbital ordering in the cooperative Jahn−Teller distorted phase.[14] On the other hand, Geck et al. find that the cooperative Jahn−Teller distorted phase (27−170 K) shows a rod-type $(3x^2 - r^2)/(3y^2 - r^2)$ orbital ordering similar to that investigated in $LaMnO_3$ using the same experimental technique.[15] RXS on the Mn *K* edge leads to Mn 1s → 4p transitions, which means that this technique allows only an indirect probe of the Mn 3d spatial distribution.[16] In the case of orbital ordering, the outermost Mn 3d orbitals are not orthogonal and arranged in two sublattices, so that X-ray linear dichroism (XLD) on the Mn *L* (Mn 2p → 3d transition) edge is able to probe the type of the uniaxial 3d electron distribution directly, which has been shown theoretically by multiplet calculations.[17−19] Moreover, very recently, the orbital ordering in the *single layered* compound $La_{1.5}Sr_{0.5}MnO_4$ has been investigated by using XLD on the Mn *L* edge (Mn 2p → 3d).[20] $La_{1.5}Sr_{0.5}MnO_4$ is a very important reference system, but it does not show ferromagnetism and colossal magnetoresistance like the system studied here, $La_{7/8}Sr_{1/8}MnO_3$, and especially these properties are necessary for possible future applications.

We report here for the first time soft XLD measurements on the Mn *L* edge of the *cubic crystal* $La_{7/8}Sr_{1/8}MnO_3$ at room temperature and in the cooperative Jahn−Teller distorted phase. In comparison with the recently published results and the available theory, we find strong indications that a predominantly cross type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering is present in the three-dimensional CMR manganite $La_{7/8}Sr_{1/8}MnO_3$. This finding is in contrast to the common view of rod-type $(3x^2 - r^2)/(3y^2 - r^2)$ orbital ordering, and we discuss our experimental result in the light of different exchange interaction models.

2. Experimental Details

A $La_{7/8}Sr_{1/8}MnO_3$ single crystal was grown by the floating zone method at the Moscow State Steel and Alloys Institute. X-ray diffraction (XRD) was used to check the structural quality and single phase nature of the specimens. The chemical composition was determined by microprobe analysis. The crystal was carefully polished with a diamond paste and oriented with help of back reflection Laue patterns. No substantial admixtures of twin domains could be identified at room temperature. By cooling the sample below $T_{JT} \approx 270$ K, one introduces a collective Jahn−Teller distortion and consequently anisotropy into the crystal. The temperature-dependent XRD measurements indicated that the *a* and *b* axes might be interchanged in parallel plates of the crystal. This is also in agreement with recent results of Alejandro et al., who found that if twinning in the *ac* and *bc* planes of $La_{7/8}Sr_{1/8}MnO_3$ is present, it is small.[12] Twinning in the *ab* plane has no essential influence on the XLD signal, as discussed below. The XLD spectroscopy was performed at the Beamline for Advanced diCHroism (BACH) at ELETTRA, Italy.[21,22]

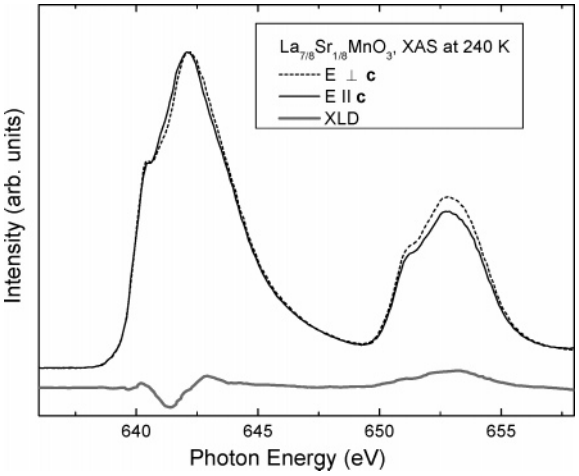

Figure 1. Polarization-dependent XAS with $E \perp c$ and $E \| c$ and the corresponding linear dichroism (LD) recorded on the Mn *L* edge of $La_{7/8}Sr_{1/8}MnO_3$ recorded in the cooperative Jahn−Teller distorted phase at 240 K.

3. Results and Discussion

Figure 1 displays the polarization dependent Mn $L_{2,3}$ XAS spectra recorded in the cooperative Jahn−Teller distorted phase at a temperature of 240 K.

The incident angle of the beam was 75° from the sample surface normal and the *c*-axis of the crystal, which was oriented perpendicular to the polished [001] surface. Hence, for a vertically polarized incoming beam, the **E**-vector of the light was orientated perpendicular to the *c*-axis of the crystal, whereas the **E**-vector of horizontally polarized light was orientated nearly parallel to the *c*-axis. The linear dichroism was then determined by subtracting the two XAS spectra from each other.

In Figure 2 we present the measured Mn *L* edge linear dichroism (LD) spectra at different temperatures, together with calculated spectra, with the $(x^2 - z^2)/(y^2 - z^2)$ and the $(3x^2 - r^2)/(3y^2 - r^2)$ orbitals occupied, respectively.[20] At room temperature, $La_{7/8}Sr_{1/8}MnO_3$ is in a paramagnetic, pseudocubic, incoherent Jahn−Teller distorted phase, and thus no LD signal can be expected. Indeed, the LD signal (Figure 2) for the measurement at room temperature is very small. If the sample is cooled below a temperature of around $T_{JT} = 270$ K, $La_{7/8}Sr_{1/8}MnO_3$ undergoes a phase transition into a coherent Q_2-type Jahn−Teller distorted, orbital-ordered phase, induced by a significant contraction of the *c*-cell parameter from 7.79 Å

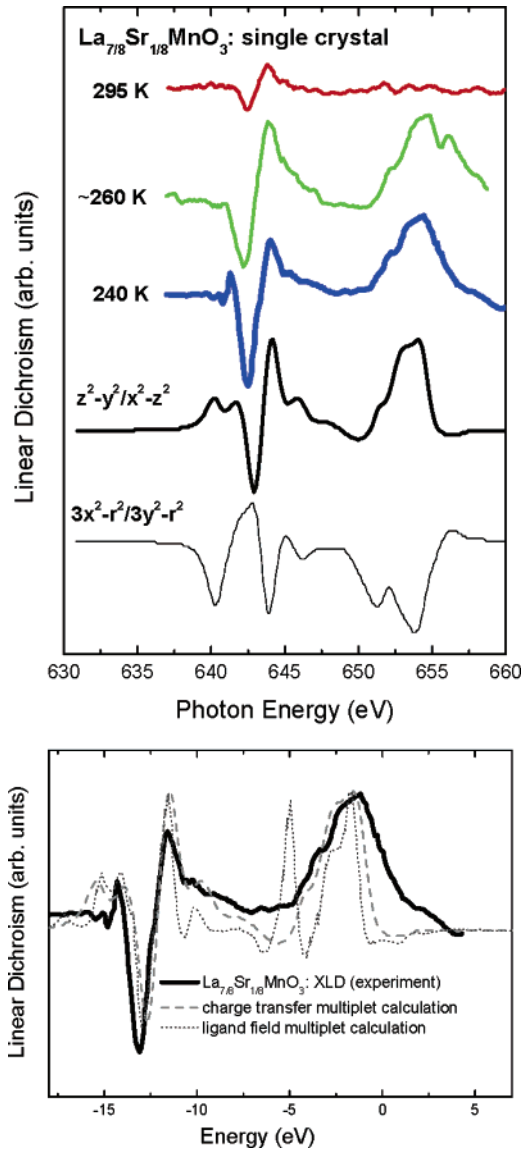

Figure 2. Upper panel: XLD signal recorded at the Mn *L* edge of a $La_{7/8}Sr_{1/8}MnO_3$ single crystal at different temperatures compared with MnO_6 cluster model calculations.[20] Lower panel: Experimental XLD recorded at 240 K in comparison with a crystal field multiplet calculation (dotted line[17] and a charge-transfer multiplet calculation (dashed line).[20]

(295 K) to 7.74 Å (240 K). Highly distorted MnO_6 octahedrons undergo a long-range ordering, accompanied by orbital ordering of the outermost Mn 3d valence electrons. Hence, a strong LD can be observed by measurements recorded at 240 K (Figure 2). An XLD spectrum obtained at around 260 K (just below the orbital ordering temperature T_{OO}) shows nearly the same shape as the XLD recorded at 240 K. The evolution of the LD signal with temperature also excludes that the dichroism is caused accidentally by disordered grains at the surface. Very recently, it has been shown that, even in the case that the *a* and *b* axes show twinning and are interchanged in parallel plates of the crystal, the averaged XLD signal over the two sublattices is observed.[19] Thus XLD is suitable for the investigation of the orbital ordering, even in crystals with this kind of twinning. With the present result we have shown that XLD, applied to the Mn *L* edge, can probe the presence of orbital ordering in *three-dimensional CMR manganites*. The comparison with the calculations shows a very good agreement with the calculated LD spectra of Mn^{3+} ions with the $(x^2 - z^2)/(y^2 - z^2)$ orbitals occupied.[20] The cluster model calculations of Huang et al. have been performed based upon a model for an Mn^{3+} ion in a cubic crystal field,[17,20] and one can qualitatively compare the present results for $La_{7/8}Sr_{1/8}MnO_3$ with these calculations. Furthermore, it is generally believed that the MnO^- planes (and the MnO_6 octahedra) have a very similar structure in layered and three-dimensional systems.[23] Hence, the cooperative Jahn−Teller distorted phase of $La_{7/8}Sr_{1/8}MnO_3$ is probably accompanied by a cross-type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering. The lower panel of Figure 2 shows a comparison of the experimental XLD signal with different multiplet calculations.[17,20] Both approaches reproduce the correct sign of the XLD spectrum, and the overall integrated intensity is positive. In the crystal field approximation, one finds a feature between the Mn L_3 and the Mn L_2 edge that is not present in the experiment. By including charge transfer in the calculation and assuming an admixture of the ground-state configuration $3d^5L$, an almost perfect fit with the experimental data is obtained.

The result above cannot be explained within the framework of the widely used exchange model or Kugel−Khomskii model.[13] Dabrowski et al. derived the Mn−O bond length for the very similar compound $La_{0.87}Sr_{0.13}MnO_3$ by means of a temperature-dependent Rietveld analysis. They found the Mn−O bond length in the cooperative Jahn−Teller distorted phase in the $x-y$ plane (equatorial) to be 2.04 and 1.94 Å, respectively, whereas the Mn−O in (apical) *z*-direction is determined to be 1.97 Å. For $La_{0.11}Sr_{0.89}MnO_3$, a similar situation was found.[9] Two short Mn−O bonds and one elongated Mn−O bond are present in moderately doped three-dimensional $La_{1-x}Sr_xMnO_3$. Applying the exchange model,[13] one would expect a rod-type $(3x^2 - r^2)/(3y^2 - r^2)$ orbital ordering. This is in contrast to the result of the soft XLD measurement on the Mn *L* edge of $La_{7/8}Sr_{1/8}MnO_3$, which strongly indicates the presence of a predominantly cross-type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering (Figure 2), as discussed above. A possible reason for this may be that the exchange interaction model is based upon an effective Hubbard model, considering only the Coulomb exchange between the degenerate d-electron states. This model describes Mott Hubbard insulators, where $\Delta \gg U_{dd}$ (Δ represents the charge-transfer energy and U_{dd} the Coulomb exchange between the transition metal (TM) 3d electrons, respectively), in a correct way. However, it is clear that the ground states of charge transfer insulators are strongly influenced by hopping of electrons between ligand and TM ions (Δ), whereas the usual exchange involves the electron transfer from one TM site to another one. The magnetic and orbital ordering in the ground state may strongly depend on the ratio U_{dd}/Δ.[24] For Mn-based oxides, one finds an intermediate behavior ($\Delta \approx U_{dd}$), this means that electronic transfer interactions between Mn ion and oxygen ligand play an essential role for the mechanism of the orbital ordering. Mostovoy and Khomskii find in a very topical and recent paper that the type of the ground state in charge transfer insulators is essentially different from that of Mott Hubbard insulators.[24] The charge transfer interaction is furthermore of purely electronic origin, independent of any electron−lattice interaction, and in general present in all TM oxides. For charge-transfer insulators with one hole per TM site, the occupation of $(x^2 - y^2)$-like orbitals is preferred. Therefore, in materials such as $La_{7/8}Sr_{1/8}MnO_3$, where ($\Delta \approx U_{dd}$), the type of orbital ordering cannot be determined by merely taking into account the Coulombic consequences of the electron−lattice interaction, but it is stabilized by a fine balance between electron−lattice and the electron−hole interactions. Thus, a predominantly cross-type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering, as indicated by the

XLD measurements, is probably present. However, it should be mentioned that an admixture of $(3x^2 - r^2)/(3y^2 - r^2)$ orbitals decreases the integrated intensity of the XLD signal but does not lead to a major change of the spectral shape.[19] Therefore, an admixture of $(3x^2 - r^2)/(3y^2 - r^2)$ orbits into the $(x^2 - z^2)/(y^2 - z^2)$ orbits cannot be excluded. However, XLD at the Mn *L* edge is in any case able to distinguish between predominantly rod-type $(3x^2 - r^2)/(3y^2 - r^2)$ and predominantly cross-type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering.

To fully understand the Mn *L* edge XLD and the orbital ordering of $La_{7/8}Sr_{1/8}MnO_3$, complementary X-ray scattering experiments on the Mn *L* edge would be very helpful, since this technique is also able to probe the type of orbital ordering in manganites directly. This has been demonstrated very recently for the half-doped single layered manganite $La_{1.5}Sr_{0.5}MnO_4$.[25,26] However, there are no soft X-ray scattering experiments on $LaMnO_3$ or other three-dimensional CMR manganites known up to now.

4. Conclusions

In summary, we have shown for the first time that it is possible to probe the type of orbital ordering in three-dimensional CMR manganites by using X-ray linear dichroism on the Mn *L* edge. We obtained rather strong indications that the coherently distorted Jahn−Teller phase in $La_{7/8}Sr_{1/8}MnO_3$ is accompanied by a predominantly cross-type $(x^2 - z^2)/(y^2 - z^2)$ orbital ordering. This result cannot be explained within the widely used framework of exchange interaction, and we find experimental evidence that, in addition to the widely used electron−phonon interaction, also the electron−hole interaction has to be taken into account in order to understand the fascinating interplay between orbital, charge, and spin order in manganites.

Acknowledgment. Financial support from EU is gratefully acknowledged. K.K. and A.T. acknowledge the PhD program of Lower Saxony, Germany, for financial support. V.R.G. acknowledges financial support of the Russian Foundation for Basic Research (Grant No 04-03-96092-Ural). We thank N. Stojic for very helpful discussions. We are grateful to B. Lemme and H. Hesse for performing back reflection Laue patterns on the crystal. We thank B. J. Zimmermann for drawing the TOC graphic.

References and Notes

(1) Millis, A. J. *Nature* **1998**, *392*, 147.

(2) Rao, C. N. R. *J. Phys. Chem. B* **2000**, *104*, 5877.

(3) Tokura, Y.; Nagaosa, N. *Science* **2000**, *288*, 462.

(4) Woodward, P. M.; Suard, E.; Karen, P. *J. Am. Chem. Soc.* **2003**, *125*, 8889.

(5) Kuepper, K.; Falub, M. C.; Prince, K. C.; Galakhov, V. R.; Troyanchuk, I. O.; Chiuzbăian, S. G.; Matteucci, M.; Wett, D.; Szargan, R.; Ovechkina, N. A.; Mukovskii, Y. M.; Neumann, M. *J. Phys. Chem. B* **2005**, *109*, 9354.

(6) Ziese, M. *Rep. Prog. Phys.* **2002**, *65*, 143.

(7) Van Aken, B. B.; Jurchescu, O. D.; Meetsma, A.; Tomioka, Y.; Tokura, Y.; Palstra, T. T. M. *Phys. Rev. Lett.* **2003**, *90*, 066403.

(8) Klingeler, R.; Geck, J.; Gross, R.; Pinsard-Gaudart, L.; Revcolevschi, A.; Uhlenbruck, S.; Büchner, B. *Phys. Rev. B* **2002**, *65*, 174404.

(9) Dabrowski, B.; Xiong, X.; Bukowski, Z.; Dybzinski, R.; Klamut, P. W.; Siewenie, J. E.; Chmaissem, O.; Shaffer, J.; Kimball, C. W.; Jorgensen, J. D.; Short, S. *Phys. Rev. B* **1999**, *60*, 7006.

(10) Nojiri, H.; Kaneko, K.; Motokawa, M.; Hirota, K.; Endoh, Y.; Takahashi, K. *Phys. Rev. B* **1999**, *60*, 4142.

(11) Korotin, M.; Fujiwara, T.; Anisimov, V. *Phys. Rev. B* **2000**, *62*, 5696.

(12) Alejandro, G.; M. C. G. Passeggi; Vega, D.; C. A. Ramos; M. T. Causa; Tovar, M.; Senis, R. *Phys. Rev. B* **2003**, *68*, 214429.

(13) Kugel, K. I.; Khomskii, D. I. *Sov. Phys. Usp.* **1982**, *25*, 231.

(14) Endoh, Y.; Hirota, K.; Ishihara, S.; Okamoto, S.; Murakami, Y.; Nishizawa, A.; Fukuda, T.; Kimura, H.; Nojiri, H.; Kaneko, K.; Maekawa, S. *Phys. Rev. Lett.* **1999**, *82*, 4328.

(15) Geck, J.; Wochner, P.; Bruns, D.; Büchner, B.; Gebhardt, U.; Kiele, S.; Reutler, P.; Revcolevschi, A. *Phys. Rev. B* **2004**, *69*, 104413.

(16) Murakami, Y.; Hill, J.; Gibbs, D.; Blume, M.; Koyama, I.; Tanaka, M.; Kawata, H.; Arima, T.; Tokura, Y.; Hirota, K.; Endoh, Y. *Phys. Rev. Lett.* **1998**, *81*, 582.

(17) Huang, H. B.; Shishidou, T.; Jo, T. *J. Phys. Jpn.* **2000**, *69*, 2399.

(18) Taguchi, M.; Altarelli, M. *Surf. Rev. Lett.* **2002**, *9*, 1167.

(19) Huang, H. B.; Jo, T. *J. Phys. Jpn.* **2004**, *73*, 2480.

(20) Huang, D.; Wu, W.; Guo, G.; Lin, H.-J.; Hou, T.; Chang, C. F.; Chen, C.; Fujimori, A.; Kimura, T.; Huang, H.; Tanaka, A.; Jo, T. *Phys. Rev. Lett.* **2004**, *92*, 087202.

(21) Zangrando, M.; Finazzi, M.; Paolucci, G.; Comelli, G.; Diviacco, B.; Walker, R. P.; Cocco, D.; Parmigiani, F. *Rev. Sci. Instrum.* **2001**, *72*, 1313.

(22) Zangrando, M.; Zacchigna, M.; Finazzi, M.; Cocco, D.; Rochow, R.; Parmigiani, F. *Rev. Sci. Instrum.* **2004**, *75*, 31.

(23) Stojic, N., private communication, 2005.

(24) Mostovoy, M. V.; Khomskii, D. I. *Phys. Rev. Lett.* **2004**, *92*, 167201.

(25) Wilkins, S. B.; Spencer, P. D.; Hatton, P. D.; Collins, S. P.; Roper, M. D.; Prabhakaran, D.; Boothroyd, A. T. *Phys. Rev. Lett.* **2003**, *91*, 167205.

(26) Dhesi, S.; Mirone, A.; Nadai, C. D.; Ohresser, P.; Bencok, P.; Brookes, N. B.; Reutler, P.; Revcolevschi, A.; Tagliaferri, A.; Toulemonde, O.; van der Laan, G. *Phys. Rev. Lett.* **2004**, *92*, 056403.