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Change in Mn 3*d* orbital state related to a metal-insulator transition in a bilayer manganite studied by magnetic Compton profile measurement

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Temperature dependence of magnetic Compton profile (MCP) has been measured on a single crystal of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ at $x=0.42$ along the *c*-axis. The spin magnetic moments of Mn 3*d* electrons in t_{2g} and e_g type orbitals are evaluated from the line-shape fitting analysis of MCP's using theoretical profiles derived from the $(MnO_6)^{8-}$ *ab initio* calculations. The experimental ratios of e_g spins to t_{2g} ones show higher values above the metal-insulator transition temperature T_c in comparison with the value expected from the electronically homogeneous state. This is understood in terms of the phase separation between electron-rich ferromagnetic and electron-poor antiferromagnetic regions. The ratios indicate that the e_g electrons are highly segregated in the ferromagnetic region. In addition, the fitting result just above T_c suggests that the e_g-orbital state involved with the colossal magnetoresistance effect is optimized by an external magnetic field.

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Perovskite Mn oxides have provided a fascinating subject such as colossal magnetoresistance (CMR) observed just around a metal-insulator transition temperature T_c,[1–4] where the charge, spin, and orbital degrees of freedom are arguably connected with each other. The ferromagnetism and metallic conductivity concurrently appeared below T_c have been understood on the basis of the double-exchange (DE) mechanism, where e_g electrons hop around Mn sites through hybridization with O-2*p* orbitals, and align the localized t_{2g} spins by the strong Hund's coupling.[5–7] However, the transport properties including CMR and the complicated magnetic phase diagrams of manganites cannot be explained by the simple DE mechanism, and some additional ingredient is required. It is currently pointed out that the lattice degree of freedom, which is strongly coupled with the orbital degree of freedom, plays an important role in understanding the physical properties of manganites.[8–12] Recent x-ray and neutron-scattering experiments have observed a short-range charge ordering (SRCO) within MnO_2 layers, suggesting the localization of e_g electrons at Mn sites accompanied by local lattice distortions.[13–16] Kubota *et al*. have reported that in bilayer manganites, SRCO appears in the wide range of hole concentration and is characterized by a bistripe order running along the [100] direction in a MnO_2 layer which forms streaks of two large and one small lattice distortions around Mn^{3+} and Mn^{4+} ions, respectively.[15,16] The temperature dependence of SRCO shows a notable change in the vicinity of T_c, and well corresponds to that of resistivity.[15] Therefore, determination of the electronic and orbital states around T_c, which are sensitive to the local structural change, will provide a clue to elucidate the mechanism of CMR.

Our previous paper demonstrated that magnetic Compton-profile (MCP) measurement is capable of determining the population of Mn-3*d* orbitals which hybridize with O-2*p* orbitals.[17] In the present study, we have measured the temperature dependence of MCP on a bilayer manganite, and made a line-shape analysis on MCP's using theoretical profiles of e_g and t_{2g} type orbitals. From the analytical results, we will discuss the change in e_g electron density depending on temperature and the effect of magnetic field on the e_g-orbital state just above T_c.

The MCP, $J_{\mathrm{mag}}(p_z)$, is defined as the double integral of the difference in momentum density between spin-up and spin-down electrons with respect to p_x and p_y,

$$J_{\mathrm{mag}}(p_z)=\int\left(\sum_i |\phi_{i\uparrow}(\mathbf{p})|^2-\sum_j |\phi_{j\downarrow}(\mathbf{p})|^2\right)dp_x dp_y, \tag{1}$$

where p_z is an electron-momentum component along the direction of the scattering vector of x rays. The $\phi_{i\sigma}(\mathbf{p})$ is a wave function in momentum space, and $|\phi_{i\sigma}(\mathbf{p})|^2$ means the momentum density of *i*th state. The subscript *i* and *j* go through all occupied spin-up and spin-down states, respectively. The MCP is sensitive only to the spin magnetic moment,[18] and its area is proportional to the magnitude of spin magnetic moment. In addition, the MCP measurement is advantageous to the study of orbital states, because the shape of MCP varies according to orbitals occupied by magnetic electrons. This feature enables us to separately determine the spin magnetic moments in e_g and t_{2g} type orbitals on manganites based on the theoretical profiles of them.[17]

The sample was a single crystal of bilayer manganite $La_{2-2x}Sr_{1+2x}Mn_2O_7$ at $x=0.42$, which was melt-grown in flowing oxygen gas in a floating zone optical image furnace.[19] This system shows two-dimensional conductivity, because a pair of MnO_2 layers is interlaced between two $(La, Sr)_2O_2$ blocking layers. According to the magnetic phase diagram obtained by neutron-diffraction measurement,[20] the magnetic structure of the present sample is canted antiferromagnetic (canted AFM) below T_c, where the magnetic moments in a MnO_2 layer are ferromagnetically aligned and slightly canted between the two layers within a bilayer. Above T_c, the sample changes to AFM-I insulator phase, where the magnetic moments are antiferro-

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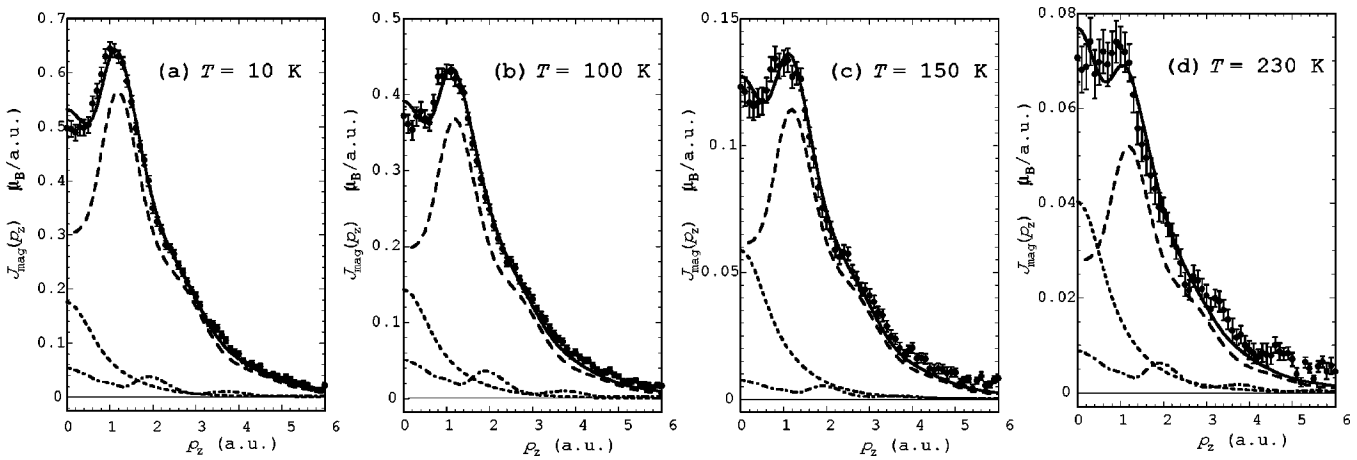

FIG. 1. The magnetic Compton profiles along the *c*-axis measured at (a) 10 K, (b) 100 K, (c) 150 K, and (d) 230 K under the external field of ± 2.5 T. The abscissa represents an electron momentum p_z in the atomic unit (a.u.). Experimental data (solid circles) are shown with fit (solid line) using the MnO_6 cluster orbitals. Error bars indicate experimental statistical errors. The t_{2g}, $e_{x^2-y^2}$, and $e_{3z^2-r^2}$ type orbital contributions are denoted by dashed, dotted, and dotted–dashed lines, respectively (Ref. 21).

magnetically ordered between the two layers, and the CMR is observed in this phase. The sample becomes paramagnetic (PM) above 170 K. We measured the magnetic susceptibility on the sample and determined T_c to be 95 K.

MCP measurements were made at 10, 100, 150, and 230 K on the beamline 08W at SPring-8, Japan. Circularly polarized x rays emitted from an elliptical multipole wiggler were monochromatized to 174 keV and incident on the sample. The Compton scattered x rays with a scattering angle of 178.5° were energy analyzed by a 10-segmented Ge solid-state detector. During the measurement, an external magnetic field of ± 2.5 T was alternatively applied along the *c*-axis of the sample to reverse the magnetization direction. Each MCP was extracted as the difference between two measured Compton profiles of the sample magnetized mutually in the opposite directions with a fixed photon polarization. The MCP's above T_c were measured on the sample with field-induced magnetization. Then, the orbital state on the condition of CMR will be reflected in the MCP particularly at 100 K.

The MCP's obtained are shown in Fig. 1. The area of each MCP is normalized to the corresponding magnetization listed in Table I. It is noticed that the dip in the low momentum region, $p_z < 1.0$ a.u., becomes shallower with increasing temperature. We can qualitatively examine the change of MCP's with atomic profiles of e_g and t_{2g} orbitals, since the magnetization of manganite is induced by the spins in Mn-3*d* orbitals. The result suggests that the ratio of e_g spin magnetic moments to t_{2g} ones increases above T_c, because the atomic e_g-orbital profile shows a peak at $p_z = 0$, while t_{2g}-one has a dent. To quantitatively evaluate the spin magnetic moments in respective orbitals, the fitting analysis of each MCP has been carried out using theoretical profiles of t_{2g}, $e_{x^2-y^2}$, and $e_{3z^2-r^2}$ type orbitals obtained from an *ab initio* molecular orbital calculation for a $(MnO_6)^{8-}$ cluster which takes the hybridization effect between Mn-3*d* and O-2*p* orbitals into account.[21] The *z*-axis is taken to be parallel to the *c*-axis. The t_{2g} profile is treated as the sum of *xy*, *yz* and *zx* orbitals because those orbitals are considered to be fully occupied. The details of the calculation are described in Ref. 17. The fitting results are shown by the lines in Fig. 1 and listed in Table I.

In the case of manganites, it is reasonable to consider that the occupation number in each Mn-3*d* orbital is proportional

TABLE I. Spin magnetic moments in respective orbitals evaluated from the fitting analysis of MCP. Each value is normalized by the magnetic moment per Mn site, $M(\mu_B/\mathrm{Mn})$, obtained by magnetization measurement at the field of 2.5 T. The results at 150 and 230 K are shown in a large number of decimals, which is due to the small normalization factor, *M*. The e_g/t_{2g} and $e_{3z^2-r^2}/e_{x^2-y^2}$ mean the ratios of e_g to t_{2g} and $e_{3z^2-r^2}$ to $e_{x^2-y^2}$ spin magnetic moments, respectively.

T(K)	$M(\mu_B/\mathrm{Mn})$	t_{2g}	$e_{x^2-y^2}$	$e_{3z^2-r^2}$	e_g/t_{2g}	$e_{3z^2-r^2}/e_{x^2-y^2}$
10	3.12	2.49 (± 0.03)	0.37 (± 0.02)	0.21 (± 0.03)	0.23	0.57
100	2.20	1.62 (± 0.02)	0.30 (± 0.02)	0.20 (± 0.03)	0.31	0.67
150	0.69	0.503 (± 0.011)	0.124 (± 0.007)	0.030 (± 0.013)	0.31	0.24
230	0.38	0.229 (± 0.009)	0.085 (± 0.006)	0.035 (± 0.011)	0.52	0.41

to the spin moment evaluated from the analysis of MCP, since the strong Hund's coupling works between t_{2g} and e_g spins. If the area of MCP is normalized to 3.58, i.e., the nominal $3d$ electron number for $x=0.42$, the orbital populations at 10 K are given as 2.86, 0.43, and 0.24 for t_{2g}, $e_{x^2-y^2}$, and $e_{3z^2-r^2}$ type orbitals, respectively, which are in good agreement with the previous result.[17] If the sample is electronically homogeneous, the ratio e_g/t_{2g} in the present sample is expected to be 0.193 on the assumption that the t_{2g} and e_g populations are 3 and 0.58, respectively. Here the e_g contribution is the sum of $e_{x^2-y^2}$ and $e_{3z^2-r^2}$ orbital populations. In the canted AFM region below T_c, the experimental ratio at 10 K deduced from the fitting results shows 0.23 that is slightly larger than the expected ratio. It is to be anticipated that in AFM-I phase, both the ratios at 100 and 150 K give a significantly large value of 0.31. The ratio at 230 K in PM phase shows an even larger value of 0.52, although it is less reliable because the measurement was made on the sample with field-induced weak magnetization resulting in poor statistics. Since the MCP measurement detects the only ferromagnetic (FM) component in the sample and does not the AFM one, these results mean that the density of e_g electrons is high in the observed FM state and the electronic inhomogeneity of the sample is remarkable particularly above T_c, and suggest the concomitance of e_g-electron poor AFM state. Yunoki *et al.* have theoretically predicted the phase separation (PS) between the electron-rich FM and the electron-undoped AFM regions in the high hole doping level.[22–26] According to this description, the increase in e_g/t_{2g} can be understood as a result of decrease in t_{2g} spin contribution to MCP. That is, in the AFM region with no e_g electrons, t_{2g} spin moments cancel each other and do not contribute to MCP. The ratio will therefore become large, if all the e_g electrons are in the FM region. The volume fraction of the FM region may be given by $M(T)/3.58$ below and just above T_c, because the thermal fluctuation of magnetic moments would be small at these temperatures. In practice, the ratios at 10 and 100 K are well explained by $0.193 \times 3.58/M(T)$. Specifically, the ratio of 0.31 at 100 K is possible when about three fifth parts of the sample is the electron-rich FM region, and the rest is the electron-undoped AFM region. However, large FM domains with high electron density could not exist because of the charge neutrality. It should be divided into small clusters. In fact, several experiments have observed magnetic clusters above T_c.[27–29] Small-angle neutron scattering (SANS) measurement has shown that the magnetic correlation length, which provides the size of the clusters, is of the order of a few lattice spacing, and rapidly diverges below T_c. In manganite, the factor contributing to the ferromagnetic small clusters would be underlying in the form of charge-segregated domains, which may originate in the local chemical and structural inhomogeneity.[30] On the other hand, SRCO, which is associated with the localization of e_g electrons, disappears below T_c. The above ratios therefore, indicate that the electronic state is comparatively homogeneous below T_c, while the e_g electrons are highly segregated in the magnetic clusters above T_c, and the degree of charge segregation varies according to the magnetic phases such as canted AFM, AMF-I, and PM states. In this regard, the PS observed in the present study would depend on temperature.

Another significant finding is the effect of external field on the e_g orbital state just above T_c. The e_g orbital state at 100 K shows a high proportion of $e_{3z^2-r^2}$ component in comparison with that at 150 K, although the ratio e_g/t_{2g} is almost the same at both temperatures. The ratio of $e_{3z^2-r^2}$ to $e_{x^2-y^2}$ spin moments makes this aspect clear as listed in Table I. The $e_{3z^2-r^2}/e_{x^2-y^2}$ at 100 K is larger than the ratio at 150 K, and shows a comparable value to the ratio at 10 K. This means that the e_g state at 150 K is dominated by the x^2-y^2 orbital character, and the e_g-orbital configuration at 100 K, just above T_c, is similar to that at 10 K under the present external field.

In zero-magnetic field, the electronic state above T_c would be a polaronic state with highly localized e_g electrons, specifically the $e_{x^2-y^2}$ electrons at least in a high hole doping region. In fact, the above result at 150 K, where the CMR effect becomes small, is consistent with this view, and well describes the AFM-I phase, i.e., the low population of $3z^2-r^2$ orbital weakens the interlayer ferromagnetic coupling within a bilayer. Then, the superexchange antiferromagnetic coupling between t_{2g} orbitals overcomes the DE interaction along the *c*-axis. Consequently, the system is in AFM-I phase. The dominance of x^2-y^2 orbital is also supported by the fact that in bilayer manganite at $x=0.4$, the Jahn-Teller distortion measured by a neutron diffraction experiment becomes small around T_c.[31] Such relaxation of lattice distortion will work for the stabilization of x^2-y^2 orbital. Hence, the MnO_2 layers in the charge-segregated domain would be substantially filled with $e_{x^2-y^2}$ electrons, because the ratio e_g/t_{2g} of 0.31 at 100 K implies that the density of e_g electrons is about 1.6 times higher in the magnetic clusters just above T_c than in the electronically homogeneous state. In such a situation, the $e_{x^2-y^2}$ electrons may be immobilized by the electron correlation between them, resulting in insulating. This is likely to be related to SRCO with local lattice distortion which will affect on the e_g orbital state. A neutron diffraction study has found that an applied magnetic field causes the collapse of SRCO,[14] while both SANS and emission Mössbauer studies have reported that above T_c, the magnetic clusters grow in size on application of a magnetic field.[27,29] These observations suggest that the percolative network of magnetic clusters, which will be a requirement for CMR, expands with decreasing SRCO. In addition to this, the ratio $e_{3z^2-r^2}/e_{x^2-y^2}$ at 100 K indicates that the change in e_g orbital state by an external field interprets the CMR phenomenon; the applied field aligns the Mn magnetic moments of the magnetic clusters. As shown by the ratio $e_{3z^2-r^2}/e_{x^2-y^2}$ at 100 K, some of the localized $e_{x^2-y^2}$ electrons move into the $3z^2-r^2$ orbitals in the combined magnetic clusters, which will play a part in the relaxation of local lattice distortion. The change in orbital configuration will simultaneously induce sufficient holes in the MnO_2 layer dominated by $e_{x^2-y^2}$ electrons. The holes correspond to the amount of e_g electrons transferred from x^2-y^2 to $3z^2-r^2$ orbital. This will effectively activate the DE interaction in the system, and metallic conductivity will be brought back in

the MnO_2 layer, thus CMR. The stabilization of $3z^2-r^2$ orbital will also facilitate conductivity along the *c*-axis and the ferromagnetic coupling between the two layers within a bilayer, and will come along with an elongation of the bond length between Mn and apical O. Indeed, the fitting result at 100 K is consistent with a large magnetostriction around T_c observed in the bilayer manganite at $x=0.4$,[32] and therefore indicates that the e_g-orbital state on the condition of CMR is optimized by external fields .

In summary, we have measured the temperature dependence of MCP for $La_{2-2x}Sr_{1+2x}Mn_2O_7$ at $x=0.42$ along the *c*-axis. The values of spin magnetic moments of t_{2g} and two e_g ($e_{x^2-y^2}$ and $e_{3z^2-r^2}$) type orbitals are obtained by the fitting analysis of each MCP using theoretical profiles derived from the $(MnO_6)^{8-}$ cluster calculation. The ratio of e_g to t_{2g} spin magnetic moments shows higher values above T_c than at 10 K. This is explained in terms of the phase separation between electron-rich FM and electron-undoped AMF regions. The ratios indicate that the e_g electrons are highly segregated in the magnetic clusters above T_c, and such electronic state with high density of e_g electrons exists as an underlying factor for CMR. In addition, the ratio of $e_{3z^2-r^2}$ to $e_{x^2-y^2}$ spin moments at 100 K suggests that the change in e_g-orbital state by external fields plays an important role in the CMR phenomenon in manganites. The e_g-orbital state around T_c may change according to the strength and the direction of applied fields. The field dependence of MCP will be able to verify the change in e_g orbital state. Measurements of anisotropy in MCP will be also effective to clarify the influence of the external field on the e_g orbital state around T_c, because MCP of each orbital changes its shape depending also on the direction of observation.

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[1] R. von Helmolt *et al.*, Phys. Rev. Lett. **71**, 2331 (1993).
[2] S. Jin *et al.*, Science **264**, 413 (1994).
[3] A. Urushibara *et al.*, Phys. Rev. B **51**, 14 103 (1995).
[4] Y. Moritomo *et al.*, Nature (London) **380**, 141 (1996).
[5] C. Zener, Phys. Rev. **82**, 403 (1951).
[6] P.W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1995).
[7] P.G. de Gennes, Phys. Rev. **118**, 141 (1960).
[8] A.J. Millis *et al.*, Phys. Rev. Lett. **74**, 5144 (1995).
[9] H. Röder *et al.*, Phys. Rev. Lett. **76**, 1356 (1996).
[10] A.J. Millis *et al.*, Phys. Rev. Lett. **77**, 175 (1996).
[11] D. Louca *et al.*, Phys. Rev. B **56**, R8475 (1997).
[12] H. Koizumi *et al.*, Phys. Rev. Lett. **80**, 4518 (1998).
[13] S. Shimomura *et al.*, Phys. Rev. Lett. **83**, 4389 (1999).
[14] L. Vasiliu-Doloc *et al.*, Phys. Rev. Lett. **83**, 4393 (1999).
[15] M. Kubota *et al.*, J. Phys. Soc. Jpn. **69**, 1986 (2000).
[16] M. Kubota *et al.*, J. Phys. Soc. Jpn. **70**, 91 (2001).
[17] A. Koizumi *et al.*, Phys. Rev. Lett. **86**, 5589 (2001).
[18] N. Sakai, J. Phys. Soc. Jpn. **63**, 4655 (1994).
[19] K. Hirota *et al.*, J. Phys. Soc. Jpn. **67**, 3380 (1998).
[20] M. Kubota *et al.*, J. Phys. Chem. Solids **60**, 1161 (1999).
[21] In this report, we use $e_{x^2-y^2}$ and $e_{3z^2-r^2}$ to denote x^2-y^2 and $3z^2-r^2$ type orbitals of the e_g state, respectively.
[22] S. Yunoki *et al.*, Phys. Rev. Lett. **80**, 845 (1998).
[23] S. Yunoki and A. Moreo, Phys. Rev. B **58**, 6403 (1998).
[24] E. Dagotto *et al.*, Phys. Rev. B **58**, 6414 (1998).
[25] S. Yunoki *et al.*, Phys. Rev. Lett. **81**, 5612 (1998).
[26] A. Moreo *et al.*, Science **283**, 2034 (1999).
[27] J.M. De Teresa *et al.*, Nature (London) **386**, 256 (1997).
[28] O. Chauvet *et al.*, Phys. Rev. Lett. **81**, 1102 (1998).
[29] V. Chechersky *et al.*, Phys. Rev. B **59**, 497 (1999).
[30] T. Shibata *et al.*, Phys. Rev. Lett. **88**, 207205 (2002).
[31] J.F. Mitchell *et al.*, Phys. Rev. B **55**, 63 (1997).
[32] T. Kimura *et al.*, Phys. Rev. Lett. **81**, 5920 (1998).