

Direct Observation of Charge and Orbital Ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$

Y. Murakami,¹ H. Kawada,¹ H. Kawata,¹ M. Tanaka,¹ T. Arima,² Y. Moritomo,³ and Y. Tokura^{4,5}

¹Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba 305-0801, Japan

²Institute of Materials Science, University of Tsukuba, Tsukuba 305-0006, Japan

³Center for Integrated Research in Science and Engineering (CIRSE), Nagoya University, Nagoya 464-0814, Japan

⁴Department of Applied Physics, University of Tokyo, Tokyo 113-0033, Japan

⁵Joint Research Center for Atom Technology (JRCAT), Tsukuba 305-0046, Japan

(Received 16 September 1997)

Charge ordering and orbital ordering in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ have been investigated by using synchrotron x-ray diffraction. The alternating pattern of $\text{Mn}^{3+}/\text{Mn}^{4+}$ in real space is observed directly by making use of their anomalous dispersion. The first clear evidence of the orbital ordering of e_g electrons on Mn^{3+} is also presented based on the measurements of ATS (anisotropy of the tensor of susceptibility) reflection near the Mn K -absorption edge. The present observations indicate that the charge ordering and orbital ordering occur simultaneously at a transition temperature higher than that of the spin ordering. [S0031-9007(98)05409-X]

PACS numbers: 71.45.Lr, 61.10.-i, 71.90.+q

Recently, it has been recognized that the charge, spin, and orbital degrees of freedom play important roles in the electric and magnetic properties of the transition-metal oxides. Especially, in perovskite-type manganites, the discovery of a wide variety of magnetic-field-induced phenomena, such as a colossal magnetoresistance [1] and a magnetostructural transition [2], has stimulated much activity in this field. Meanwhile, in a system with a smaller one-electron bandwidth, a charge-ordering (CO) transition has been observed, in which the doped carriers are ordered in real space [3]. A typical example is a layered-perovskite system $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ in which the average manganese valence is $\text{Mn}^{3.5+}$. Moritomo *et al.* [4] and Bao *et al.* [5] have studied the CO transition of this system by measurements of resistivity, magnetic susceptibility, and electron diffraction. Sternlieb *et al.* [6] have also presented clear nuclear and magnetic neutron diffraction spectra below the CO temperature ($T_{\text{CO}} \approx 217$ K) and the Neel temperature ($T_N \approx 110$ K), respectively. However, it was difficult to directly observe an alternating $\text{Mn}^{3+}/\text{Mn}^{4+}$ pattern, because superlattice peaks of CO in neutron and electron diffraction measurements include the intensity arising from the distortion of crystalline lattice, as a result of oxygen displacement, etc.

In this Letter we present the first direct evidence of an alternating $\text{Mn}^{3+}/\text{Mn}^{4+}$ pattern of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ by using the anomalous dispersion of the scattering factor for Mn^{3+} and Mn^{4+} in synchrotron x-ray diffraction measurements. Below the T_{CO} there is one e_g electron on the Mn^{3+} site and no e_g electron on the Mn^{4+} site. The e_g electron on Mn^{3+} has an orbital degree of freedom, that is, $(3z^2 - r^2)$ - and $(x^2 - y^2)$ -type orbital. The orbital-ordering (OO) configuration of the e_g electrons on Mn^{3+} is clearly demonstrated for the first time by making use of the anisotropy of the tensor of susceptibility (ATS) reflection technique. It is found that the CO and OO

occur simultaneously, and then the spin ordering occurs at a lower temperature.

The synchrotron x-ray diffraction measurements were performed at beam line-4C at the Photon Factory, KEK, Tsukuba. The incident beam is monochromatized by a Si(111) double crystal and focused by a bent cylindrical mirror. X rays with an energy near the manganese K -absorption-edge (E_A) were used, and the energy resolution was about 2 eV. The energy was calibrated by using the absorption edge of a manganese metal foil. Single crystals of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ were grown by the floating-zone method. The (110) plane was polished with diamond paste to a flat surface. The sample size was approximately $1.5 \times 1.0 \times 2.0$ mm, and the FWHM mosaic was about 0.5° . The crystal was mounted in a closed cycle ^4He refrigerator on a six-axis diffractometer.

The proposed CO model by Sternlieb *et al.* is included in Fig. 1. The resulting CO unit cell has dimensions $\sqrt{2}a \times \sqrt{2}a \times c$ relative to the room-temperature structure with the crystal space group $I4/mmm$, and $a = 3.86$ Å, $c = 12.44$ Å. We have directly confirmed this $\text{Mn}^{3+}/\text{Mn}^{4+}$ pattern through the use of the anomalous dispersion of Mn^{3+} and Mn^{4+} , as follows. The atomic-scattering factor near E_A is generally represented by

$$f(E) = f_0 + f'(E) + if''(E), \quad (1)$$

depending on the x-ray energy (E), where f_0 , f' , and f'' are the Thomson scattering factor and the real and imaginary parts of anomalous scattering factor, respectively. Since E_A of Mn^{4+} will be slightly different from that of Mn^{3+} , we can expect an anomaly of the peak intensity of the CO superlattice near E_A , which is attributed to the anomalous scattering term. Such an anomaly of the superlattice peak $(3/2, 3/2, 0)$ was observed near E_A , as exemplified for the case at $T = 29.6$ K in Fig. 2. In order to analyze the energy dependence in terms of the CO model, we obtained

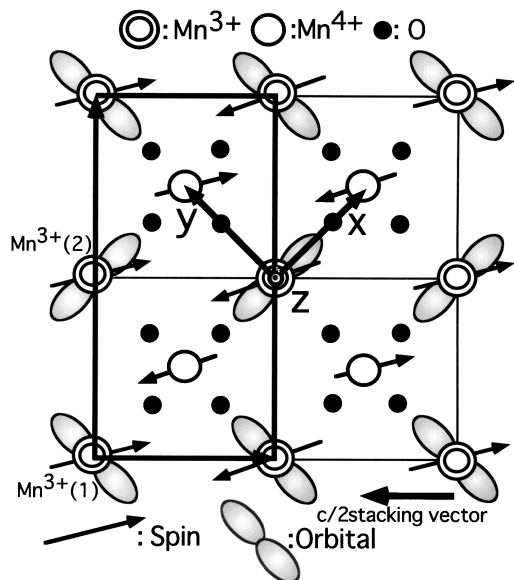


FIG. 1. Schematic view of the charge, spin, and orbital ordering in a layered perovskite manganite, $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$. The stacking vector along the c axis is shown in the figure.

the anomalous dispersion terms for Mn^{3+} and Mn^{4+} , that is, f^{3+} , f^{4+} , f'^{3+} , and f''^{4+} . The f'^{3+} and f''^{4+} could be directly obtained from the room-temperature absorption spectra of LaSrMnO_4 (Mn^{3+}) and $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ ($\text{Mn}^{3+} + \text{Mn}^{4+}$), which is shown in Fig. 3. The energy difference between the E_A 's of Mn^{3+} and Mn^{4+} was about 4 eV. The f^{3+} and f^{4+} can be transformed by the Kramers-Kronig transformation of the f'^{3+} and f''^{4+} , respectively, in which Cromer and Liberman's calculation was applied to estimate the region outside the absorption measurements [7]. The $f'(E)$ obtained by this procedure is also shown in Fig. 3. Making use of these $f'(E)$ and $f''(E)$, we can calculate the energy dependence of the structure factor of the CO superlattice. The structure fac-

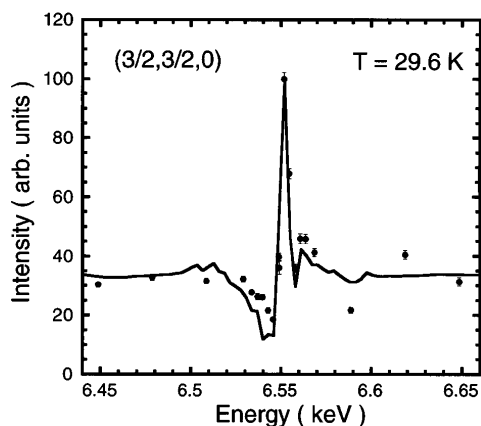


FIG. 2. Energy dependence of the charge-ordering superlattice reflection $(3/2, 3/2, 0)$ near the manganese K -absorption edge at $T = 29.6$ K. The solid curve is a calculated one based on $f'(E)$ and $f''(E)$ of Mn^{3+} and Mn^{4+} .

tor $F(h/2, h/2, 0)$ at odd h , is given by

$$F(h/2, h/2, 0) \propto (f^{3+} - f^{4+}) + i(f'^{3+} - f''^{4+}) + C, \quad (2)$$

where C is independent of the energy, contributed by $(f_0^{3+} - f_0^{4+})$ plus the term from the oxygen distortion which is due to the CO. The solid curve in Fig. 2 shows the calculated energy dependence for the $(3/2, 3/2, 0)$ superlattice after absorption correction, which agrees with the experimental data very well. This is direct evidence that the alternating $\text{Mn}^{3+}/\text{Mn}^{4+}$ pattern is formed in the CO state at a sufficiently low temperature ($T = 29.6$ K $\ll T_{\text{CO}}$). Namely, this CO state is not a small modulation of the manganese valence, but represents an integer charge of valence from site to site.

In order to probe the possible OO configuration of e_g electrons on the Mn^{3+} site, we adopt the model shown in Fig. 1. This assumption is based on the spin ordering configuration observed by neutron diffraction [6]; the spins should be parallel in the direction of extension of the orbitals as a result of the double-exchange mechanism [8]. The unit cell of this OO model is $\sqrt{2}a \times 2\sqrt{2}a \times c$, as shown by thick solid lines in Fig. 1. We used the ATS reflection technique in order to observe such a OO. ATS reflection means that "forbidden" reflections may, in fact, be observed due to the anisotropy of the x-ray susceptibility of atoms, that is, the atomic-scattering factor (\hat{f}), which is attributed to the asphericity of the atomic electron density [9]. This anisotropy is so small in the x-ray region that in conventional x-ray diffraction theories \hat{f} is treated as a scalar. Near E_A , however, the ATS

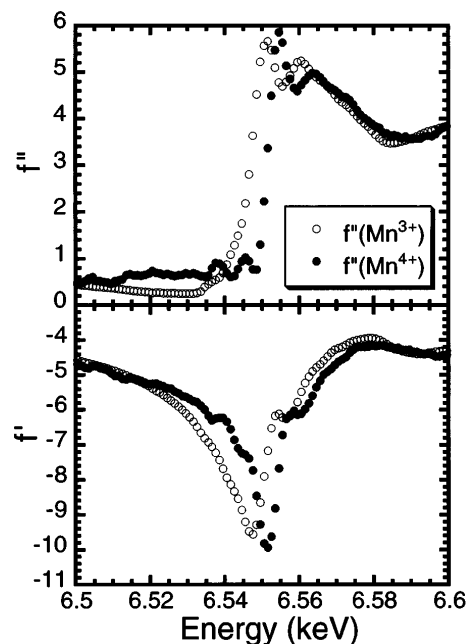


FIG. 3. Energy dependence of the anomalous scattering factor f' and f'' of Mn^{3+} and Mn^{4+} .

reflections become measurable, since the effect of the anisotropy is dramatically enhanced at resonance [10]. Since the \hat{f} of $\text{Mn}^{3+}(1)$ in Fig. 1 is not equivalent to that of $\text{Mn}^{3+}(2)$ due to the anisotropy of the e_g electron wave function in the OO state, an ATS reflection is expected to occur. Figure 4 shows the energy dependence of the integrated intensity of the $(3/4, 3/4, 0)$ reflection, which reflects a superlattice of OO. We successfully observed a striking enhancement of the reflection at $E = 6.552$ keV. It seems likely that this resonant diffraction results from electric dipole transitions, because the resonant energy is about 5 eV higher than the E_A of Mn^{3+} . The dipole transitions would correspond to the $1s$ core levels to the $4p$ band, which is hybridized with the polarized $3d$ band.

In order to confirm that this reflection is indeed an ATS reflection arising from the OO, we measured the angular dependence around the scattering vector (azimuthal scan) of this reflection. For a normal charge reflection, the intensity is independent on the azimuthal angle, but an ATS reflection shows a characteristic oscillation. The atomic-scattering tensors of $\text{Mn}^{3+}(1)$ and $\text{Mn}^{3+}(2)$ take the following form, respectively, assuming the $(y^2 - z^2)$ - and $(z^2 - x^2)$ -type orbital based on the xyz coordinates shown in Fig. 1:

$$\hat{f}_1 = \begin{pmatrix} f_{\parallel} & 0 & 0 \\ 0 & f_{\perp} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix}, \quad \hat{f}_2 = \begin{pmatrix} f_{\perp} & 0 & 0 \\ 0 & f_{\parallel} & 0 \\ 0 & 0 & f_{\perp} \end{pmatrix}. \quad (3)$$

Thus, the crystal-structure factor is also calculated as a tensor. Taking into account the transformation introduced by the azimuthal scan, we calculated the azimuthal angle dependence of the OO superlattice intensity;

$$I(\theta, \varphi) \propto (f_{\parallel} - f_{\perp})^2 \cos^2 \theta \sin^2 \varphi, \quad (4)$$

in the configuration shown in the inset of Fig. 5, where θ is the Bragg angle of the OO superlattice and φ the azi-

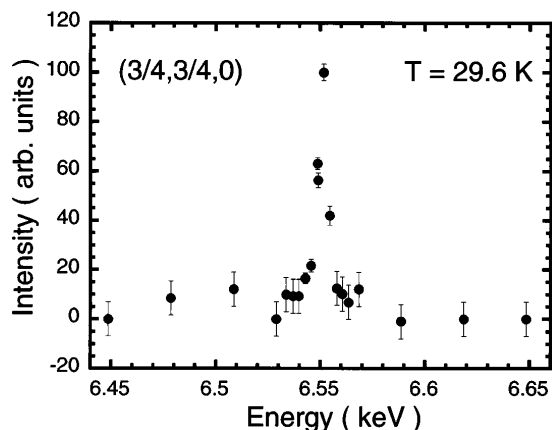


FIG. 4. Energy dependence of the orbital-ordering superlattice reflection $(3/4, 3/4, 0)$ near the manganese K -absorption edge at $T = 29.6$ K.

muthal angle. The detailed procedure of the calculation is the same as described in Ref. [11]. The calculation indicates that the intensity has a 180° period in the azimuthal angle and that the polarization is rotated in the scattering process ($\sigma_0 \rightarrow \pi$; see the inset of Fig. 5). In Fig. 5, we show the experimentally obtained azimuthal-angle dependence of the superlattice intensity of $(5/4, 5/4, 0)$ reflection normalized by the fundamental reflection $(1, 1, 0)$. The azimuthal angle $\varphi = 0^\circ$ corresponds to the configuration in which the sum of the wave vectors of the incident and diffracted beams ($k_0 + k$) is parallel to the a axis. The solid curve was calculated by Eq. (4), which fit well the experimental data with only a scaling factor for the intensity axis. This is the first firm evidence of OO in this system. At this stage, however, we could not uniquely determine the OO pattern because we can deduce the same calculated results assuming the $(3y^2 - r^2)$ - and $(3x^2 - r^2)$ -type orbital instead of the $(y^2 - z^2)$ - and $(z^2 - x^2)$ -type orbital for $\text{Mn}^{3+}(1)$ and $\text{Mn}^{3+}(2)$ in Fig. 1, respectively. In order to determine the orbital uniquely, we may need the careful measurements of the other orbital superlattice.

Figure 6 shows the temperature dependence of the normalized intensity of superlattices $(1/2, 1/2, 0)$ and $(5/4, 5/4, 0)$ at $E = 6.552$ keV, $\varphi = 110^\circ$, which represent the order parameters of CO and OO, respectively. Thus, the CO and OO occur concomitantly (and perhaps cooperatively) at a higher critical temperature ($T \approx 210$ K) than that of spin ordering ($T \approx 110$ K) [6]. This result indicates that the spin ordering configuration is ruled by the OO configuration. Earlier electron diffraction studies by Moritomo *et al.* reported evidence of $(1/4, 1/4, 0)$ and $(3/4, 3/4, 0)$ structural scattering at $T = 110$ K [4]. Bao *et al.* also observed these reflections

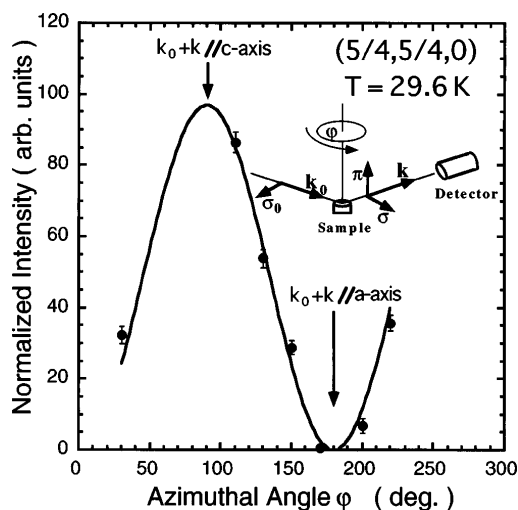


FIG. 5. Azimuthal-angle dependence of the intensity of the OO superlattice reflection $(5/4, 5/4, 0)$ normalized by the fundamental reflection $(1, 1, 0)$ at $E = 6.552$ keV, $T = 29.6$ K. The solid curve is the calculated intensity of Eq. (4). Inset: Schematic view of the experimental configuration and definition of the polarization directions.

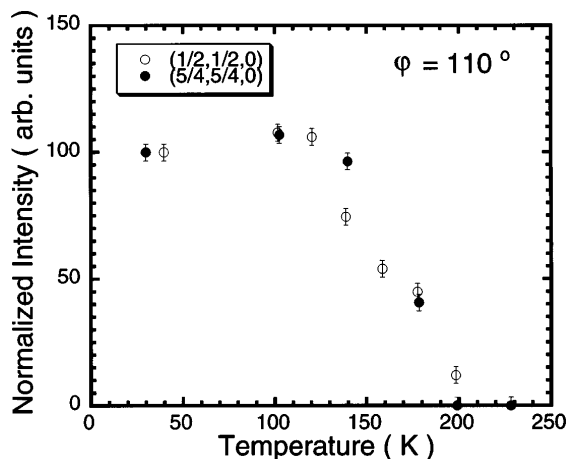


FIG. 6. Temperature dependence of the normalized intensity of the charge-ordering superlattice $(1/2, 1/2, 0)$ and the orbital-ordering superlattice $(5/4, 5/4, 0)$ at $E = 6.552$ keV, the azimuthal angle $\varphi = 110^\circ$.

below $T \approx 250$ K [5]. Their observed reflections may be attributed to the OO.

In conclusion, we have presented direct evidence for the CO and OO in a layered perovskite manganite $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ by using novel synchrotron x-ray diffraction techniques. In this system, the orbital degree of freedom of e_g electrons on Mn^{3+} plays an important role in the CO and spin ordering transitions and their configurations.

The authors thank Y. Endoh, J.P. Hill, D. Gibbs, and M. Blume for fruitful discussions. This work was supported by a Grant-In-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan, and by the New Energy and Industrial Technology Development Organization (NEDO).

[1] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, *Physica (Amsterdam)* **155B**, 362 (1989);

- K. Chabara, T. Ohno, M. Kasai, and Y. Kozono, *Appl. Phys. Lett.* **63**, 1990 (1993); R. von Helmolt, J. Wocker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993); S. Jin, T.H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L.H. Chen, *Science* **264**, 413 (1994); Y. Tokura, A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and N. Furukawa, *J. Phys. Soc. Jpn.* **63**, 3931 (1994); A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, *Phys. Rev. B* **51**, 11 103 (1995); Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *J. Phys. Soc. Jpn.* **64**, 3626 (1995).
- [2] A. Asamitsu, Y. Moritomo, Y. Tomioka, T. Arima, and Y. Tokura, *Nature (London)* **373**, 407 (1995).
- [3] C.H. Chen, S-W. Cheong, and A.S. Cooper, *Phys. Rev. Lett.* **71**, 2461 (1993); S-W. Cheong, H.Y. Hwang, C.H. Chen, B. Batlogg, L.W. Rupp, Jr., and S.A. Carter, *Phys. Rev. B* **49**, 7088 (1994); Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, *Phys. Rev. Lett.* **74**, 5108 (1995); Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, *Phys. Rev. B* **53**, 1689 (1996); H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, *Science* **270**, 961 (1995).
- [4] Y. Moritomo, Y. Tomioka, A. Asamitsu, Y. Tokura, and Y. Matsui, *Phys. Rev. B* **51**, 3297 (1995).
- [5] Wei Bao, C.H. Chen, S.A. Carter, and S-W. Cheong, *Solid State Commun.* **98**, 55 (1996).
- [6] B.J. Sternlieb, J.P. Hill, U.C. Wildgruber, G.M. Luke, B. Nachumi, Y. Moritomo, and Y. Tokura, *Phys. Rev. Lett.* **76**, 2169 (1996).
- [7] D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53**, 1891 (1970); *Acta Crystallogr. A* **37**, 267 (1981); S. Sasaki, *KEK Rep.* **88-14**, 1 (1989).
- [8] J.B. Goodenough, *Phys. Rev.* **100**, 564 (1955).
- [9] V.E. Dmitrienko, *Acta Crystallogr. A* **39**, 29 (1983).
- [10] D.H. Templeton and L.K. Templeton, *Acta Crystallogr. A* **41**, 133 (1985); **41**, 365 (1985); **42**, 478 (1986).
- [11] T. Nagano, J. Kokubun, I. Yazawa, T. Kurasawa, M. Kuribayashi, E. Tsuji, K. Ishida, S. Sasaki, T. Mori, S. Kishimoto, and Y. Murakami, *J. Phys. Soc. Jpn.* **65**, 3060 (1996).