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Orbital order induced ferromagnetic insulating properties

J Geck¹, P Wochner², S Kiele^{1,3}, R Klingeler¹, A Revcolevschi⁴,
M v Zimmermann³, B Büchner¹ and P Reutler⁴

¹ Leibniz Institute for Solid State and Materials Research Dresden at the IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany

² Max-Planck-Institut für Metallforschung, Heisenberg Str. 3, 70569 Stuttgart, Germany

³ Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22603 Hamburg, Germany

⁴ Laboratoire de Physico-Chimie de l'Etat Solide, Université de Paris-Sud, 91405 Orsay Cedex, France

E-mail: j.geck@ifw-dresden.de

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Abstract. At temperatures below the metal–insulator transition of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $0.1 < x < 0.15$, a peculiar ferromagnetic and insulating phase is observed which has been intensively discussed over the last few years. We present a detailed investigation of this phase by means of resonant and high energy x-ray scattering along with measurements of the electrical resistivity, thermal expansion, magnetization, and specific heat. Interestingly, the data show that the metal–insulator transition of lightly doped manganites is accompanied by an orbital rearrangement. The microscopic information provided by the x-ray scattering studies together with the analysis of the macroscopic properties implies that the orbital reordering maximizes the gain of double exchange energy and, at the same time, induces an insulating behaviour. The relevance of the double-exchange mechanism for the stabilization of the ferromagnetic insulating phase is further substantiated by studies of $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$: with increasing praseodymium content, the metal–insulator transition is dramatically suppressed which can naturally be explained by a reduction of the band width upon praseodymium doping.

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1. Introduction

The itinerant magnetism of simple metals can qualitatively be understood in terms of independent electron models, which predict a tendency of metallic systems towards ferromagnetic spin correlations. This result agrees well with the experimental observation that most ferromagnetic materials display metallic properties. However, in some rare cases nature confronts us with a puzzling coexistence of ferromagnetic and insulating properties, which cannot be reconciled by any independent electron picture, pointing to the relevance of strong electron correlations. These correlations are particularly pronounced in doped manganites, leading to a variety of intriguing phenomena like the Colossal Magnetoresistance (CMR), charge order, and orbital order [1]–[4]. In particular, the lightly doped perovskite manganites $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x \sim 1/8$, which will be at the focus of the present paper, represent one specific example of materials where a ferromagnetic insulating phase is observed.

In the following, the physics of these compounds will be briefly reviewed, starting with the lattice structure which is illustrated in figure 1. The observed lattice structures of $\text{A}_{1-x}\text{B}_x\text{MnO}_3$ (where A represents the trivalent cation and B the divalent cation) can be deduced from the aristotype cubic perovskite structure, displayed in the left part of the figure. The (A,B)-cation site is surrounded by eight corner sharing MnO_6 -octahedra which build up a three-dimensional network. However, due to a misfit of the mean (A,B)- and Mn-site radii, this ideal structure is not observed in nature. Instead, distortions and tilts of the MnO_6 -octahedra lead to rhombohedral, orthorhombic, monoclinic and even triclinic modifications of the cubic perovskite [6]–[8]. In the right part of figure 1, the orthorhombic modification observed for LaMnO_3 is shown, where a pronounced octahedral tilting occurs.

The octahedra in LaMnO_3 are not only tilted, but also Jahn–Teller distorted: referring to formal valences, LaMnO_3 contains only Jahn–Teller active Mn^{3+} -ions with a $3d^4$ -configuration. Since the MnO_6 -octahedra are connected to each other, it is intuitively clear that cooperative distortions can occur. This is illustrated in figure 2, where a cooperative ordering of Q_2 -distorted octahedra is shown [9]. As the long axis of a distorted octahedron points to the short axes of its neighbours, this antiferro-distortive ordering reduces the elastic energy of the crystal. In

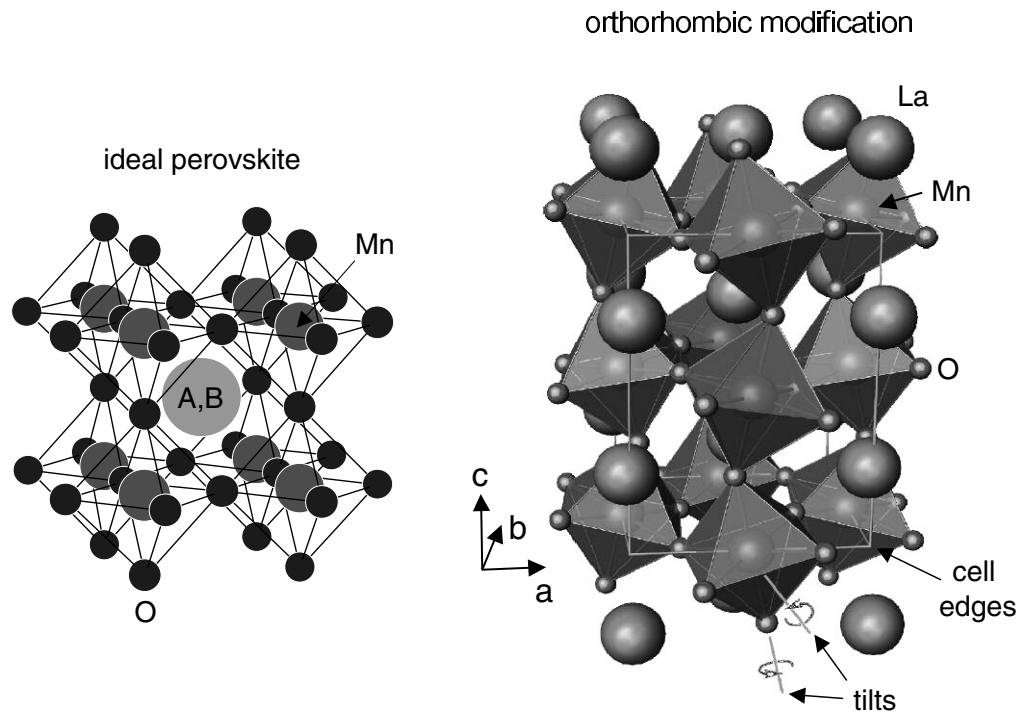


Figure 1. Left: ideal cubic perovskite structure. Right: lattice structure in the orthorhombic phase of LaMnO₃, where a pronounced tilting of the MnO₆-octahedra occurs [5]. Cell edges and lattice directions corresponding to the Pbnm-setting are also indicated.

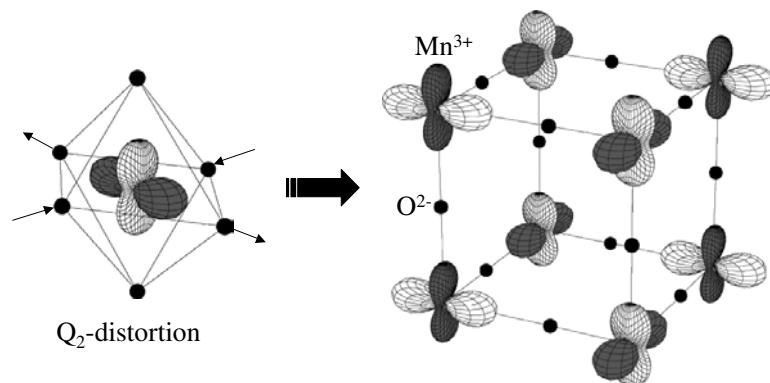


Figure 2. Left: Q_2 -distorted MnO₆-octahedron. Right: three-dimensional network of cooperatively Jahn–Teller distorted MnO₆-octahedra, which is connected to an antiferro-orbital ordering.

other words, elastic interactions significantly contribute to the stabilization of the cooperative Jahn–Teller distorted phase of LaMnO₃.

The cooperative Jahn–Teller distortions correspond to an orbital ordering, which in turn determines the magnetic superexchange interactions between neighbouring manganese sites. The dependence of the superexchange interaction on the orbital occupation is summarized

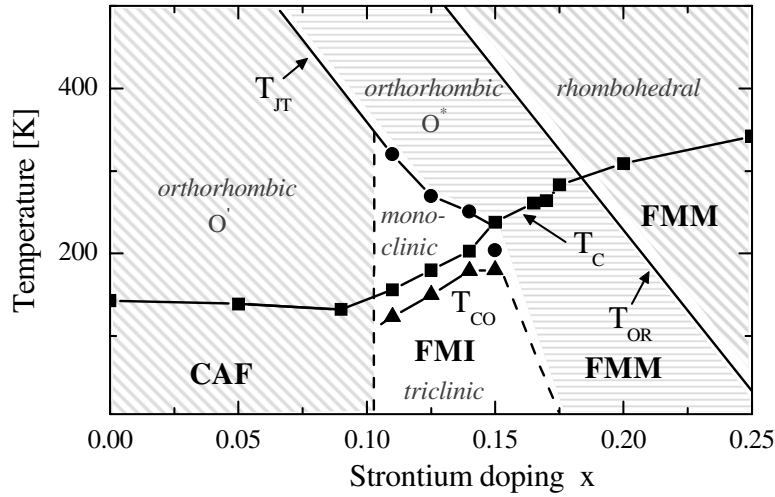


Figure 3. Phase diagram of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [15, 16]. CAF, FMI and FMM indicate the canted antiferromagnetic (insulating), the ferromagnetic insulating and the ferromagnetic metallic phase, respectively. O' and O^* denote orthorhombic modifications [14, 17]. At T_{JT} , T_{OR} , and T_{CO} structural phase transitions occur. T_C indicates the magnetic-ordering temperature.

by the so-called Goodenough–Kanamori–Anderson (GKA) rules [10, 11]. In the specific case illustrated in figure 2, two GKA rules are relevant: firstly, the 180° -superexchange between an empty and a half-occupied orbital gives rise to a ferromagnetic nearest-neighbour interaction within the ab -plane. Second, the 180° -superexchange between two half-filled orbitals along the c -direction is antiferromagnetic. It follows that the orbital order shown in figure 2 is connected to the A-type antiferromagnetic ordering, consisting of ferromagnetic ab -planes which are antiferromagnetically aligned along the c -axis. In fact, below $T_{JT} \simeq 780$ K a cooperative Jahn–Teller distorted phase similar to that shown in figure 2, as well as the A-type antiferromagnetic order below $T_N \simeq 140$ K are experimentally observed for LaMnO_3 [12]–[14]. Note that, although the antiferro-orbital ordering in LaMnO_3 is well established, the e_g -states $|3d_i\rangle = \alpha_i|3z^2 - r^2\rangle + \beta_i|x^2 - y^2\rangle$ occupied at a site i have not been determined unambiguously so far. Therefore, the orbital ordering shown in figure 2 represents only an illustrative example.

Referring to the ionic picture, the substitution of trivalent lanthanum by divalent strontium in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ introduces Jahn–Teller inactive Mn^{4+} -ions. Therefore, the movement of a hole turns a Jahn–Teller active site into a Jahn–Teller inactive site, implying that the holes are always dressed with lattice distortions. In addition to this, the presence of doped holes gives rise to ferromagnetic interactions due to the double exchange (DE) mechanism [18]. According to this model, the e_g -hopping amplitude is given by $t = t_0 \cos(\vartheta/2)$, where ϑ denotes the angle between two neighbouring t_{2g} -spins [19]. This means that the holes are completely localized, if the neighbouring spins are antiparallel, while they are delocalized in the ferromagnetic case. This implies that the doped holes in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ introduce ferromagnetic interactions, since ferromagnetic spin alignment reduces the kinetic energy of the charge carriers. Indeed, this prediction of the DE model corresponds to the general trend, as can be observed in figure 3: there are antiferromagnetic insulating phases at low x and ferromagnetic metallic phases at

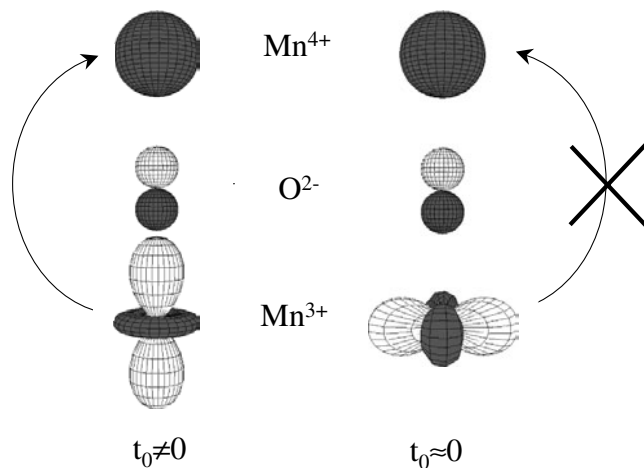


Figure 4. In the case of adjacent Mn³⁺ and Mn⁴⁺ sites along the c -axis the σ -overlap between the oxygen 2p and the manganese 3d states vanishes, if the $3d_{x^2-y^2}$ orbital is occupied (right); i.e. $t_0 \simeq 0$. If the $3d_{3z^2-r^2}$ orbital is occupied there is a non-vanishing overlap of the O2p and Mn3d states leading to $t_0 \neq 0$ (left).

higher x . However, this evolution is far from gradual. In particular, around the commensurate doping $x = 1/8$, the phase diagram in figure 3 becomes rather complex and, moreover, a ferromagnetic insulating ground state is observed, which conflicts the bare DE model described above. In addition to this, the lattice properties display a complex behaviour around $x = 1/8$. As described above, the lattice symmetry strongly depends on correlated octahedral tilts and distortions. Since the latter are directly connected to the orbital occupation (figure 2), the changes of the lattice symmetry provide a first hint for the relevance of orbital ordering phenomena at the respective phase transitions. But not only do the structural properties couple to the orbital degree of freedom, the orbital occupation also influences the hopping processes between neighbouring manganese sites, because the hopping integral t_0 depends on the orbital occupation (see figure 4). Therefore, the orbital degree of freedom can lead to localization of charge carriers as well, suggesting that the orbitals might play a crucial role for the FMI phase of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$.

Based on experimental as well as theoretical studies, quite a number of publications argue that charge and orbital ordering take place in this FMI phase but, to date, there is no consensus about the microscopic ordering pattern [20]–[26]. Quite a large variety of microscopic models for the FMI phase of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ has been proposed in the literature, and some of them are given in figure 5. In order to clarify the role of the orbital degree of freedom for the FMI phase of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$, we performed a resonant x-ray scattering (RXS) study at the Mn K-edge. Our RXS results, which will be presented in this paper, reveal an orbital rearrangement at the metal–insulator transition. Moreover, the analysis of the macroscopic properties implies that the DE mechanism is essential for the stabilization of the FMI phase, despite the fact that the system is macroscopically insulating. This conclusion is further supported by our studies of $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ which will also be presented in this paper.

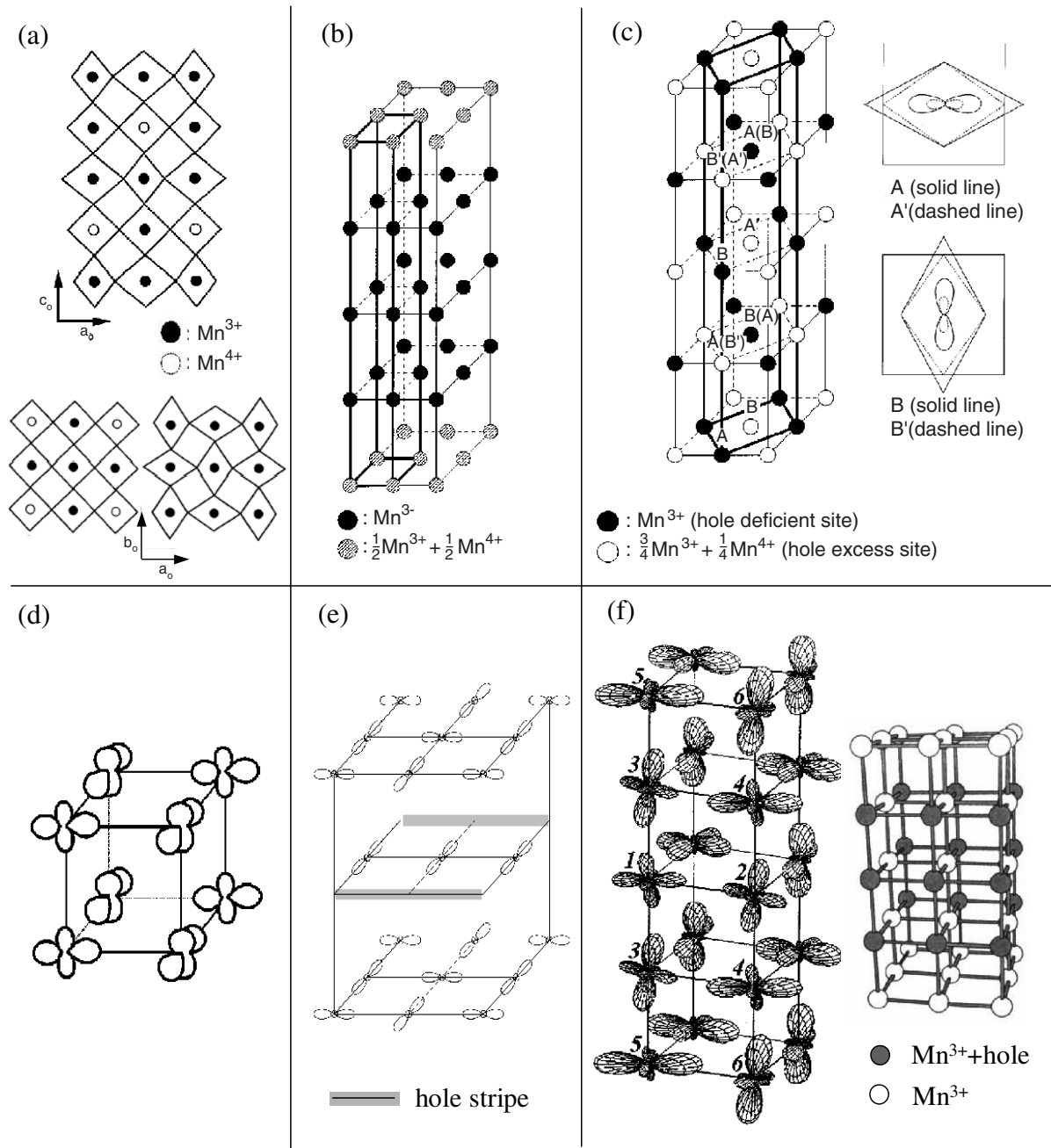


Figure 5. Proposed models for the FMI-phase of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$: (a) charge and polaron ordering. Undoped MnO_2 -planes alternate with quarter doped planes [20]. (b) Segregation into half doped and undoped planes [21]. (c) Checkerboard-like charge ordering accompanied by static orbital waves along the c -axis [22]. (d) Orbital ordering without charge order [23]. (e) MnO_2 -planes containing hole stripes alternate with undoped planes [24]. (f) Long-range orbital-ordered phase with three-line hole stripes. Hole rich planes are separated by undoped planes [25].

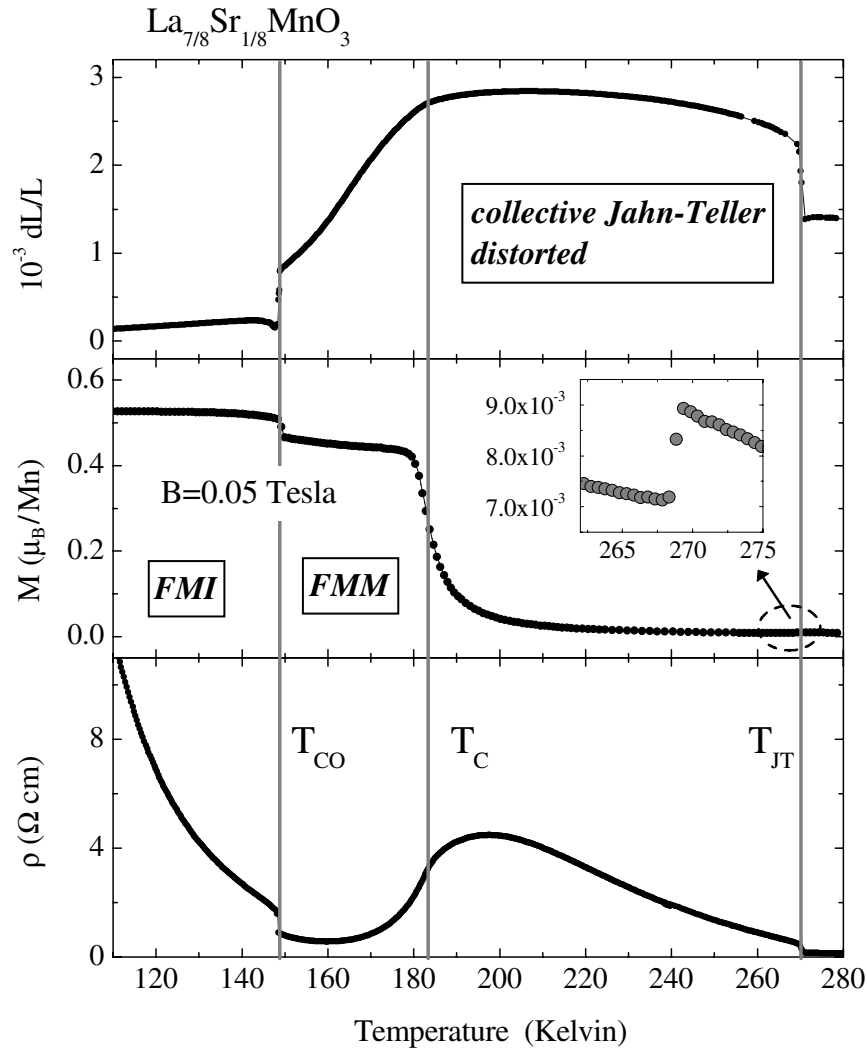


Figure 6. Comparison between the temperature dependencies of the relative changes of the macroscopic sample length dL/L (top), the magnetization (middle) and the electrical resistivity (bottom) of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$. Further explanations are given in the text.

2. Macroscopic measurements on $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$

In order to discuss the different phase transitions, which can be observed in $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ in the temperature range between 4.2 and 300 K, the relative changes of the macroscopic sample length dL/L , the magnetization M , and the electrical resistivity ρ of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ are compared in figure 6. Three successive phase transitions at $T_{JT} \simeq 270$ K, $T_C \simeq 183$ K and $T_{CO} \simeq 150$ K are clearly visible in all three quantities: upon cooling, a discontinuous phase transition into the cooperative Jahn–Teller distorted phase takes place at T_{JT} [14, 17, 27], as signalled by the pronounced anomaly in dL/L . The arrangement of the distorted MnO_6 -octahedra in this phase corresponds to the cooperative Jahn–Teller distorted phase of the undoped parent compound (cf section 3). This structural phase transition is also reflected in the temperature dependences

of M and ρ , which show a step-like decrease and increase, respectively. Between T_{JT} and the magnetic ordering temperature T_C the resistivity displays an insulating behaviour [28]. With further decrease in temperature, the onset of ferromagnetic order at T_C is signalled by the increase of M . The ferromagnetic spin alignment is connected to the change from an insulating to a metallic characteristic of ρ upon cooling, in agreement with the DE picture. Therefore, this phase is called ferromagnetic metallic (FMM), although the resistivity is still three orders of magnitude larger than that of a typical metal. The enhanced charge carrier mobility in the FMM-phase correlates with a continuous reduction of the cooperative Jahn–Teller distortions, which is indicated by the reduction of dL/L below T_C . Finally, the jump-like decrease of dL/L at T_{CO} reflects the vanishing of the cooperative Jahn–Teller distortions. Moreover, both the magnetization and the resistivity display an abrupt increase at this phase transition; i.e. a ferromagnetic insulating phase is observed. This FMI phase will be the main focus of the following sections.

3. Orbital rearrangement in $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$

The resonant x-ray scattering (RXS) technique is well suited for the investigation of orbital order phenomena in doped manganites. Nonetheless, it is important to note that RXS at the Mn K-edge provides only an indirect probe for the ordering of the relevant e_g -states. More specifically, the RXS at the Mn K-edge involves a $1s \rightarrow 4p$ transition; i.e. RXS at this energy does not probe the 3d states but the 4p states. Recent band structure calculations show, however, that the 4p states are strongly influenced by distortions of the MnO_6 -octahedra [29]–[31]. Since these distortions correspond to the occupation of a specific e_g -orbital, the resonant scattering at the Mn K-edge reflects the orbital occupation at a manganese site. Within the dipole–dipole approximation, the virtual $1s \rightarrow 4p_{x,y,z}$ transitions lead to a polarization dependence of the resonant scattering process which can be described by an atomic scattering tensor f_{Mn} . Taking the specific example of the undoped parent compound LaMnO_3 (cf figure 2), the orbital ordering in the cooperative Jahn–Teller distorted phase causes two manganese sites with different anisotropic atomic scattering tensors $f_{\text{Mn}}^{1,2}$ [12]. This leads to the occurrence of symmetry forbidden reflections at the Mn K-edge which display distinct polarization-dependent features.

More specifically, undoped LaMnO_3 has Pbnm-symmetry which implies that the (300) reflection is forbidden [13]. However, in the cooperative Jahn–Teller distorted phase of LaMnO_3 the symmetry forbidden (300) reflection can be observed at the Mn K-edge [12]. Moreover, if the polarization of the incoming beam is perpendicular to the scattering plane (σ -polarization), the scattered beam of the (300) reflection is polarized parallel to the scattering plane (π -polarization). In the following, this rotation of the beam polarization will be referred to as $\sigma\pi$ scattering. Accordingly, the term $\sigma\sigma$ scattering refers to scattering processes without a rotation of the incident polarization. The polarization dependence of the resonant scattering at the (300) position implies a variation of the intensity upon rotating the sample around the scattering vector. In the case of the cooperative Jahn–Teller distorted phase of LaMnO_3 , the intensity of the (300) reflection is found to vary as $I \propto \sin^2 \psi$, where ψ is the rotation angle [12]. This variation of the resonant intensity will be called azimuthal dependence hereafter.

Next, we describe the RXS results obtained from a (100)-oriented $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ single crystal. It is important to note that the perovskite manganite single crystals are twinned in general. In the case of this particular sample, however, only twins with interchanged a - and b -axis exist [32]. As a result, only the (300) and the (030) reflection are superimposed at

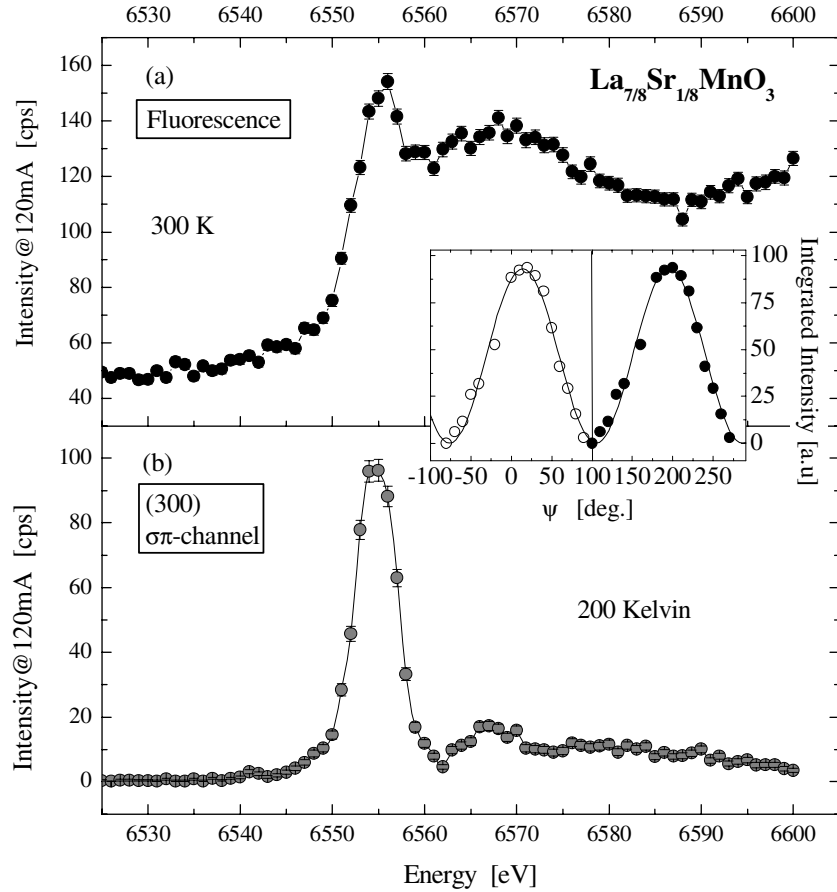


Figure 7. Measurements on the (100)-oriented $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ sample. (a) Fluorescence measurement taken at room temperature. (b) Energy dependence of the (300) reflection at 200 K in the $\sigma\pi$ channel. The polarization analysis has been performed using the (220) reflection of copper, yielding a cross-talk between $\sigma\sigma$ and $\sigma\pi$ channels of 3%. The solid lines in (a) and (b) are guides to the eyes. The azimuthal dependence of the (300) reflection also taken at 200 K is given in the inset. Here, the solid line represents a fit to a $\sin^2 \psi$ behaviour.

the nominal (300) position, which substantially simplifies the analysis of the obtained RXS data. In figure 7, a fluorescence measurement at room temperature, the energy dependence of the symmetry forbidden (300)/(030) reflection at 200 K in the $\sigma\pi$ -channel and the azimuthal dependence of the resonant intensity at 200 K are shown. A comparison of the fluorescence measurement given in figure 7(a) and the energy dependence displayed in figure 7(b) shows that a strong intensity increase at the Mn K-edge takes place. Furthermore, the intensity of the (300)/(030) reflection displays a pronounced azimuthal dependence which can be well described by a $\sin^2 \psi$ behaviour. Note that the data points represented by closed circles have been obtained from the measured data (open symbols) by a translation along the ψ -axis by about 180° . Within the experimental errors, the polarization analysis, which has been carried out using the (220) reflection of Cu, revealed pure $\sigma\pi$ -scattering at the nominal (300) position. These polarization-dependent features, namely the $\sigma\pi$ -scattering and the $\sin^2$ -azimuthal dependence, agree with

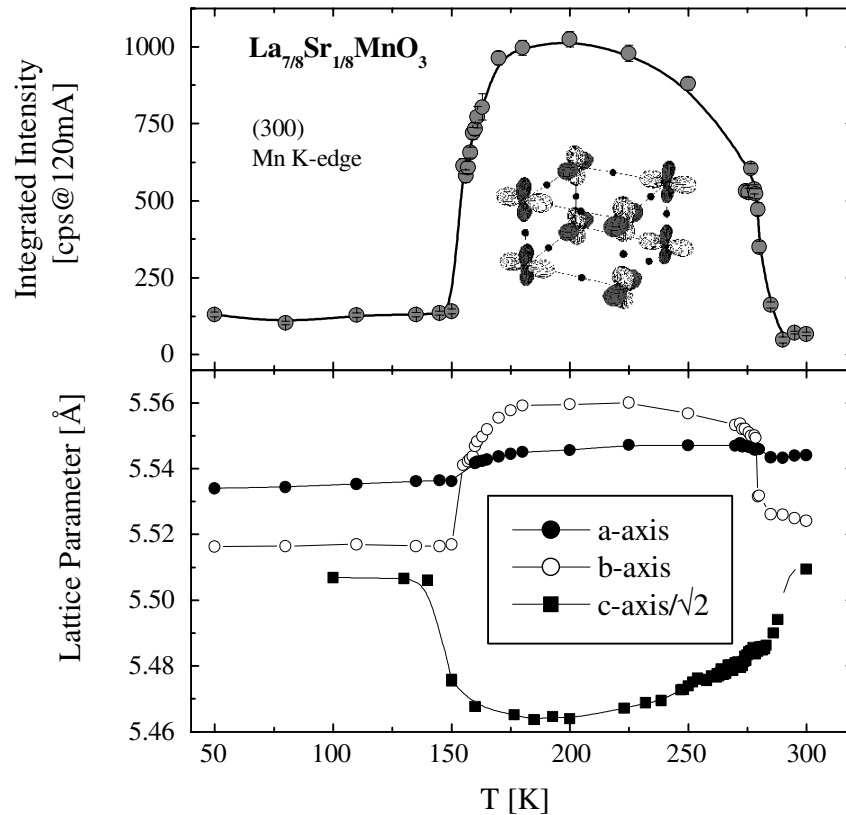


Figure 8. Top: temperature dependence of the integrated intensity of the (300) reflection at 6555 eV for $\psi = 0^\circ$. The integrated intensity has been calculated by integrating over radial, rocking and χ -scans. Bottom: temperature dependence of the lattice parameters (Pbnm-setting). The a and b parameters have been measured using the (100)-oriented sample. The c -parameter has been measured using the (001)-oriented sample.

the above-mentioned RXS results for the orbital-ordered phase of LaMnO_3 [12]. Moreover, the above observations can be reproduced by a model calculation based on this type of orbital order and on the energy splitting of atomic 4p-states [12, 32]. It can therefore be concluded that a cooperative Jahn–Teller distorted phase exists in $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ at 200 K, which is similar to that in the undoped parent compound LaMnO_3 .

The temperature dependence of the (300)/(030) reflection and of the lattice parameters is given in figure 8. It is evident that the integrated intensity I_{300} at the (300) position strongly increases in the cooperative Jahn–Teller distorted phase between T_{CO} and T_{JT} [14], which is also signalled by pronounced anomalies of the lattice parameters. We mention that the anomalies observed in the lattice parameters are due to cooperative Jahn–Teller distortions in the presence of octahedral tilts [33, 32]. For example, no anomaly of the lattice parameters is expected to occur for the ideal antiferro-distortive ordering shown in figure 2. Below T_{JT} , the cooperative Jahn–Teller distortions increase, reaching a maximum at T_{C} . With the onset of ferromagnetic order and enhanced charge carrier mobility below T_{C} , the cooperative Jahn–Teller distortions are gradually reduced and disappear abruptly at T_{CO} . It is evident from the temperature dependences shown in figure 8 that I_{300} and the anomalies in the lattice constants are directly connected;

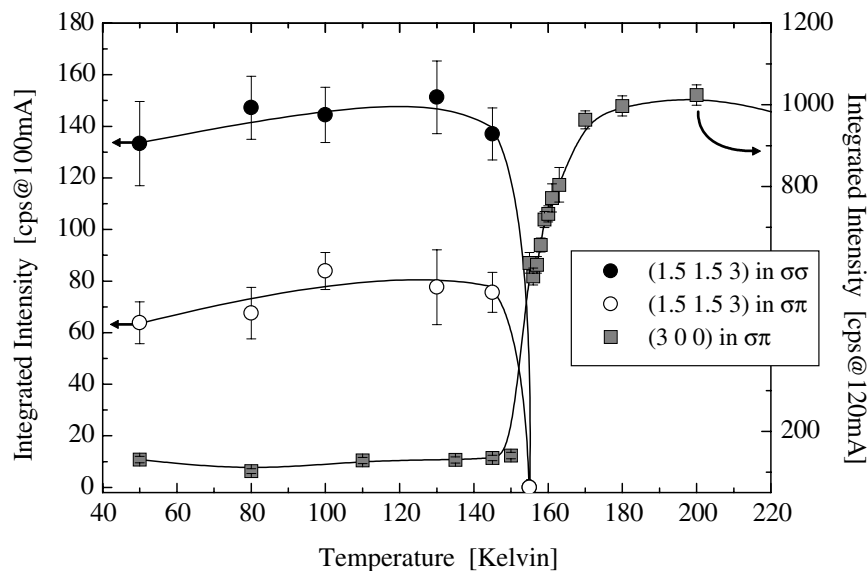


Figure 9. Temperature dependence of the integrated intensity of the (1.5 1.5 3) reflection in the $\sigma\sigma$ and the $\sigma\pi$ channel (open and filled circles). The polarization analysis of this measurement has been performed using the (002) reflection of graphite, yielding a cross-talk of 15%. For the corrected data $I_{\sigma\sigma}/I_{\sigma\pi} \simeq 2.25$ is obtained. The integrated intensity of the (300) reflection is also shown (grey squares). All intensities have been obtained by integrating over radial, rocking and χ -scans.

i.e. both quantities reflect the same order phenomenon, namely the antiferro-distortive ordering of Jahn–Teller distorted MnO_6 -octahedra between T_{CO} and T_{JT} .

The temperature dependence of the (300)/(030) reflection shown in figure 8 is in glaring contradiction to previously published RXS results of $\text{La}_{0.88}\text{Sr}_{0.12}\text{MnO}_3$ [23]. In that study, the (030) reflection has been observed only at temperatures below T_{CO} . Between T_{JT} and T_{CO} , where we find the largest intensity at the (300) position, the (030) reflection has not been observed in the previous study reported in [23]. It is important to note that the integrated intensity shown in figure 8 corresponds to the sum of the intensities at the (300) and the (030) positions, because both reflections have been observed around the same position in reciprocal space. Furthermore, our measurements reveal the same temperature dependences for the (300) and the (030) reflections.

This contradiction can be resolved by taking into account the twinning of the perovskite samples: due to the twinning, the (400) and the (224) reflections of different twin domains can occur close to a common position in reciprocal space. Consequently, the (300) position of one twin domain corresponds to the (1.5 1.5 3) position of another domain. Taking into account the reduced twinning of our samples, we were able to prepare a (112)-oriented sample, in order to investigate the resonant scattering at the (1.5 1.5 3) position. In fact, the (1.5 1.5 3) reflection has been observed, in agreement with results of a recent electron diffraction study [34]. In figure 9, the integrated intensities of the (1.5 1.5 3) and the (300)/(030) reflections are compared. Upon cooling, the (300)/(030) reflection collapses at T_{CO} , while the (1.5 1.5 3) reflection appears below the metal–insulator transition in $\sigma\pi$ as well as in the $\sigma\sigma$ channel. The (1.5 1.5 3) reflection also

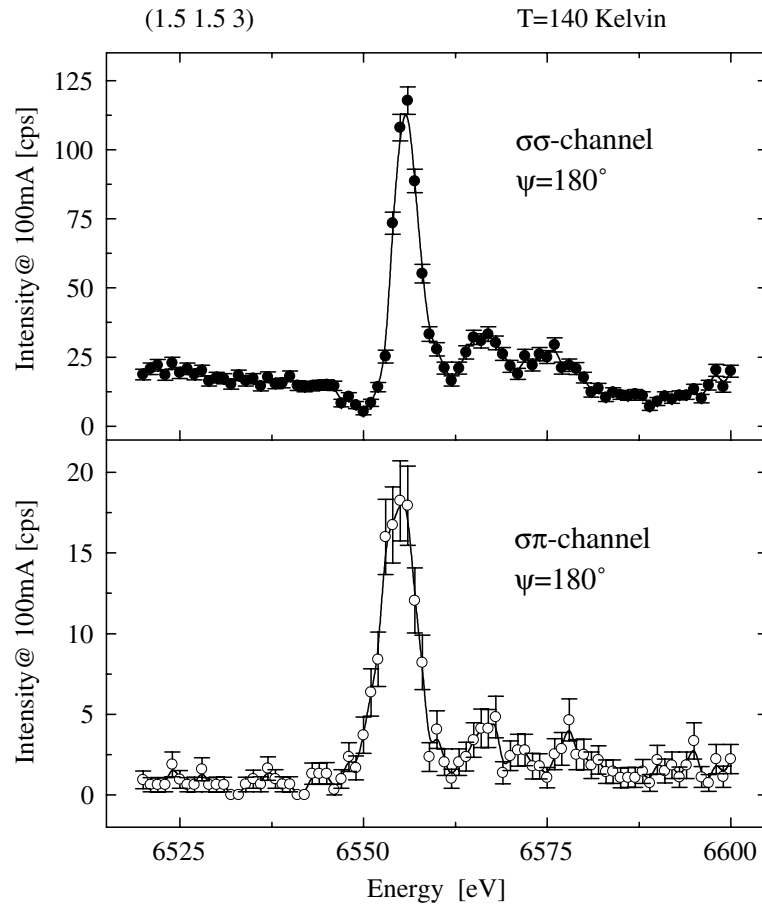


Figure 10. Energy dependence of the (1.5 1.5 3) reflection in the $\sigma\sigma$ and $\sigma\pi$ channels at 140 K. The polarization analysis has been performed using the (220) reflection of copper. Note that maximum intensities are shown which differ from the integrated intensities given in figure 9.

displays a strong azimuthal dependence in both the $\sigma\pi$ and the $\sigma\sigma$ channels, which can be well described by a $\sin^2 \psi$ dependence [32]. The energy dependence of the (1.5 1.5 3) reflection is given in figure 10. In both channels, a strong resonance at 6554 eV and a typical structure at higher energies are observed. Note that there is also a significant non-resonant scattering in the $\sigma\sigma$ channel far below and above the Mn K-edge, which is caused by a static superstructure modulation.

To summarize, the azimuthal dependence, the rotation of the beam polarization, the energy dependence, and the non-resonant scattering observed at the (1.5 1.5 3) position imply the presence of an anisotropic form factor of manganese which is related to a structural modulation. Since the orbital order parameter couples to both the anisotropic form factor and the structure, we conclude that the occurrence of the (1.5 1.5 3) reflection at the Mn K-edge signals a new type of orbital order in the FMI-phase. In other words, the collapse of the (300)/(030) reflection and the appearance of the (1.5 1.5 3) reflection at T_{CO} reveal an orbital rearrangement at the metal–insulator transition of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$.

4. Orbital order between T_{Co} and T_{C}

In the course of our RXS studies we also investigated the (003) reflection, which is screw-axis forbidden in the orthorhombic Pbnm-symmetry. The investigations have been performed using a (001)-oriented sample with the same reduced twin structure as the (100)-oriented sample. We have observed the (003) reflection in the whole temperature regime under investigation in both the $\sigma\sigma$ and the $\sigma\pi$ channels. In figure 11, the energy dependences observed at the (003) position in the $\sigma\sigma$ and the $\sigma\pi$ channels at different temperatures are compared. Focusing on the $\sigma\sigma$ channel, a strong non-resonant signal is superimposed to a resonant contribution at 200 and 50 K, i.e. below T_{JT} , whereas at 300 K $> T_{\text{JT}}$ only a weak resonant peak is observed. The non-resonant scattering at the (003) position below T_{JT} is in agreement with the observed reduction of the orthorhombic lattice symmetry, which implies that the (003) reflection becomes allowed in this temperature regime [16, 32]. A comparison of the energy dependences for 200 and 50 K reveals that the non-resonant scattering in the $\sigma\sigma$ channel is considerably enhanced at the metal–insulator transition. In the $\sigma\pi$ channel, a clear resonance is observed at the Mn K-edge for all investigated temperatures, although there is a considerable contamination of the signal due to cross-talk effects.

The temperature dependence of the integrated intensity in the $\sigma\sigma$ and the $\sigma\pi$ channels at the Mn K-edge is shown in figure 12. After the $\sigma\pi$ intensity has been corrected for cross-talk effects, the temperature dependence resembles the one observed for the (300) reflection (figure 8). This demonstrates that the anisotropic form factor of Mn, which reflects changes of the cooperative Jahn–Teller distortions, determines the $\sigma\pi$ intensity at the (300) and the (003) positions. The temperature dependence of the integrated $\sigma\sigma$ intensity, which is given in the lower panel of figure 12, starts to increase at T_{C} upon cooling; i.e. the suppression of the cooperative Jahn–Teller effect is accompanied by an additional structural modulation. Taking into account that the change of the kinematic structure factor (only the Thomson term is considered) reads for small displacements $\mathbf{d}_l$

$$\Delta F(\mathbf{Q}) = i\mathbf{Q} \sum_l f_l e^{i\mathbf{Q} \cdot \mathbf{b}_l} \mathbf{d}_l, \quad (1)$$

where the $\mathbf{b}_l$ describe the position of the lattice site in the orthorhombic phase, the observation of the non-resonant $\sigma\sigma$ scattering at the (003) position implies a continuous increase of the $\mathbf{d}_l$ -component parallel to the c direction below T_{C} .

One may argue that the reduction of the (300) reflection and the increase of the non-resonant intensity of the (003) reflection between T_{C} and T_{Co} is related to phase separation. In order to address this point, radial scans at the (400) and (300) positions have been taken without analyser at temperatures between T_{C} and T_{Co} (figure 13). A comparison of the radial scans at 156 K, i.e. 1 K above the metal–insulator transition shows that the FWHM of the (400)/(040) and the (300)/(030) reflections are almost the same. In fact, the FWHM of the (300)/(030) reflection is even smaller than that of the (400)/(040) peak, which can be attributed to the $\mathbf{Q}$ -dependence of the experimental resolution. When the intensity profile consists of two separated peaks, the radial scans in figure 13 are always centred on the reflection at the larger 2Θ -angle. This ensures that the reflections at the nominal (300) and (400) positions belong to the same twin domain. As the FWHM of the (400)/(040) reflection provides a measure of the experimental resolution, the data shown in figure 13 indicate that no pronounced disorder of the cooperative Jahn–Teller

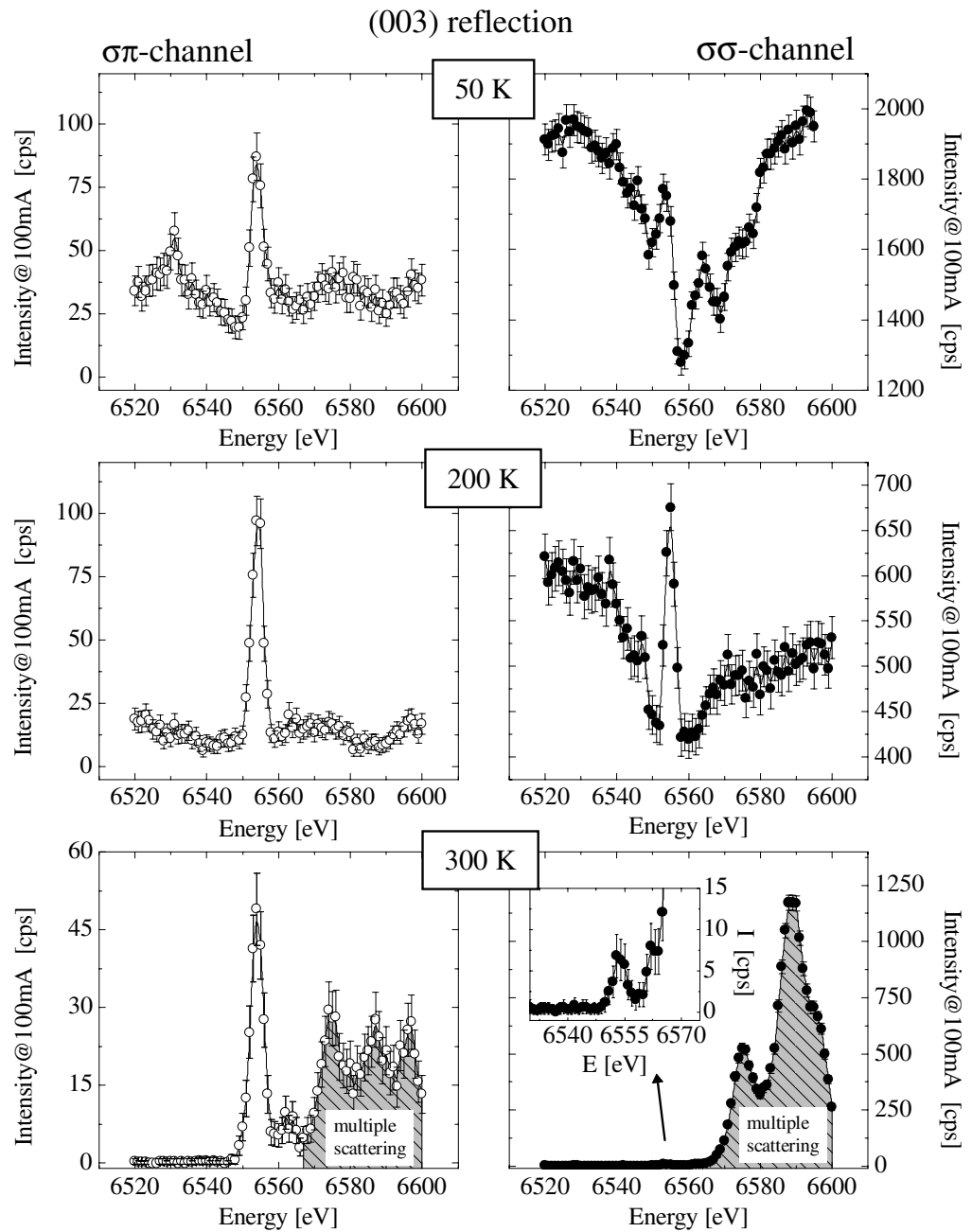


Figure 11. Energy dependence of the (003) reflection in the $\sigma\sigma$ (●) and the $\sigma\pi$ channels (○) at different temperatures. A strong non-resonant signal superimposed to a resonance at the Mn K-edge has been observed in the $\sigma\sigma$ channel below T_{JT} . The intensity in the $\sigma\pi$ channel displays a resonant behaviour (the intensity below and above the Mn K-edge is due to the finite cross-talk). At 300 K, a strong multiple scattering contribution is observed. The polarization analysis has been performed using the (220) reflection of copper (cross-talk: 3%).

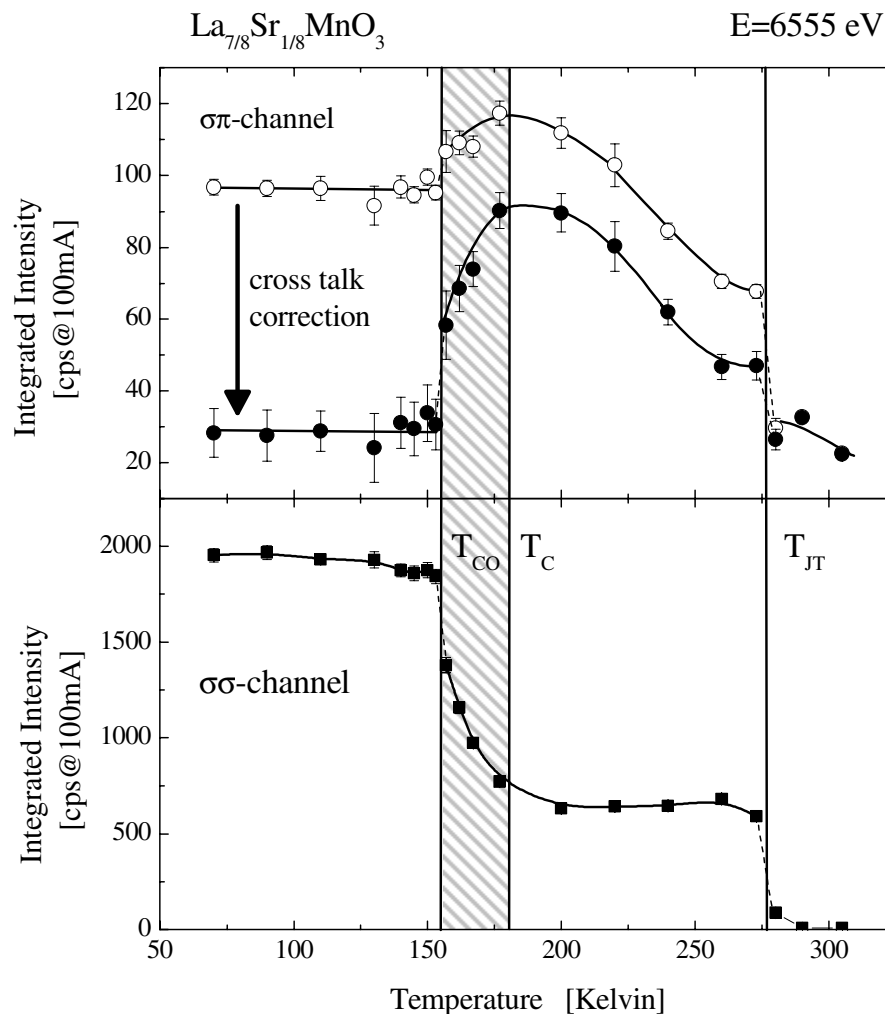


Figure 12. Temperature dependence of the (003) reflection observed in the $\sigma\pi$ (top) and the $\sigma\sigma$ (bottom) channels. The two curves in the upper panel show the results with (●) and without (○) cross-talk correction. The cross-talk correction for the $\sigma\sigma$ scattering can be neglected.

distortions occurs between T_{CO} and T_{C} . A similar conclusion can be drawn by comparing the FWHM of the (004) and the (003) reflections. Consequently, the data described above point to a continuous reduction of the cooperative Jahn–Teller distortions between T_{C} and T_{CO} , which is accompanied by the onset of additional structural distortions parallel to the c -direction. From this data we find no evidence for a spatial inhomogeneity.

5. Thermodynamics of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x \simeq 1/8$

An interesting observation concerns the entropy changes at T_{CO} . In figure 14, the anomalies observed in the specific heat c_p of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.11, 1/8, 0.14$, and 0.15 around T_{C} and T_{CO} are displayed. The thick arrows indicate the jump Δc_m at T_{C} , which is expected for a

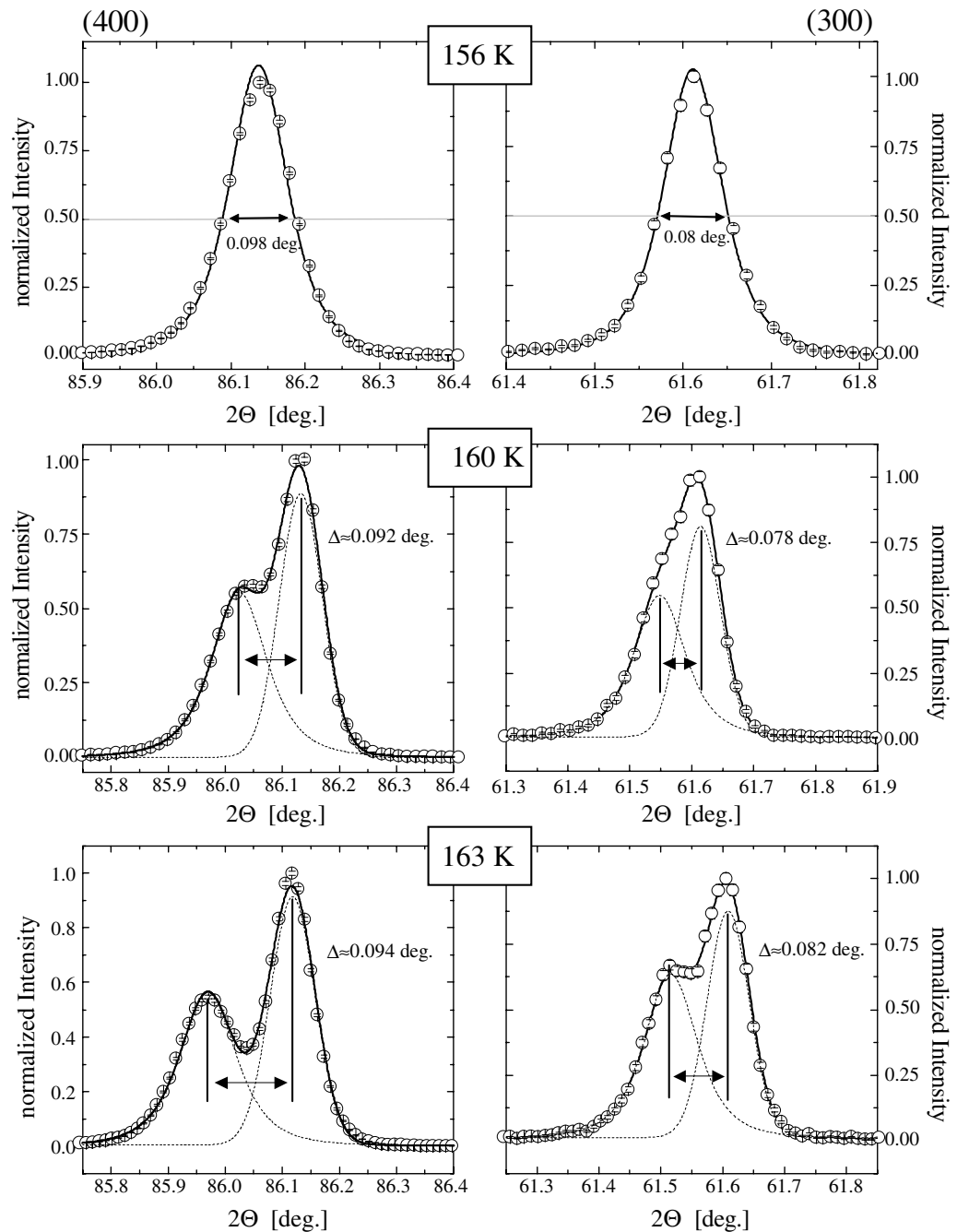


Figure 13. Comparison between the intensity profiles observed in radial scans at the (300) (right) and (400) (left) position taken at different temperatures. The measurements were performed in the temperature regime between T_C and T_{CO} , where the cooperative Jahn–Teller distortions are continuously suppressed upon cooling. The continuous lines are fits to the data, consisting of the two peaks represented by the dotted curves. The Δ -value given in the two lower panels corresponds to FWHM of the stronger (the centred) peak.

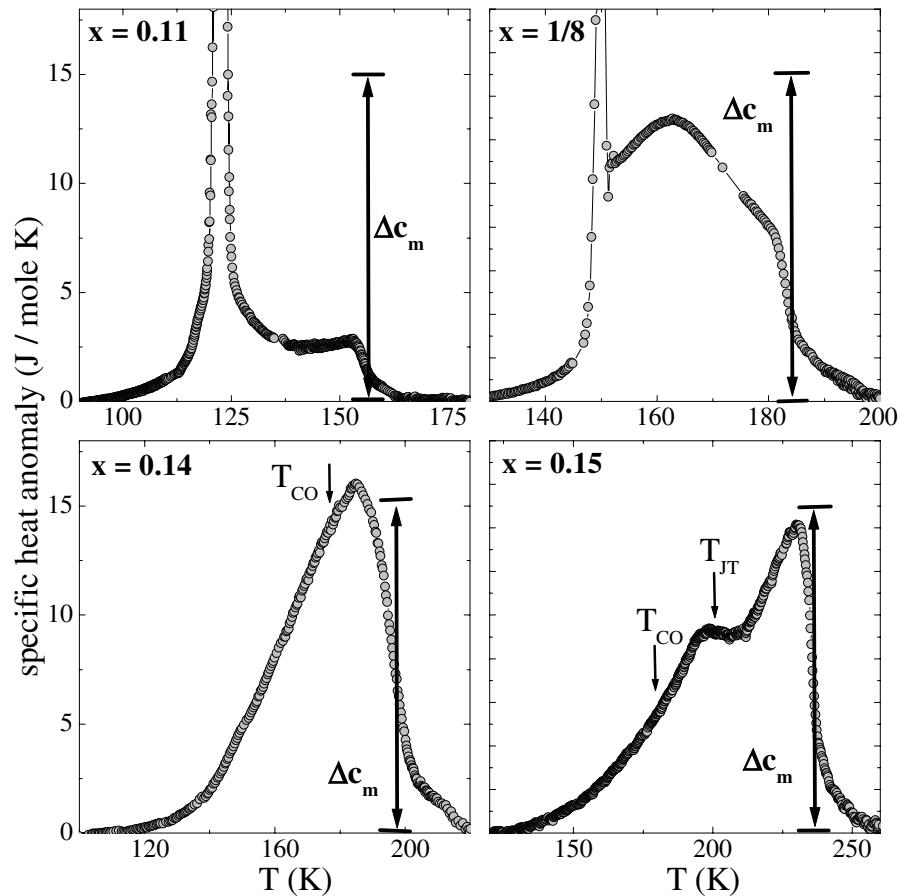


Figure 14. Specific heat anomaly observed in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.11, 1/8, 0.14$ and 0.15 [15]. The arrows at T_C indicate the anomalies Δc_m of the specific heat which are expected for a usual ferromagnetic transition. The transition temperature T_{CO} has been determined by HXS measurements [26].

ferromagnetic ordering transition according to a mean field description of a pure spin system (for details see [15]). The parameters necessary for the calculation of Δc_m have been determined by measurements of the macroscopic magnetization. Focusing on the samples with $x = 0.11$ and $1/8$, it is evident that the anomaly of c_p at the magnetic ordering temperature T_C is considerably smaller than Δc_m . A comparison of the measured c_p -anomalies and the calculated c_m thus reveals a suppressed ferromagnetic order between T_C and T_{CO} . On the other hand, a pronounced anomaly is observed at the metal–insulator transition. In the case of $x = 0.14$ and 0.15 , a large anomaly of c_p is found at T_C , while no anomaly has been observed at T_{CO} within the errors of the experiment. Note that the sample with 15% strontium doping constitutes a particular case, because at this doping level the cooperative Jahn–Teller distorted phase occurs below T_C , i.e. $T_{JT} < T_C$. For $x = 0.14, 0.15$, the observed anomaly in c_p at T_C is in fair agreement with the calculated Δc_m , indicating the onset of long-range ferromagnetic order at T_C .

The comparison given in figure 14 reveals that the specific heat anomaly at T_C increases upon strontium doping until it reaches the magnitude which is expected for the onset of ferromagnetic order. The opposite behaviour is observed at T_{CO} , where the specific-heat anomaly is found to

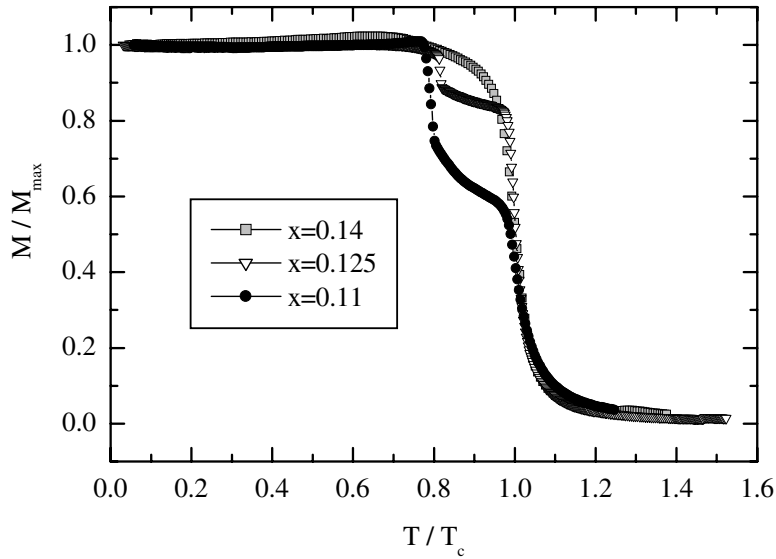


Figure 15. Comparison between the temperature dependences of the macroscopic magnetization for $x = 0.11$, $1/8$ and 0.14 in reduced units for an external field of 0.05 Tesla. M_{max} is the low temperature value at 4.2 K. The temperature has been normalized to the corresponding $T_C = T_C(x)$.

decrease with increasing strontium content. In the case of the 14% strontium doped sample, the analysis of the specific-heat measurement reveals that ΔS^Σ is almost entirely given by magnetic entropy changes ΔS^M alone. Since the total entropy changes $\Delta S^\Sigma(x)$ derived from the data given in figure 14 are almost independent of x , it follows that also $\Delta S^\Sigma(x = 0.11)$ and $\Delta S^\Sigma(x = 1/8)$ are largely dominated by the magnetic degrees of freedom. In particular, the pronounced anomalies of c_p observed at T_{CO} for $x = 0.11$ and 0.125 are, to a large extent, of magnetic origin [15]. This conclusion is further supported by the magnetization data given in figure 15. By comparing the data displayed in figures 14 and 15, it can be observed that the specific heat anomaly at T_{CO} scales with the jump ΔM of the magnetization. This qualitative observation is confirmed by a quantitative analysis of the macroscopic measurements. In particular, the quantitative analysis for $x = 1/8$ shows that the entropy jump at T_{CO} can almost entirely be explained by the magnetization jump at this temperature [15]. To summarize, analysis of the macroscopic measurements unambiguously shows that the entropy changes below T_C are dominated by the magnetic contributions.

The observation $\Delta S^\Sigma \simeq \Delta S^M$ implies that the orbital degrees of freedom do not significantly contribute to the entropy changes in the temperature regime below T_C . This result is consistent with the orbital rearrangement which has been described in the preceding section. More specifically, the orbitals are already ordered in the cooperative Jahn–Teller distorted phase. Therefore, the reordering in the orbital sector at T_{CO} does not lead to pronounced entropy changes, if the disorder during the order–order transformation is small. In fact, the RXS-measurements at the (300) position indicate that no pronounced disorder in the orbital sector develops below T_C upon cooling (cf figure 13); i.e. the thermodynamic properties fairly agree with the results of the RXS study.

Another conclusion which can be drawn from the analysis of the specific heat concerns the stabilization of the FMI-phase: thermodynamically speaking, the equilibrium state of a system

is determined by the minimum of the free energy $F = E - TS$. As shown by the specific-heat measurements in figure 14 and the magnetization data shown in figure 15, entropies of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x = 0.11$ and $x = 1/8$ are strongly reduced at T_{CO} upon cooling. This implies an increase of the free energy due to the entropy term $-T\Delta S \simeq -T\Delta S^M$ which must be overcompensated by a decrease in the inner energy ΔE . This is exactly what is known as the double-exchange mechanism. According to the double exchange (DE) theory [18, 19, 35], the transfer integral t is connected to the normalized magnetization m via

$$t = t_0 \langle \cos \Theta / 2 \rangle \simeq t_0 \sqrt{(1 + m^2)/2}, \quad (2)$$

where Θ is the angle between nearest-neighbour spins. Thus, an increase of the ferromagnetic order results in a decreased kinetic energy of the charge carriers or, in other words, in a reduction of the inner energy. However, as already stated above, a bare double-exchange picture without taking into account the orbital degrees of freedom cannot account for the coexistence of ferromagnetic and insulating properties. A possible scenario, which can reconcile the experimental results presented above, refers to the formation of orbital polarons [24, 36] and will be discussed below.

6. Effects of chemical pressure

The above results provide strong experimental evidence for the relevance of the DE mechanism for the stabilization of the FMI phase in $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$. This motivates the investigation of the metal–insulator transition of $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ as a function of y : the substitution of lanthanum by smaller praseodymium leads to a chemical pressure, which induces changes in the Mn–O–Mn bond angles and, therefore, modifies the transfer integral t_0 [11]. More precisely, the tolerance factor of the perovskite structure decreases as a function of y which is expected to lead to increased octahedral tilt angles and reduced Mn–O–Mn bond angles [7, 8, 37, 38].

In figure 16, the temperature dependences of the electrical resistivity ρ and the macroscopic magnetization M of $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ are compared for $y = 0, 0.1, 0.25$, respectively. Focusing on the resistivity data shown in the top panel of figure 16, it can be observed that ρ strongly increases upon praseodymium doping with a concomitant suppression of the anomalies in the electrical resistivity. More specifically, the metal-like resistivity which correlates to the development of ferromagnetic order is significantly suppressed on increasing y . Moreover, the jump-like increase of ρ at T_{CO} which is observed for $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ vanishes upon praseodymium doping. Turning to the magnetization shown in the bottom panel of figure 16, it can be seen that the magnetic ordering temperature T_{C} considerably decreases upon praseodymium doping. While the step-like increase of M below T_{C} signals the development of the FMI phase for $y = 0, 0.1$, no additional anomaly is observed for the sample with $y = 0.25$. Since all samples display a ferromagnetic insulating behaviour at low temperatures, the FMI phase which has been discussed for $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ will be referred to as the ordered FMI phase, in order to distinguish this phase from FMI phases without charge and/or orbital order.

Note that the gross behaviour of ρ and M as a function of y is in agreement with a reduction of the transfer integral t_0 . To be specific, a smaller t_0 is expected to lead to a larger ρ and reduced ferromagnetic interactions. The effect of praseodymium doping on the transition temperatures is summarized in table 1. However, the macroscopic data given in figure 16 do not allow us to

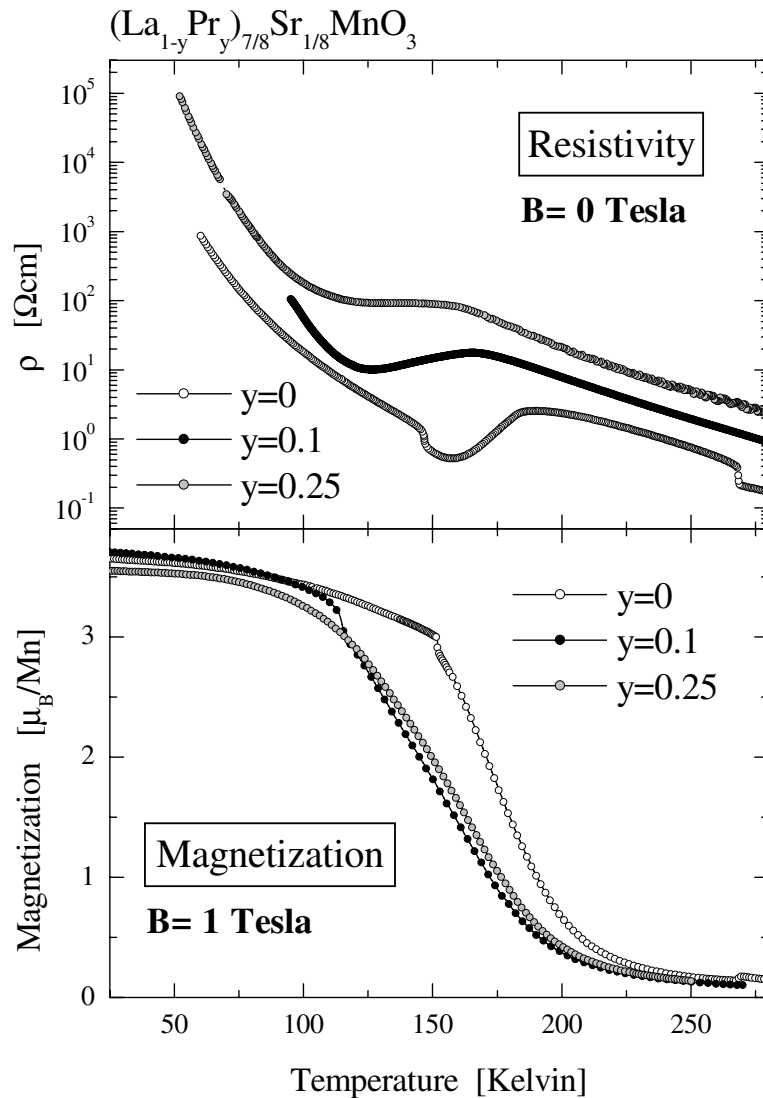


Figure 16. Temperature dependence of the electrical resistivity (top) and the macroscopic magnetization (bottom) for $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ at different praseodymium concentrations y .

decide whether the ordered FMI phase of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ is completely suppressed for $y = 0.25$ or not. Therefore, the samples with $y = 0.1$ and $y = 0.25$ have been examined by means of x-ray diffraction in order to clarify this issue.

6.1. X-ray diffraction study on $(\text{La}_{0.9}\text{Pr}_{0.1})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$

The low-temperature phase of a $(\text{La}_{0.9}\text{Pr}_{0.1})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ single crystal has been investigated by means of high energy x-ray scattering. The HXS measurements at 10 K reveal the presence of superlattice modulations which are characteristic of the ordered FMI phase. The temperature dependence of the (0.75 0.75 2.5) superlattice reflection is shown in figure 17. It can be observed that the integrated intensity at the (0.75, 0.75, 2.5) position displays a rather continuous

Table 1. Transition temperatures for $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$. T_{JT} for $y = 0$ and 0.25 have been obtained from x-ray powder-diffraction measurements. T_{JT} for $y = 0.1$ has been deduced from specific-heat and magnetization measurements. T_{C} and T_{CO} have been determined from magnetization and HXS-measurements, respectively.

y	T_{JT} (K)	T_{C} (K)	T_{CO} (K)
0	$\simeq 280$	$\simeq 183$	$\simeq 155$
0.1	$\simeq 296$	$\simeq 168$	$\simeq 110$
0.25	$\simeq 290$	$\simeq 169$	–

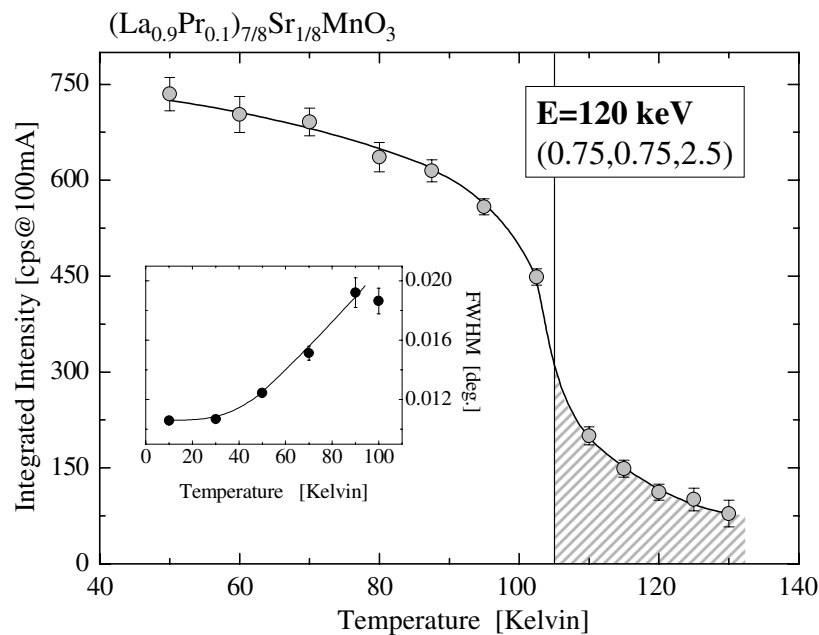


Figure 17. Temperature dependence of the integrated intensity of the $(0.75, 0.75, 2.5)$ reflection determined by high-energy x-ray diffraction using a low-resolution setup. The shaded area indicates the temperature regime where short-range charge and orbital ordering have been observed. The inset shows the FWHM of a radial scan through this reflection which has been measured in a high-resolution setup.

behaviour which makes it difficult to define a transition temperature based on the integrated intensity. However, the steepest decrease of the integrated intensity upon warming occurs at about 110 K which corresponds to the temperature where the magnetization displays a jump-like behaviour (figure 16). Therefore, this temperature will be identified as the transition temperature T_{CO} for this sample. In order to characterize the correlation length corresponding to the ordered FMI-phase, high-resolution measurements at the $(0.75, 0.75, 2.5)$ position have been performed.

The temperature dependence of the FWHM determined from a radial scan through the $(0.75, 0.75, 2.5)$ reflection is shown in the inset of figure 17. Although the mosaicity spread

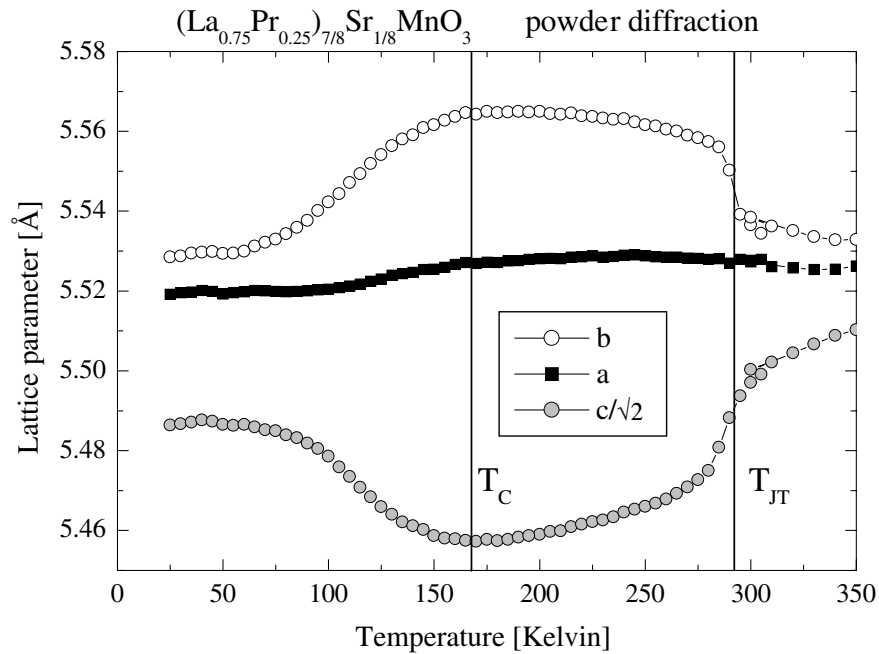


Figure 18. Temperature dependence of the lattice parameters for $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ as determined by x-ray powder diffraction. The lattice parameters are given in the orthorhombic Pbnm-setting.

of the investigated sample was too large to obtain a reliable value for the correlation length, a pronounced broadening of the $(0.75\ 0.75\ 2.5)$ superstructure reflection has been observed already at temperatures well below 110 K. Above 110 K the $(0.75, 0.75, 2.5)$ peak gets too weak and too broad to be detected in the high-resolution measurements. However, in this temperature range a broad intensity distribution is detected at the $(0.75\ 0.75\ 2.5)$ reflection in the low-resolution setup. This indicates the presence of short-range correlations.

To summarize the above results, the observed superstructure reflections verify the development of the ordered FMI phase in $(\text{La}_{0.9}\text{Pr}_{0.1})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$. However, the reduced transition temperature, the temperature dependence of the integrated intensity, and the FWHM determined at the $(0.75, 0.75, 2.5)$ position indicate that the ordered FMI phase is considerably destabilized in $(\text{La}_{0.9}\text{Pr}_{0.1})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$.

6.2. X-ray diffraction study on $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$

In figure 18, the temperature dependences of the lattice parameters for $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ are shown, which have been obtained from x-ray powder diffraction measurements. The behaviour of the lattice constants around $T_{JT} \simeq 290$ K is similar to that observed for $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ (figure 8). However, the increase in T_{JT} from 280 K for $y = 0$ to 290 K for $y = 0.25$ reveals the stabilization of the cooperative Jahn–Teller distorted phase upon praseodymium doping. Upon cooling, the splitting between the a , b and the c axes increases, reflecting the increase of the cooperative Jahn–Teller distortions. With the onset of ferromagnetic order below $T_C \simeq 169$ K, the splitting of the lattice parameters is reduced which indicates the

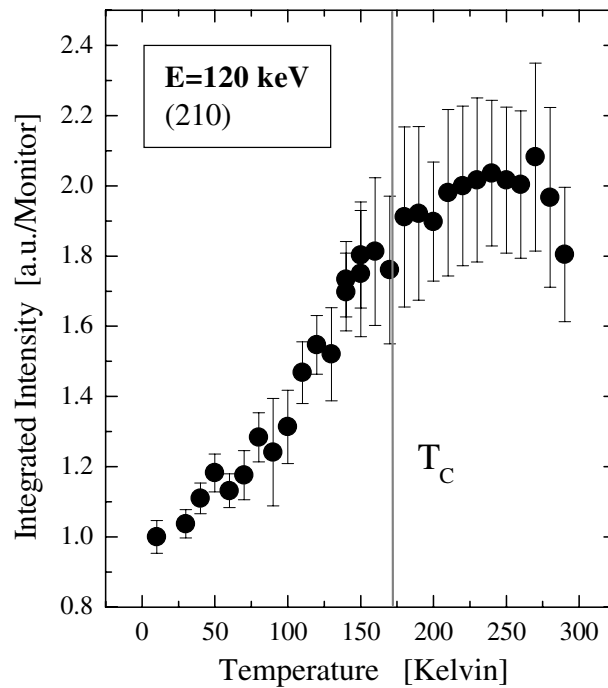


Figure 19. Temperature dependence of the integrated intensity observed at the (210) position for $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$. The large error bars at higher temperatures are the result of a pronounced peak splitting which occurs at elevated temperatures.

reduction of the cooperative Jahn–Teller distortions. However, there is no sign of a discontinuous phase transition below T_C , which already indicates the absence of the ordered FMI phase for this sample.

In order to further characterize the low temperature phase of $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$, the sample has been investigated by means of HXS. No superlattice reflections have been found at 10 K which reveals the absence of the ordered FMI phase for $y = 0.25$. However, the (210) reflection has been observed which is sensitive to the cooperative Jahn–Teller distortions [26]. A decrease in the integrated intensity of the (210) reflection below T_C reveals the suppression of the cooperative Jahn–Teller distortions in the ferromagnetic phase upon cooling (figure 19).

The sample has also been studied by RXS. Again, no superstructure reflections corresponding to the FMI phase have been found. Instead, the resonant (300) reflection has been observed as demonstrated in figure 20. The resonant behaviour as well as the $\sigma\pi$ -scattering at this position are clear signatures of the cooperative Jahn–Teller distorted phase [12].

To summarize the above results, examination of $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ by means of HXS and RXS unambiguously revealed the absence of the ordered FMI phase. Instead, the data indicate that the cooperative Jahn–Teller distorted phase persists in the ferromagnetic phase down to low temperatures. It is worth noting that the ferromagnetic phase in $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ is also insulating, although the experimental data given above shows that no superlattice modulation corresponding to the ordered FMI phase occurs in this phase. Therefore, this phase will be referred to as the ferromagnetic cooperative Jahn–Teller disordered phase (abbreviated to the FMJT phase).

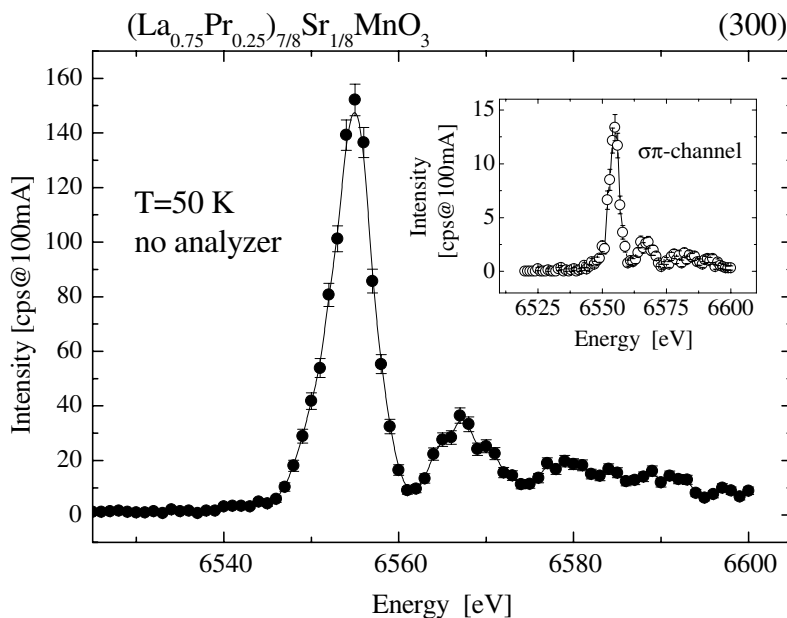


Figure 20. Energy dependence of the (300) reflection of $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ taken without analyser. The inset shows the energy dependence of the (300) reflection in the $\sigma\pi$ channel (Cu220 analyser).

7. Discussion and conclusion

The experimental study of $\text{La}_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ shows that the metal–insulator transition in this compound is connected to a reordering in the orbital sector. More precisely, the antiferro-orbital order of the cooperative Jahn–Teller distorted phase changes discontinuously to another type of orbital order. These results lead to the conclusion that the coexistence of ferromagnetic and insulating properties at low temperatures is related to a particular orbital order.

In addition to this, an analysis of the macroscopic properties implies that the DE mechanism is essential for the stabilization of the FMI phase in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x \simeq 1/8$. This result is further supported by the effect of chemical pressure on the metal–insulator transition. Substituting strontium by smaller praseodymium in $(\text{La}_{1-y}\text{Pr}_y)_{7/8}\text{Sr}_{1/8}\text{MnO}_3$ leads to a decrease of the transfer integral via an increase of the octahedral tilts. The presented data show that the ordered FMI phase is drastically suppressed upon praseodymium doping, verifying the relevance of the DE mechanism for the stabilization of the ordered FMI phase.

At first sight, the stabilization of an insulating phase by the DE mechanism is puzzling. We argue that this apparent contradiction can be resolved by taking into account the orbital degree of freedom. To be specific, all experimental observations presented in this article can be reconciled within an orbital polaron picture [24, 36]. An illustration of an orbital polaron, which constitutes a ferromagnetic object and is stabilized by the DE mechanism, is shown in figure 21. At the same time, the holes are trapped when an orbital polaron is formed, leading to a pronounced reduction of the charge carrier band width [36]. Consequently, the orbital polaron picture provides a natural explanation for the coexistence of ferromagnetic and insulating properties. It is important to note that our RXS results imply the formation of an orbital polaron lattice, since we observe

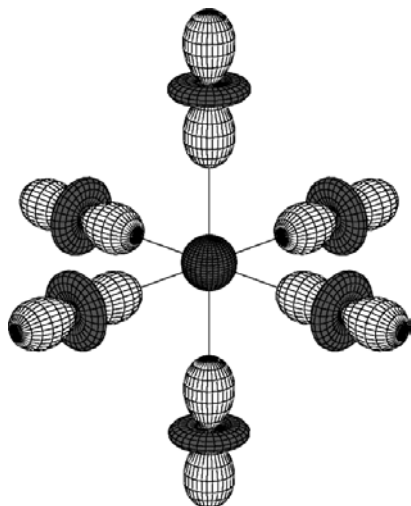


Figure 21. Orbital polaron around a Mn^{4+} -site (sphere) in the strong coupling limit [36]. The orbitals at the surrounding Mn^{4+} sites are directed towards the hole. The orbital polaron formation reduces the kinetic energy of the charge carriers due to local DE processes between the participating lattice sites.

well-defined resonant reflections at the Mn K-edge. This conclusion is strongly supported by recent Hartree–Fock model calculations [24].

It is interesting to speculate about the mechanisms which lead to the development of the orbital polaron lattice: Since the orbital occupation at a given manganese site is influenced by several interactions like electron–phonon, superexchange and DE interactions, it is reasonable to assume that the balance between these energies changes with the onset of ferromagnetic order. To be more specific, the energy gain due to DE processes is suppressed in the paramagnetic phase. Therefore, the cooperative Jahn–Teller distorted phase may be stable, because it is not stabilized by the DE mechanism, but by the energy gain connected to electron–phonon and superexchange interactions [39]. Note that the doping dependence of T_{JT} , which is given in table 1, supports this scenario. In a ferromagnetic phase, however, the situation is completely different. Although the system is ferromagnetic, the orbital order as well as the electron–phonon coupling suppress charge hopping: referring to figure 22(a), the electron hopping along x and y is prevented by the electron–phonon coupling. Moreover, along x the hopping is further suppressed, because the σ -overlap along this direction is small (cf figure 4). As a result, the gain of DE energy is expected to be small in this phase, despite the ferromagnetic ordering. In the situation sketched in figure 22(b), the formation of an orbital polaron maximizes the local DE processes at the expense of the electron–phonon coupling. We argue that in the ferromagnetic phase the loss of electron–phonon coupling energy is overcompensated by the DE energy gain, leading to the observed orbital rearrangement at T_{CO} .

The above conclusions may also be applied for low doped $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.1 < x < 0.2$) and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.15 < x < 0.3$): in these systems also a ferromagnetic and insulating phase is observed at low temperatures [40, 41]. However, in contrast to the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system, the development of superstructure modulations corresponding to the ordered FMI phase has not been reported yet. Instead, the orbital order in these systems is believed to be similar to that of the undoped parent compound [42]. This corresponds to the development of the FMJT phase

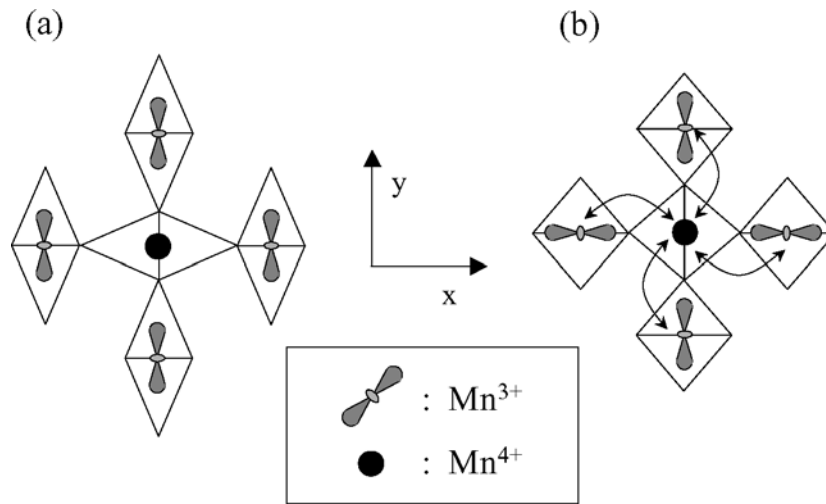


Figure 22. Cartoon of two possible local environments in the ab -planes next to a hole. (a) Hole in the cooperative Jahn–Teller distorted phase. Even if the spins of all manganese sites are ferromagnetically aligned, the hopping processes of the hole are strongly suppressed. (b) Orbital polaron in the absence of octahedral distortions. In this case, the hole gains kinetic energy in a ferromagnetic phase due to DE processes.

which we observe for $(\text{La}_{0.75}\text{Pr}_{0.25})_{7/8}\text{Sr}_{1/8}\text{MnO}_3$. In fact, the tilt angles in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ are expected to be larger than in the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system, because of the smaller praseodymium and calcium ions. According to the above conclusions, this considerably destabilizes the ordered FMI phase due to a reduction of the transfer integral t_0 . Thus the picture of the orbital polaron formation, which has been developed above, qualitatively explains the absence of the ordered FMI phase for low-doped $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ and agrees with the reported orbital ordering of the LaMnO_3 -type.

To conclude, the FMI phase observed in low-doped perovskite manganites provides a fascinating example of how different electronic degrees of freedom can cooperate to stabilize phases with stupendous properties. The data presented above provide a glimpse of how orbital physics can participate in the complex ordering mechanisms observed in strongly correlated electron systems.

Acknowledgments

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References

- [1] Kusters R M, Singleton J, Keen D E, McGreevy R and Hayes W 1989 *Physica B* **155** 362
- [2] Coey J M D, Viret M and von Molnár S 1999 *Adv. Phys.* **48** 167

- [3] Cheong S-W 1998 *Charge Ordering and Related Properties of the Manganese Oxides* (Singapore: World Scientific)
- [4] Tokura Y and Nagaosa N 2001 *Science* **288** 462
- [5] Loa I, Adler P, Grzechnik A, Syassen K, Schwarz U, Hanfland M, Rozenberg G K, Gorodetzky P and Pasternak M P 2001 *Phys. Rev. Lett.* **87** 125501
- [6] Glazer A M 1975 *Acta Crystallogr. A* **31** 756
- [7] Woodward P M 1997 *Acta Crystallogr. B* **53** 32
- [8] Woodward P M 1997 *Acta Crystallogr. B* **53** 44
- [9] Kanamori J 1960 *J. Appl. Phys. Suppl.* **31** 14S
- [10] Anderson P W 1963 *Exchange in Insulators: Superexchange, Direct Exchange, and Double Exchange, vol I: Magnetic Ions in Insulators. Their Interactions, Resonances, and Optical Properties of Magnetism* ed G T Rado and H Suhl (New York: Academic)
- [11] Goodenough J B 1976 *Magnetism and the Chemical Bond* (Huntington, NY: RE Krieger)
- [12] Murakami Y *et al* 1998 *Phys. Rev. Lett.* **81** 582
- [13] Rodriguez-Carvajal J, Hennion M, Moussa F, Moudden A H, Pinsard L and Revcolevschi A 1998 *Phys. Rev. B* **57** R3189
- [14] Pinsard L, Rodriguez-Carvajal J and Revcolevschi A 1997 *J. Alloys Compounds* **262–263** 152
- [15] Klingeler R, Geck J, Gross R, Pinsard-Gaudart L, Revcolevschi A, Uhlenbruck S and Büchner B 2001 *Phys. Rev. B* **65** 174404
- [16] Cox D E, Iglesias T, Moshopoulou E, Hirota K, Takahashi K and Endoh Y 2001 *Phys. Rev. B* **64** 024431
- [17] Kawano H, Kajimoto R, Kubota M and Yoshizawa H 1996 *Phys. Rev. B* **53** R14709
- [18] Zener C 1951 *Phys. Rev.* **82** 403
- [19] de Gennes P-G 1960 *Phys. Rev.* **118** 141
- [20] Yamada Y, Hino O, Nohdo S, Kanao R, Inami T and Katano S 1996 *Phys. Rev. Lett.* **77** 904
- [21] Inami T, Ikeda N, Murakami Y, Koyama I, Wakabayashi Y and Yamada Y 1999 *Japan. J. Appl. Phys. Suppl.* **38** 212
- [22] Yamada Y, Suzuki J, Oikawa K, Katano S and Fernandez-Baca J A 2000 *Phys. Rev. B* **62** 11600
- [23] Endoh Y *et al* 1999 *Phys. Rev. Lett.* **82** 4328
- [24] Mizokawa T, Khomskii D I and Sawatzky G A 2000 *Phys. Rev. B* **61** R3776
- [25] Korotin M, Fujiwara T and Anisimov V 2000 *Phys. Rev. B* **62** 5696
- [26] Niemoeller T *et al* 1999 *Eur. J. Phys. B* **8** 5
- [27] Dabrowski B *et al* 1999 *Phys. Rev. B* **60** 7006
- [28] Uhlenbruck S *et al* 1999 *Phys. Lett.* **82** 185
- [29] Elfimov I S, Anisimov V I and Sawatzky G A 1999 *Phys. Rev. Lett.* **82** 4264
- [30] Benfatto M, Joly Y and Natoli C R 1999 *Phys. Rev. Lett.* **83** 636
- [31] Benedetti P J, van den Brink J, Pavarini E J, Vigliante A and Wochner P 2001 *Phys. Rev. B* **63** 060408(R)
- [32] Geck J, Wochner P, Bruns D J, Büchner B, Gebhardt U, Kiele S, Reutler P and Revcolevschi A 2004 *Phys. Rev. B* **69** 104413
- [33] Proffen T, DiFrancesco R, Billinge S J L, Brosha E L and Kwei G H 1999 *Phys. Rev. B* **60** 9973
- [34] Tsuda K, Tanaga M, Hirota K and Endoh Y 2001 *J. Phys. Soc. Japan* **70** 1010
- [35] Anderson P W and Hasegawa H 1955 *Phys. Rev.* **100** 675
- [36] Kilian R and Khaliullin G 1998 *Phys. Rev. B* **58** R11841
- [37] Goldschmidt V M 1926 *Naturwissenschaften* **14** 477
- [38] Alonso J A, Martinez-Lope M J, Casais M T and Fernandez-Diaz M T 2000 *Inorg. Chem.* **39** 917
- [39] Feiner L F and Oleś A M 1999 *Phys. Rev. B* **59** 3295
- [40] van Aken B B, Jurchescu O D, Meetsma A, Tomioka Y, Tokura Y and Palstra T T M 2003 *Phys. Rev. Lett.* **90** 066403
- [41] Jirak Z, Krupica S, Simsa Z, Dlouha M and Vratislav S 1985 *J. Magn. Magn. Mater.* **53** 153
- [42] Zimmermann M *et al* 2001 *Phys. Rev. B* **64** 195133