

The charge ordered phase in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ studied by means of high energy X-ray diffraction

T. Niemöller^{1,a}, M. von Zimmermann¹, S. Uhlenbruck², O. Friedt², B. Büchner², T. Frello³, N.H. Andersen³, P. Berthet⁴, L. Pinsard⁴, A.M. De León-Guevara⁴, A. Revcolevschi⁴, and J.R. Schneider¹

¹ Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22603 Hamburg, Germany

² II. Physikalisches Institut, Universität zu Köln, Zùlpicher Strasse 77, 50937 Köln, Germany

³ Condensed Matter Physics and Chemistry Department, Risø National Laboratory, 4000 Roskilde, Denmark

⁴ Laboratoire de Chimie des Solides^b, Bâtiment 414 Université Paris-Sud, 91405 Orsay Cedex, France

Received 23 February 1998

Abstract. Superstructure reflections due to charge ordering have been observed in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ single crystals using X-ray diffraction. The critical temperatures for the ordering process are 150 K and 180 K in samples with Sr concentrations of 12.5% and 15%, respectively. For $x = 0.125$ the charge order transition correlates with a drastic resistivity enhancement, while a much smaller change of the resistivity is found for $x = 0.15$. It is argued that the onset of charge ordering in the sample with $x = 0.125$ is related to the suppression of co-operative Jahn-Teller distortions which is initiated by rising ferromagnetism.

PACS. 61.10.Nz Single-crystal and powder diffraction – 71.38.+i Polarons and electron-phonon interactions

1 Introduction

The physics of LaMnO_3 based perovskites have been studied intensively in the last few years due to the colossal negative magnetoresistance found in samples where La is partially replaced by divalent cations as Sr or Ca. The strongly reduced resistivity obtained upon application of a magnetic field can qualitatively be understood in terms of a double exchange process. To which extend this double exchange process does explain the anomalous properties of the manganates is discussed controversially in the literature [1, 2]. According to Millis, it is in addition necessary to take into account a strong coupling between charges and lattice due to the Jahn-Teller (JT) effect [1]. The parent compound LaMnO_3 is a Mott insulator with co-operative JT distortions below $T_{JT} = 750$ K [3]. Upon substituting a divalent ion on the La site e_g electrons are removed from Mn^{3+} , resulting in JT inactive Mn^{4+} ions. Thus the JT transition temperature is reduced, e. g. in the sample with 12.5% of Sr T_{JT} amounts to 270 K. It has been suggested that the co-operative JT effect is constricted to Sr concentrations less than $x \sim 0.15$ [4]. This prediction is in good agreement with experiments, the only deviations are found in the charge ordered regime. Charge ordering phenomena in the manganites are known from Ca doping with concentrations of $x = 0.35$, $x = 0.5$, and $x = 0.67$ for

example [5–7]. In Sr-doped samples, charge ordering has been observed in single crystal neutron diffraction studies for stoichiometries corresponding to $x = 0.1$ and $x = 0.15$ [8]. In this doping regime around $x = 0.125$, a subtle interplay of charge ordering, co-operative JT effect, and magnetism is responsible for the physical properties. In this paper, we present results obtained by means of high energy synchrotron radiation diffraction. Charge ordering has been found in stoichiometries with $x = 0.125$ and $x = 0.15$, whereas it has not been observed in a sample with $x = 0.06$. The interaction of charge ordering and the co-operative JT effect has been studied by mapping the intensity of superstructure reflections which are sensitive to the structural distortions.

2 Experimental

We have studied single crystal samples with Sr concentrations of 6%, 12.5%, and 15%. They were grown by a floating zone method [9]. A characterization of the samples shows different domains so that a , b , and c directions cannot be distinguished. Transport and structural properties as well as details of the growing process are given in references [10, 11]. The crystals have a cylindrical shape with a diameter of 4 mm. The lengths are 0.4 mm for the 6% sample, 6 mm for the 12.5% sample, and 7 mm for the 15% sample. The measurements were performed at the beamlines BW5 and PETRA2, both located at

^a e-mail: niemoell@x4u2.desy.de

^b CNRS – URA 446

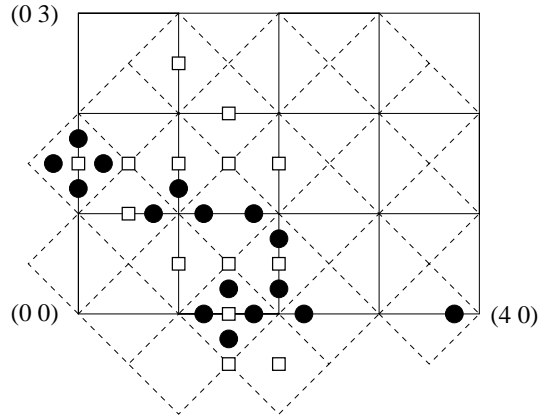


Fig. 1. The surveyed area in reciprocal space. The solid lines belong to the cubic reciprocal lattice, whereas the dashed lines show the h, k plane of an orthorhombic setting. The corners represent the fundamental reflections. Charge peaks (●) and superstructure reflections (□) due to the Sr-doping have been observed at the indicated positions.

HASYLAB in Hamburg. Triple axis diffraction in horizontal Laue geometry can be performed at both beam-lines [12]. The (1 1 1) reflection of an imperfect Si crystal (PETRA2) or of a Si/TaSi₂ [13] crystal (BW5) was used to monochromatize the beam. The analyzer has always been a Si/TaSi₂ crystal with a mosaicity of 60", also using the (1 1 1) reflection. The photon energies were 100 keV at PETRA2 and 100 keV or 120 keV at BW5. The high energies result in penetration depths of ~ 0.5 mm or ~ 0.8 mm. A solid state Ge detector with a resolution of 500 eV at 100 keV has been used allowing electronical suppression of higher harmonics in the beam. The longitudinal resolution is $\sim 0.02 \text{ \AA}^{-1}$, measured at the (2 0 0) reflection of the studied samples. The transverse resolution (0.005 \AA^{-1}) is determined by the mosaicity of the crystals with $x = 0.125$ and $x = 0.15$, which is $\sim 0.1^\circ$. The rocking curve of the 6% sample is narrower and has a FWHM value of $\sim 0.07^\circ$. The samples were mounted on the coldfinger of a closed cycle which itself was fixed on a standard Huber Eulerian cradle. Temperatures between 8 K and 300 K could be reached.

3 Results

In the doping and temperature range under study $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has an orthorhombic $Pbnm$ symmetry [11,14,15]. Because of the twinning, a pseudo-cubic setting valid for the undistorted perovskite structure was used. Projections of peak positions to the $(h k 0)$ plane for the $x = 0.125$ sample in reciprocal space are shown in Figure 1.

At low temperatures 16 superstructure reflections were detected at positions $(h \pm 0.25 k 0)$ and $(h k \pm 0.25 0)$, h and k being integer or half-integer values (filled circles, from now on called charge peaks). These charge peaks disappear above 150 K in the $x = 0.125$ sample. In Figure 2,

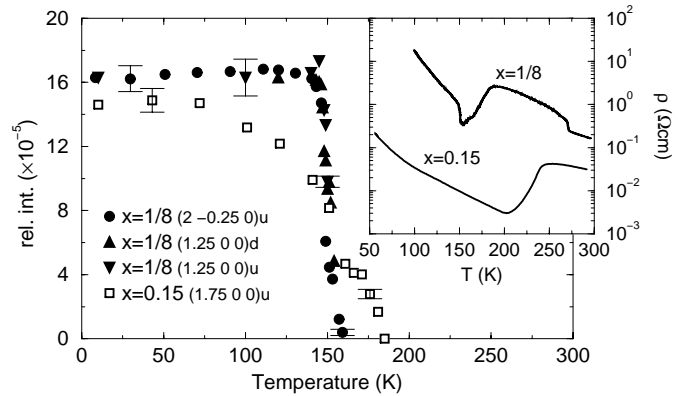


Fig. 2. Comparison of the charge peak intensities in the $x = 0.125$ and the $x = 0.15$ sample. The intensities are normalized relative to the adjacent Bragg-reflections, *i.e.* the intensity of the (1.25 0 0) reflection is divided by (1 0 0) and (1.75 0 0) by (2 0 0). The inset shows resistivity measurements from the same samples on a logarithmic scale. A positive jump in the resistivity of the $x = 0.125$ sample marks the transition into the charge ordered phase.

the variation of the integrated intensities with temperature is shown. No hysteresis was found upon heating (in Fig. 2: u) or cooling (d). For the $x = 0.125$ sample, charge ordering vanishes abruptly, which indicates a first order transition. Transport measurements on the same sample show an increase in resistivity of about a factor 3 at 150 K upon cooling (see inset Fig. 2). Together with the occurrence of the observed reflections, this is a strong hint for charge ordering. In particular, the charge peaks are at positions which can be explained with a Sr doping of 0.125 following a model of Yamada *et al.* [8]. These authors describe the charge ordered phase in alternate layers with JT distorted, hole-free layers and undistorted layers where 25% of the Mn sites contain a hole. In Figure 2, results for the $x = 0.15$ stoichiometry are also displayed. In this sample, charge peaks appear at exactly the same positions as in the specimen with $x = 0.125$. To get a rough estimate of the intensities of the charge peaks in different stoichiometries, values normalized to the adjacent fundamental Bragg-reflections are plotted. Although we do not know the correct structure factors for the charge peaks, it can be inferred that charge ordering is of the same strength in both samples. The optimal doping level for charge order seems to be 12.5% in Sr-doped LaMnO_3 , but charge order in the $x = 0.15$ sample is not considerably suppressed. The onset temperature of 180 K is even about 30 K larger than in the $x = 0.125$ sample. Whereas a first order transition at 150 K is observed in the sample with $x = 0.125$, the transition in the higher doped crystal is more continuous according to our X-ray data. This is supported by the resistivity data for $x = 0.15$ which does not show any jump-like increase due to charge order. Instead a broad minimum of ρ below 200 K is observed followed by a semiconductor-like increase at lower temperature. While this temperature dependence of ρ signals charge order as in the case for the lower doping of $x = 0.125$,

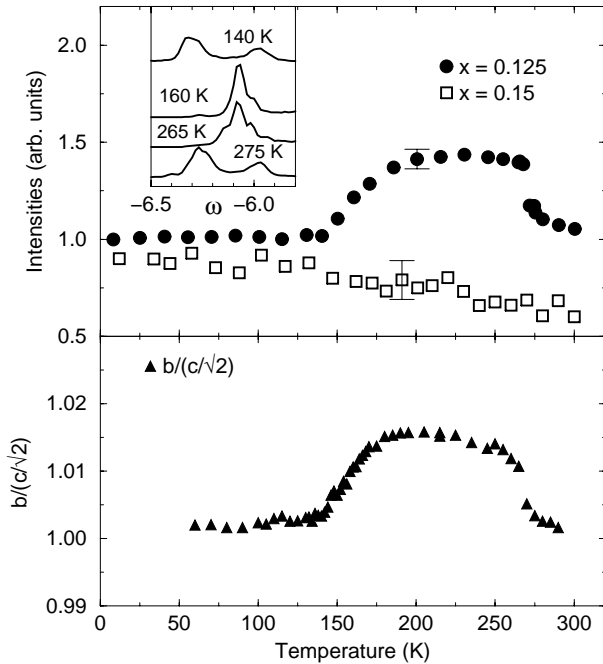


Fig. 3. Top: Intensities of half-integer peaks for the stoichiometries $x = 0.125$ ($1.5 \overline{0.5} 0$) and $x = 0.15$ ($\overline{1.5} 0.5 0$) in arbitrary units. The increased intensity between 150 K and 270 K (filled circles, $x = 0.125$) reflects an increased Jahn-Teller distortion. The inset shows ω scans below and above the transition temperatures in $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$. Bottom: Lattice distortion due to the co-operative Jahn-Teller effect in $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ obtained by X-ray powder diffraction.

there is a strong difference in the absolute values of ρ . In the crystal with $x = 0.15$ the resistivity is about three orders of magnitude smaller than for $x = 0.125$. It is apparent from the resistivity that charge order is not perfect for $x = 0.15$. We stress that this correlates well with our X-ray data. The positions of the superstructure reflections in the charge ordered phase fit well to a doping of $x = 0.125$. These peak positions do, however, not change when increasing the Sr content to $x = 0.15$, which indicates that not all holes are ordered for this higher doping. This suggests that the $x = 0.15$ crystal should be regarded as a charge ordered $x = 0.125$ compound doped by a small amount of additional holes. Due to these additional charges the resistivity remains relatively small in the "charge ordered phase" and the charge ordering, which is clearly seen in the X-ray data, does not lead to drastic anomalies of ρ but only causes a moderate increase of the resistivity.

In addition to the charge peaks, superstructure reflections were found in all studied samples at $(h \pm 0.5, k \pm 0.5, l \pm 0.5)$ positions, h, k, l being integer or half-integer values. These reflections are observed in the entire temperature range. The open squares in Figure 1 show the positions in reciprocal space for the sample with 12.5% of Sr. The peak intensities are smaller by a factor of approximately 10^{-4} in comparison with fundamental Bragg-reflections. These reflections originate from imperfect de-

structive interference of adjacent layers in the perovskite structure due to the Sr-doping which introduces distortions in the tilt pattern of the oxygen octahedra. The intensities of these superstructure reflections are sensitive to changes in the crystal structure.

Figure 3 shows the integrated intensities of the $(1.5 \overline{0.5} 0)$ and the $(\overline{1.5} 0.5 0)$ reflections for the samples with $x = 0.125$ and $x = 0.15$, respectively. The intensities are normalized arbitrarily to be 1.0 and 0.9 at low temperatures. The influence of the JT distortions on the peak intensity of the studied half-integer reflections can be seen in the $x = 0.125$ sample. Starting from the high temperature side, a positive jump in intensity at 270 K is followed by a decrease of intensity in the range from ~ 190 K to 150 K. At lower temperatures, the integrated intensity remains constant and is about the same as at room temperature. In the inset of Figure 3 the raw data from the $x = 0.125$ sample obtained by rotating the crystal (ω scan) is shown. At the two temperatures of 270 K and 150 K an abrupt change from two peaks to one peak can be observed. This indicates two structural transitions which are observed by Kawano *et al.* [15]. These authors mention a reentrant structural behaviour which is reflected in the same peak intensities at temperatures below 150 K and at 300 K. The structural phases at room temperature and below 150 K are not identical since charge order only occurs at low temperatures, but both phases are pseudo-cubic. Between 270 K and 150 K, a co-operative Jahn-Teller effect is responsible for anomalies in the lattice parameters [16]. A comparison of the anomalous peak intensity of the $(1.5 \overline{0.5} 0)$ reflection in the $x = 0.125$ sample with the relative change of the lattice constants b and c (Fig. 3, bottom) proves that the enhanced peak intensity is a measure of the co-operative JT effect. The smooth decrease below ~ 190 K sets in where rising ferromagnetism reduces the resistivity as can be seen in the inset of Figure 2. The increased itinerancy of the charge carriers leads to a suppression of the JT distortions [15]. The results for the sample with $x = 0.15$ also displayed in Figure 3 show a slightly rising intensity with decreasing temperature. Neither the synchrotron X-ray data nor the temperature dependence of the lattice constants give any evidence for a co-operative JT effect in this sample.

4 Discussion

When discussing the charge ordering in weakly doped $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ one has to take into account hole doping, the mobility of the charges which is related to ferromagnetic order and the JT energy. For $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ two different kinds of cooperative JT distortions have to be considered. At high temperatures, *i.e.* below 270 K, a JT distortion similar to that in undoped LaMnO_3 is present causing *e.g.* the anomalies of the lattice constants as shown in Figure 3. In the charge ordered phase the lattice constants do not show a cooperative JT effect. However, the fact that the sites with Mn^{4+} ions form a sublattice leads to the conclusion that orbital ordering with a different arrangement of JT distorted Mn^{3+}O_6 octahedra

is also present in this low temperature phase. Focusing on $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ we find that at 150 K, where the high temperature co-operative JT effect is strongly suppressed by ferromagnetism, charge ordering sets in abruptly. This might indicate that the co-operative JT effect as present below 270 K and the ordering of charges compete with each other. A relationship between the high temperature JT effect and charge order was also inferred from recent specific heat measurements in external fields, performed on the same crystal [17]. In particular these data show an increase of the charge order transition temperature with increasing magnetic field, *i.e.* with increasing mobility of the holes. Our data on the crystal with $x = 0.15$ reveals further indications for a competition between the usual co-operative JT effect and the charge ordered phase. Assuming that this cooperative JT effect reduces the charge order temperature for $x = 0.125$ naturally explains the higher onset temperature for charge ordering in the compound with $x = 0.15$ which is not JT distorted at high temperatures.

Thus, our data indicate a strong interplay between different cooperative JT distortions, ferromagnetism and charge mobility. In a small range of Sr doping around $x = 1/8$, where both, the JT effect and ferromagnetism play an important role, an increase of the charge mobility enhances the tendency of charge ordering at low temperatures. Mobile holes reduce the usual JT distortions of the oxygen octahedra which are measured *e.g.* by the lattice constants. The suppression of the corresponding JT energy then enhances charge ordering which allows the sample to retain JT distortions in every second layer whereas the holes segregate into the intermediate planes.

5 Conclusions

We have observed charge ordering in Sr doped $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ and $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ by means of hard X-ray synchrotron radiation diffraction. The occurrence of these charge peaks correlates with resistivity enhancements which is much more pronounced for $x = 0.125$. In this sample with 12.5% of Sr charge ordering is reflected in a large positive jump in resistivity. The positions of the charge peaks in reciprocal space confirm the charge ordering model suggested by Yamada *et al.* [8]. In $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ a co-operative JT effect leads

to structural distortions which do not support charge ordering. This possibly leads to a reduction of the onset temperature down to 150 K compared with charge ordering below 180 K found in $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$.

References

1. A.J. Millis, P.B. Littlewood, B.I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
2. E. Müller-Hartmann, E. Dagotto, Phys. Rev. B **54**, R6819 (1996).
3. J. Rodriguez-Carvajal, M. Hennion, F. Moussa, L. Pinsard, A. Revcolevschi, Physica B **234-236**, 848 (1997).
4. A.J. Millis, Phys. Rev. B **53**, 8434 (1996).
5. K. Liu, X.W. Wu, K.H. Ahn, T. Sulchek, C.L. Chien, J.Q. Xiao, Phys. Rev. B **54**, 3007 (1996).
6. C.H. Chen, S.-W. Cheong, Phys. Rev. Lett. **76**, 4042 (1996).
7. A.P. Ramirez, P. Schiffer, S.-W. Cheong, C.H. Chen, W. Bao, T.T.M. Palstra, P.L. Gammel, D.J. Bishop, B. Zegarski, Phys. Rev. Lett. **76**, 3188 (1996).
8. Y. Yamada, O. Hino, S. Nohdo, R. Kanao, T. Inami, S. Katano, Phys. Rev. Lett. **77**, 904 (1996).
9. A. Revcolevschi, R. Collongues, C. R. Acad. Sci., Paris **266** 1767.
10. A. Anane, C. Dupas, K. Le Dang, J.P. Renard, P. Veillet, A.M. de Leon Guevara, F. Millot, L. Pinsard, A. Revcolevschi, J. Phys.-Cond. **7**, 7015 (1995).
11. L. Pinsard, J. Rodriguez-Carvajal, A. Revcolevschi, J. of Alloys and Compounds **262-263**, 152 (1997).
12. R. Bouchard, D. Hupfeld, T. Lippmann, J. Neuefeind, H.-B. Neumann, H. Poulsen, U. Rütt, T. Schmidt, J.R. Schneider, J. Süßenbach, M. von Zimmermann, J. Synchrotron Rad. **5**, 90 (1998).
13. H.-B. Neumann, J.R. Schneider, J. Süßenbach, S.R. Stock, Z.U. Rek, Nucl. Instr. Methods A **372**, 551 (1995).
14. J.F. Mitchell, D.N. Argyriou, C.D. Potter, D.G. Hinks, J.D. Jorgensen, S.D. Bader, Phys. Rev. B **54**, 6172 (1996).
15. H. Kawano, R. Kajimoto, M. Kubota, H. Yoshizawa, Phys. Rev. B **53**, 14709 (1996).
16. L. Pinsard, J. Rodriguez-Carvajal, A.H. Moudden, A. Anane, A. Revcolevschi, C. Dupas, Physica B **234-236**, 856 (1997).
17. S. Uhlenbruck *et al.*, submitted to Phys. Rev. Lett.