La-site shift as probe for Jahn-Teller effect

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We observe two consecutive transitions in La$_{1-x}$Ca$_x$MnO$_3$, $x = 0.19$: ferromagnetic ordering at $T_c = 177$ K and Jahn-Teller orbital ordering at $T_{JT} = 150$ K. The presence of a ferromagnetic insulating state below $T_{JT}$ shows that the metallic phase is bound by ferromagnetic and Jahn-Teller ordering, and not induced by a critical doping concentration. The A-site shift is found to be a good indicator of Jahn-Teller ordering. Furthermore, the A-site shift does not disappear above $T_{JT}$, indicating a dynamical behaviour of the distorted MnO$_6$ octahedra.

The basic interactions in the manganite perovskites allow three phases: a ferromagnetic metal, a charge/orbital ordered antiferromagnetic insulator and a paramagnetic polaronic liquid. Metallicity is obtained by introducing holes by doping in antiferromagnetic, insulating LaMnO$_3$. This doping renders La$_{1-x}$Ca$_x$MnO$_3$, for 0.20 $< x < $ 0.50, both metallic and ferromagnetic, as the interactions are dominated by double exchange. However, La$_{1-x}$Ca$_x$MnO$_3$, with 0.10 $< x < $ 0.20, has a ferromagnetic insulating ground state. This unexpected coexistence of ferromagnetic and insulating behaviour seems to contradict the conventional double and super exchange models. Originally the magnetic state was thought to be a canting antiferromagnetic phase, but experiments determined the magnetic state to be ferromagnetic. The origin of the coexistence of ferromagnetism with insulating behaviour is not clear, but might stem from a delicate balance of charge localisation by orbital ordering (OO), due to the Jahn-Teller (JT) effect, and ferromagnetic interactions between Mn$^{3+}$-Mn$^{4+}$. The exact position of the phase line of the JT ordering transition in the composition-temperature phase diagram of doped LaMnO$_3$ is not known, and may depend on other variables, such as the tolerance factor and the magnetic ordering.

The phase diagram of Sr doped manganites has been explored in great detail. Here the situation is more complicated than for Ca doping, because the number of phases is larger due to the rhombohedral structure at $x > 0.18$ and the pronounced charge ordering (CO) at $x \sim 1/8$. Several authors reported a JT related structural phase transition above the magnetic ordering temperature, $T > T_c$ at $x \sim 0.12$. Below $T_c$, a transition to CO or OO is observed, where the cooperative JT distortion is significantly reduced. As the transition temperatures are extremely concentration dependent, a comparison between the various reports is not straightforward. It is claimed that the intermediate phase is both ferromagnetic and metallic and exhibits static cooperative JT distortions. Some reports clearly distinguish these two properties and combine short range order of JT distortions with metallic behaviour. However, a general relation between the JT ordered phase and the nature of the conductivity has not been established. Also, a coincidence of the CO transition and the re-entrant insulator-metal transition is claimed. The common metal-insulator transition is indisputably associated with the ferromagnetic ordering at $T_c$.

The Ca doped phase diagram is somewhat less complex, as there is no orthorhombic-rhombohedral structural transition. Furthermore, the phase transitions take place at higher concentrations. As a result we can probe the ferromagnetic insulating phase at concentrations far away from $x = 1/8$ to prevent charge ordering. In this Letter we explore the region where the JT ordering phase line has crossed the magnetic ordering phase line. We will show that the transition to the ferromagnetic metallic phase is not at fixed carrier concentration, but is controlled by the suppression of JT ordering. Conventionally, the JT ordering is observed via the Mn-O distances. We will provide evidence that the La-site shift is a more accurate tool for JT ordering, as the La position is sensitive to a change in the oxygen environment. Our measurements suggest that above the JT ordering phase line both the metallic phase and the paramagnetic phase exhibit strong JT like fluctuations. These fluctuations become long range ordered below $T_{JT}$.

The experiments were carried out on single crystals of La$_{1-x}$Ca$_x$MnO$_3$, $x = 0.19$, obtained by the floating zone method at the MISIS institute, Moscow. Although all crystals were twinned, small mosaicity and sharp diffraction spots were observed. Furthermore, the sharp magnetic and electronic transitions indicate the good quality of the crystals. Simultaneous measurements of resistance $R$ and magnetisation $M$ were performed in a MPMS magnetometer to find the exact transition temperatures for this composition. A thin piece was cut from the crystal to be used for single crystal diffractometry. Initial measurements were carried out on an Enraf-Nonius CAD4 single crystal 4-circle diffractometer to determine the twin fraction volume. Temperature dependent measurements between 90 K and 300 K were performed on a Bruker APEX diffractometer with an ad-
justable temperature set-up.

In Fig. 1 the temperature dependence of the resistivity is shown in zero, small and large magnetic fields. The resistance has a clear maximum at 177 K. At significantly lower temperatures, \( T \approx 160 \) K, the resistivity shows a subtle and wide transition to activated behaviour. This maximum can be suppressed by applying small fields (\( H < 0.1 \) T). Upon applying larger fields the resistence decreases not only in the local maximum but in the whole temperature range, both below the local minimum at \( T \approx 160 \) K and above \( T_c \).

In the inset of Fig. 1, magnetisation curves are plotted in the temperature range \( 170 < T < 180 \) K with temperature steps of 1 K. For \( T \leq 177 \) K the initial slope is constant and determined by the demagnetisation factor. Therefore, we establish \( T_c \) to be 177 K. Both the magnetisation curves and resistance measurements indicate a sharp transition at 177 ± 0.5 K.

![Resistance vs Temperature](image)

**FIG. 1.** Temperature dependence of the resistance at \( H = 0, 0.01 \) and 1 T. The inset shows the magnetisation vs. applied magnetic field in temperature steps of 1 K between 170-180 K. Both measurements establish that \( T_c = 177 \) K.

We propose that the observed upturn in resistance at \( T \leq 160 \) K is a result of re-entrant insulating behaviour caused by JT ordering. The well-known phase diagram by Cheong et al. is modified as shown in Fig. 2. We propose that the FMM phase, hatched area, should be extended to the phase line, which indicates the JT ordered to JT disordered transition. Obviously, JT ordering and metallicity are mutually exclusive. In analogy to conventional ferromagnetic metallic \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) systems, with \( x \sim 0.3 \), we expect to see a narrowing of the distribution of Mn-O bond lengths below \( T_c \) as a result of the itinerancy in the ferromagnetic, metallic regime. As soon as the JT orbital ordering sets in there will be a separation of the Mn-O bond lengths, as observed for \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) with \( 0.11 < x < 0.165 \). The difference in bond lengths should become less pronounced in the charge ordered phase at the lowest temperatures.

![Phase Diagram](image)

**FIG. 2.** Sketched phase diagram in the FMI-FMM transition region, modified from Cheong et al. The critical concentration, \( x_c \), only indicates the doping induced insulator to metal transition at \( T = 0 \).

From our full structure refinement, we can clearly observe the difference in in-plane Mn-O bond lengths, *i.e.* Mn-O2, both in the paramagnetic phase and in the insulating phase. However, we can not observe a decrease in this difference in the metallic regime, \( 160 < T < 177 \) K. The error bars on the bond lengths are quite large, due to the relatively low X-ray scattering factor of oxygen and the influence of the twinning, common in many perovskite materials. As we explained in detail elsewhere, the reflections of the various twin fractions overlap indistinguishably, which averages the calculated \( \sqrt{2a}, b \) and \( \sqrt{2c} \) parameters. Therefore the accuracy of the lattice parameter determination is not as good as for neutron powder diffraction.

However, the refinement of the relative atomic positions within the unit cell, which are reflected in the observed intensities, is extremely accurate. Therefore it makes more sense to focus on the refined atomic positions instead of the bond lengths. This holds especially for the O2 (in-plane) oxygen position, since it completely determines the Jahn-Teller distortion. For the full structure determination, we had to derive the twin relations, which are reported elsewhere. The temperature dependence of the O2 fractional coordinates show a transition in \( x_{O2} \), but this provides little insight into the physical mechanism.

More insight is gained by using the parameters \( x+z \) and \( x-z \) as sketched in Fig. 3. Here, a movement of the O2 ion parallel to \( x-z \), keeping \( x+z = \frac{1}{2} \), results in equal bond lengths but a Mn-O-Mn angle smaller than 180°. We interpret this movement, along \( x-z \), as the GdFeO3 rotation. Similarly, a shift of the O-ion along \( x+z \), fixing \( x-z = 0 \), results in different in-plane bond lengths and therefore indicates a Jahn-Teller distortion. The undistorted cubic structure obeys \( x+z = \frac{1}{2} \) and \( x-z = 0 \).
orbital ordering in LaMnO$_3$. The basic argument favouring the A-site shift is that the covalency between A and O can be optimised by decreasing the A-O distances for the three shortest bonds. Any GdFeO$_3$ distortion will result in a distorted polyhedron and therefore it will cause an A-site shift. Marezio et al. have studied the structure of the AFeO$_3$ compounds in great detail and their data allows us to focus on the correlation between the rotation and the A-site shift. The relevant atomic parameters, $x$ and $z$ of both the O$_2$ and the A-site, are all fully correlated as shown in Fig. 3. The figure shows a perfect linear relation between the A-site shift and the rotation parameter. Thus the shift of the A-site atom is, in this system, fully determined by the rotation of the FeO$_6$ octahedron. A fixed rotation will result in a constant A-site shift. An extra shift of the A-site at fixed rotation must therefore indicate the presence of a further influence on the oxygen positions. In the La$_{1-x}$Ca$_x$MnO$_3$ system the extra influence is the ordering of the Mn$^{3+}$ $e_g$ orbitals. The observed increase of 0.0027 in the rotation corresponds to an increase of 0.0021 in the La-site shift, using the relation between rotation and A-site shift. The observed shift is much larger.

We interpret our data as follows. Between 90 and $T_{JT} = 150$ K the average Mn environment is distorted, and the $e_g$ orbitals are ordered in the d-type fashion. Due to the orbital ordering, the charge carriers are localised and the material behaves as an insulator. We have

FIG. 3. Sketch of the GdFeO$_3$ rotation and the JT distortion in the ac-plane, obeying Pnma symmetry. Mn and O are represented by large and small circles, respectively. The shift associated with JT is shown as a closed arrow (shift along $x+z$). Open arrows indicate the GdFeO$_3$ rotation, with a shift along $x-z$. The basic argument favouring the A-site shift is that the covalency between A and O can be optimised by decreasing the A-O distances for the three shortest bonds. Any GdFeO$_3$ distortion will result in a distorted polyhedron and therefore it will cause an A-site shift. Marezio et al. have studied the structure of the AFeO$_3$ compounds in great detail and their data allows us to focus on the correlation between the rotation and the A-site shift. The relevant atomic parameters, $x$ and $z$ of both the O$_2$ and the A-site, are all fully correlated as shown in Fig. 3. The figure shows a perfect linear relation between the A-site shift and the rotation parameter. Thus the shift of the A-site atom is, in this system, fully determined by the rotation of the FeO$_6$ octahedron. A fixed rotation will result in a constant A-site shift. An extra shift of the A-site at fixed rotation must therefore indicate the presence of a further influence on the oxygen positions. In the La$_{1-x}$Ca$_x$MnO$_3$ system the extra influence is the ordering of the Mn$^{3+}$ $e_g$ orbitals. The observed increase of 0.0027 in the rotation corresponds to an increase of 0.0021 in the La-site shift, using the relation between rotation and A-site shift. The observed shift is much larger.

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FIG. 4. Jahn-Teller distortion and GdFeO$_3$ rotation as a function of temperature. The JT-distortion increases linearly down to $T_{JT} = 150$ K. A kink in the GdFeO$_3$ rotation appears at $T = 180$ K.

Recently, Mizokawa et al. reported on the interplay between the GdFeO$_3$ rotation, the orbital ordering and the A-site shift in ABO$_3$, with B=Mn$^{3+}(3d^4)$ or V$^{3+}(3d^2)$. Their theoretical calculations suggest that the observed orbital ordering in LaMnO$_3$ is stabilised by both a large GdFeO$_3$ rotation and a shift of the A-site ion. 12 Conversely, if a Jahn-Teller distortion is present, then the energy will be lowered if it is accompanied by a shift of the A-site. In Fig. 5 we show the temperature dependence of the A position, $(x_A, \frac{1}{2}, z_A)$, with respect to the ideal position $(0, \frac{1}{2}, +)$. Note that the error bars and scatter are much smaller than for the O positions, due to the higher electron density at the A-site.

FIG. 5. $x_{La}$ and $z_{La}$ positions vs. $T$. Drawn lines are linear, $T > 150$ K, and constant, $T < 150$ K, fits of $x_{La}$. For the $z_{La}$ a fixed ratio of 1:5 with respect to $x_{La}$ is assumed.

Fig. 5 shows a linear increase of $x_A$ with $T$ down to $T_{JT} = 150$ K. $x_A$ is roughly 5 times larger than $z_A$ for all temperatures. Below $T_{JT}$, $x_A$ and $z_A$ are temperature independent. This La-site shift along [1 0 5] is in good agreement with the [1 0 7] direction which was assumed by Mizokawa et al. 12 Furthermore, the observed temperature dependence is in excellent agreement with the temperature dependence of the JT effect.

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We interpret our data as follows. Between 90 and $T_{JT} = 150$ K the average Mn environment is distorted, and the $e_g$ orbitals are ordered in the d-type fashion. 13 Due to the orbital ordering, the charge carriers are localised and the material behaves as an insulator. We have
not observed any super lattice reflections. Any charge ordering phase either exists at lower temperatures, \( T < 90 \) K, or at a hole concentration closer to \( x = 1/8 \). In the phase diagram of \( \mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{MnO}_3 \), the CO phase borders the FMM phase, as observed by superlattice reflections in single crystal neutron experiments. [3] In contrast, for \( \mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3 \) the CO phase is suppressed by the orbital ordered FMI phase.

Above \( T_f T = 150 \) K the La-site shift and the parameter for JT ordering begin to decrease. The rotation remains constant, as does the magnetic ordering. One expects equal Mn-O distances in the metallic, itinerant phase. [2] The absence of equal bond lengths indicates that the structure on average is not a fully itinerant phase, although the JT parameter decreases. The low conductivity in the metallic regime agrees well with this interpretation. However, the decrease in the JT parameter signals the destruction of long range orbital ordering, although medium-range correlations remain. This orbital ordering melting is sufficient to render the material metallic, though the metallicity is not associated with the absence of Jahn-Teller distortions, only with the absence of long range orbital order. The Bragg peaks signal this order because the time scale of diffraction is very small, \( \sim 10^{-15} \) s. A decrease of the integrated intensity can thus be attributed to a decrease in phase coherence on length scales 100 – 1000 Å. The decrease of the La-site shift and the JT parameter indicates that the long range orbital ordering is broken. Locally the distortions are still present, but ordered on smaller length scales, in good agreement with experiments probing the local distortions. [4] This implies that metallic behaviour and long range JT ordering can not coexist in the same phase, in contradiction to the interpretation of [1,2].

Above \( T_c \), we observe no further change in the structure, except the continuous decrease of the La-site shift and the JT parameter. The magnetic ordering is broken, which decreases the 'bare' electron kinetic energy and the conduction becomes semiconducting as the electron-phonon coupling is the leading term. [5] The effect of the magnetic ordering on the structure is smaller than can be observed via single crystal X-ray diffraction. The magnetically ordered state allows metallic conduction, but the mobility is impeded by JT fluctuations. Eventually, the breaking of the magnetic ordering leads to a semiconducting state, with localised charge carriers due to the JT fluctuations. With increasing temperature the average structure will have less and less the signature of the JT ordered phase.

We have demonstrated that the ferromagnetic metallic phase is obtained, in a limited temperature range, by the suppression of the long range Jahn-Teller ordering. This contrasts with the common opinion that metallicity occurs if the charge carrier density exceeds a critical concentration. Furthermore, we have shown that we can study the Jahn-Teller ordering by observing the La-site shift. The JT ordering is no longer long range above \( T_f T \), but on shorter length scales the JT distortions do not disappear. With increasing temperature there is a simultaneous reduction of the JT parameter and the La site shift. The metallic state of \( \mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3 \) is bound by ferromagnetic ordering and the absence of orbital ordering.

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