

Role of structurally and magnetically modified nanoclusters in colossal magnetoresistance

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It is generally accepted that electronic and magnetic phase separation is the origin of many of exotic properties of strongly correlated electron materials, such as colossal magnetoresistance (CMR), an unusually large variation in the electrical resistivity under applied magnetic field. In the simplest picture, the two competing phases are those associated with the material state on either side of the phase transition. Those phases would be paramagnetic insulator and ferromagnetic metal for the CMR effect in doped manganites. It has been speculated that a critical component of the CMR phenomenon is nanoclusters with quite different properties than either of the terminal phases during the transition. However, the role of these nanoclusters in the CMR effect remains elusive because the physical properties of the nanoclusters are hard to measure when embedded in bulk materials. Here we show the unexpected behavior of the nanoclusters in the CMR compound $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.4 \leq x < 0.5$) by directly correlating transmission electron microscopy observations with bulk measurements. The structurally modified nanoclusters at the CMR temperature were found to be ferromagnetic and exhibit much higher electrical conductivity than previously proposed. Only at temperatures much below the CMR transition, the nanoclusters are antiferromagnetic and insulating. These findings substantially alter the current understanding of these nanoclusters on the material's functionality and would shed light on the microscopic study on the competing spin-lattice-charge orders in strongly correlated systems.

nanoscale inhomogeneities | superlattice

It is widely believed that electronic inhomogeneities due to the complex spin-lattice-charge interplay (1–9) and the percolation of the conducting phase in manganites (10–18) are essential to the understanding of the colossal magnetoresistance (CMR) mechanism (19–21). However, the competing magnetic, lattice, and charge orders result in very intricate phase-separation scenarios in the materials and, therefore, it is difficult to unravel the role of individual phases in the CMR effect. Firstly, the dimension of the percolative phases that yields the CMR effect is under intensive debate. Submicron percolating network was observed using several imaging techniques (10–12), although evidence by various diffraction techniques and scanning tunneling microscopy (STM) supports nanoscale phase separation to be the key to study the CMR (3–9, 15–18). Secondly, among the nanoscale phases, a phase in form of nanoclusters with unique structural characteristic has attracted great attention because its appearance coincides with the CMR effect in a wide range of doped manganites without exception (3–9). This nanoscale phase was found to have satellite-superlattice reflections detected by neutron scattering, synchrotron X-ray, and electron diffractions during a paramagnetic (PM) to ferromagnetic (FM) phase transition upon cooling (3–9). The superstructure modulation exhibits in the nanoclusters with maximum density in the intermediate temperature range and very small density in both the high-temperature PM-insulating phase and the long-range-ordered low-temperature FM-metallic phase. Nevertheless, the role of these nanoclusters is still mysterious due to the difficulty of measuring their physical properties in bulk materials. Indeed, the structurally modified

nanoclusters were hypothesized to be antiferromagnetic (AFM) and insulating to establish a possible relationship between the nanoclusters and CMR in the previous works (3–9). Without further observation of the phases at various length scales and direct measurement of the properties of these phases, understanding of the mechanism of the CMR effect as well as basic properties of manganites remains a daunting task.

In this article, we report the evolution of the intrinsic phases in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO, $0.4 \leq x < 0.5$) as a function of temperature and doping level using a number of transmission electron microscopy (TEM) techniques. In order to explain the measured physical properties of the materials, we correlated the bulk measurements with the TEM observations over the length scales from nanometers to microns. In particular, we explored the role of the FM submicron domains (without superstructure) and the nanoclusters (with superstructure) in the CMR effect in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ materials and provided strong evidences for the unexpected relationship between those phases and the CMR effect in these compounds (see Fig. S1).

Results and Discussion

Fig. 1A shows the magnetization as a function of temperature for LCMO samples at $0.4 \leq x \leq 0.5$ under a magnetic field $H = 10$ kOe ($1 \text{ Oe} = 1 \times 10^{-4} \text{ T}$ in a vacuum). The magnetization monotonically increases upon cooling for $0.4 \leq x \leq 0.45$. However, it peaks at intermediate temperatures with large hysteresis for $x = 0.48$ and 0.50 . The drop of the magnetic moment in these compositions at approximately 120 K has been usually ascribed to the emergence of some AFM volume in the bulk material (19). As demonstrated in Fig. 1B, the sample at $x = 0.48$ exhibits very unusual magnetic properties. Below the PM–FM transition at $T_1 \sim 240$ K, an unexpected transition at $T_2 \sim 120$ K occurs where the magnetic moment increases at nearly zero field (5 Oe) but decreases at slightly larger magnetic field (200 Oe). The transition temperature T_2 upon cooling differs from warming due to strong thermal hysteresis, and only the dataset upon cooling process is discussed here (see Fig. S2). The magnetic transition at T_2 cannot simply be explained by the previous theory (e.g., the appearance of the AFM volume in the bulk material).

In order to understand the magnetic properties of the $x = 0.48$ sample, we used a dedicated Lorentz microscope (JEOL 2100F-LM) that has a negligible magnetic field at sample position (22). Fig. 2A shows that the FM domains form at $T^* \sim 227$ K and the domain-wall intensity continuously increases upon cooling. It is worthy of mentioning that, because Lorentz imaging is a low electron-dose method, beam-heating effect can be ignored and the temperature determination is sufficiently accurate for

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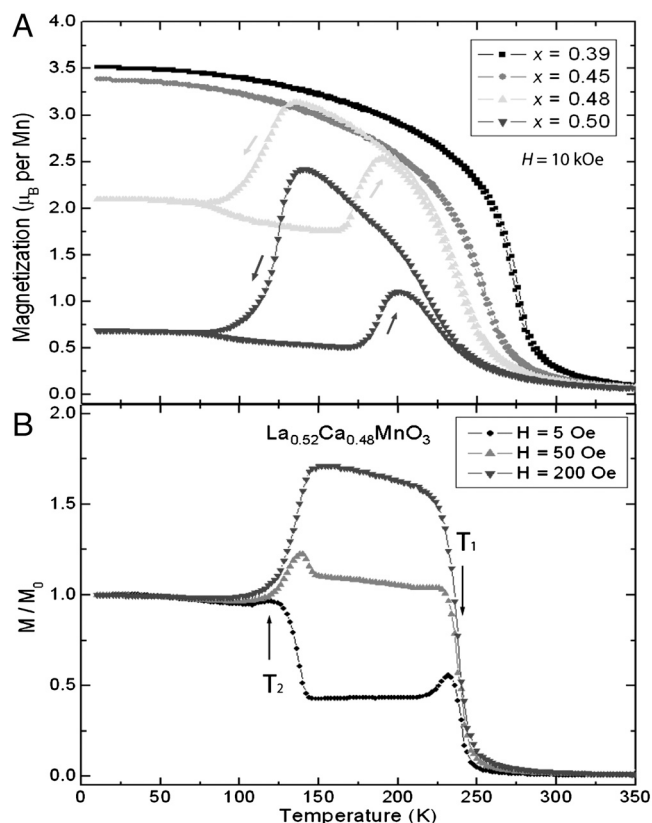


Fig. 1. Magnetization measurements for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ bulk samples. (A) Magnetization as a function of temperature for bulk LCMO $0.4 \leq x \leq 0.5$ under a magnetic field $H = 10$ kOe. (B) Magnetization (normalized to the low temperature value M_0) as a function of temperature upon cooling with various applied magnetic fields ($H = 5, 50, 200$ Oe) for LCMO, $x = 0.48$.

the formation of the FM submicron domains. Because the local magnetization of the FM domains is directly reflected by the domain-wall intensity and the observed formation of the FM submicron domains does not have abrupt change* below T^* , we may conclude that the FM submicron domains are not responsible for the transition at T_2 for $x = 0.48$. Moreover, the magnetic hysteresis curve measured as a function of applied field, shown in Fig. 2B, unambiguously illustrates that the FM submicron domains are not the only FM phase at $T = 200$ K, a temperature between T^* and T_2 . Deviating from a standard hysteresis loop, the magnetic hysteresis behavior only appears at the very center part of the M-H curve, enlarged in the inset of Fig. 2B. Such features could be interpreted as a combination of two types of FM phases, one as conventional FM submicron domains (with hysteresis) and the other as single-domain FM nanoclusters (without observable hysteresis).

On the other hand, the existence of a nanoscale phase, or the structurally modified nanoclusters, in the sample $x = 0.48$ was revealed by electron diffraction as diffused superlattice reflections (SLRs) in the $[010]$ zone (Fig. 2C). The correlation length of the nanoclusters is *ca.* 3–4 nm measured from the full width at half maximum of the SLRs in electron diffraction. The wavenumber of the superstructure, q_S/a^* , was further determined as a function of temperature, as shown in Fig. 2D. Interestingly, there are two temperatures where the structural characteristic of the nanoclusters (the value of q_S/a^*) drastically changes: one is approximately

240 K and the other is approximately 120 K, both coinciding with the magnetic transitions observed in the same sample. Moreover, the resistivity measurement of the sample (Fig. 2E) shows a metal-insulator transition at T_2 .

What could we learn from the above experimental evidences? At room temperature, the system is mainly PM. Upon cooling, the density of the structurally modified nanoclusters rapidly increases at a temperature around T_1 (240 K) and FM submicron domains (without superstructure) are formed at T^* (227 K). At the temperature range between T^* and T_2 , the structurally modified nanoclusters emerge and coexist with the FM submicron domains. The magnetic property measurements and the TEM observations strongly indicate the role of these nanoclusters in the magnetic transitions, and the magnetic order of the nanoclusters could be possibly derived as follows. Firstly, if these nanoclusters are PM or AFM in the temperature range between T^* and T_2 , they would give negligible contribution to the total magnetization. Because the other phase, FM submicron domains, was observed to be irresponsible for the transition at T_2 (Fig. 2A), there would be no abrupt increase (at 5 Oe) or decrease (at 200 Oe) in magnetization at T_2 (Fig. 1B). Hence, this possibility is not supported by the experimental results. Secondly, if the nanoclusters are FM, then the magnetic behavior between T^* and T_2 can be well explained by the scenario proposed in Fig. 3. For very small magnetic fields ($H < 50$ Oe, Fig. 3A), the spin direction of the structurally modified FM nanoclusters is opposite to their surrounding (i.e., the FM nanoclusters are coupled antiparallelly to the magnetization of the FM submicron domains), possibly resulting from a superexchange interaction at the interfaces of the nanoclusters, giving negative contribution to the total magnetization. Small magnetic fields could easily align the spin orientations of the FM nanoclusters to the field direction, making the total magnetization greater than that of the FM submicron domains (Fig. 3B, $H = 200$ Oe). Moreover, the observation of the coexistence of the FM nanoclusters and the FM submicron domains in the temperature range between T^* and T_2 (Fig. 2B and Fig. S3) also supports the notion that the structurally modified nanoclusters are FM.[†] At $T_2 \sim 120$ K, the structurally modified FM nanoclusters transform into the AFM state and give no more contribution to the magnetization—i.e., the total magnetization of the material at temperature below T_2 only arises from the contribution of the FM submicron domains. We note that a previous study on the LCMO system ($x = 0.47$) by neutron scattering found the transition temperature to the AFM state is lower than the transition temperature associated with the structural superlattice (23), which is in consistent with the scenario we proposed here.

The volume fraction of the structurally modified nanoclusters (FM between T^* and T_2 ; AFM below T_2) is hard to measure precisely by TEM in this case. Experiments using the scanning electron nanodiffraction technique developed in ref. 8, which provides the capability to map the nanoclusters in real space, were performed for $x = 0.48$. However, the results show that the superlattice reflections appear in the electron nanodiffraction patterns nearly at every location during the scanning of the electron beam over the sample below T^* . Considering the incident electrons probe the projection of the three-dimensional distribution of the nanoclusters that are homogeneously arranged, we arrive at the volume fraction of the structurally modified nanoclusters close to 50%, or even larger in the bulk sample for $x = 0.48$. This significant volume-fraction value was indeed consistent with the estimation using bulk property measurements

*Although we observed that the FM domain walls are not pinned on the samples through various thermal cycling, the average domain width and the orientation of the FM domains remain statistically the same once they form swiftly at the formation temperature ~ 227 K in $x = 0.48$ upon cooling.

[†]It is also possible that the nanoclusters are AFM at intermediate temperatures with uncompensated moments at the nanocluster surface. However, the magnetic property measurements suggest that $\sim 40\%$ of the total magnetization of the material comes from the FM component inside the nanoclusters (see figure S3). This significant fraction implies that it is more likely that the whole nanoclusters are FM than the scenario of uncompensated FM moments at the nanocluster surface.

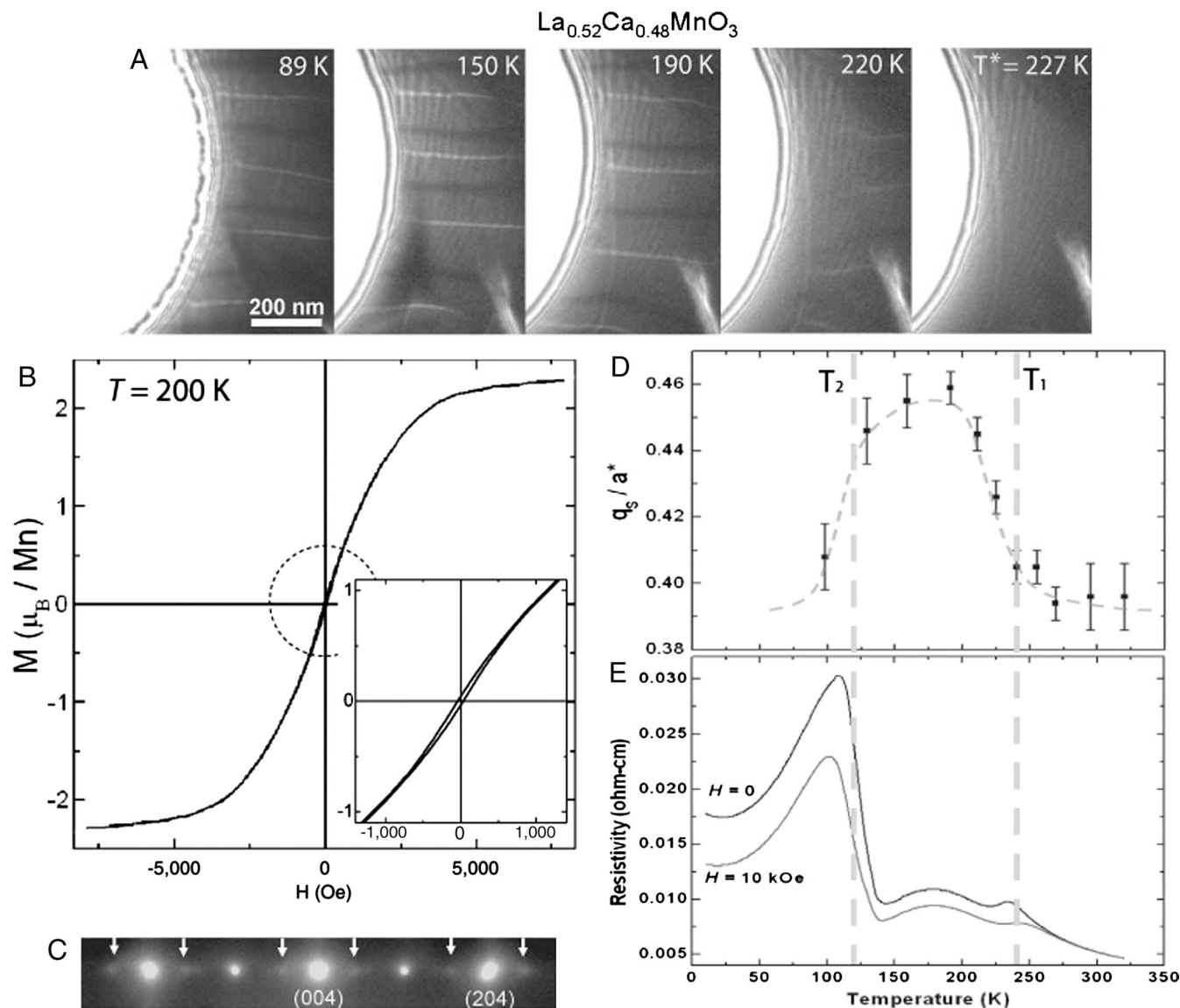


Fig. 2. Microscopic observations and property measurements of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.48$). (A) A series of Lorenz Fresnel images showing the evolution of the FM-CD submicron domains upon cooling (from right to left) for LCMO $x = 0.48$. The images show the typical FM domains with the black (divergent wall) and white lines (convergent wall) as 180° FM-domain walls. The transition temperature of the FM submicron domains T^* is determined to be 227 K. A reversal evolution was also observed with the same transition temperature during warming process. (B) Magnetization vs. field measurement for $x = 0.48$. The center part of the measurement is enlarged shown in the inset. (C) Typical electron diffraction pattern at the [010] zone at intermediate temperature showing diffused SLRs from the structurally modified nanoclusters at $x = 0.48$, as satellites surrounding the fundamental reflections. (D) The wavenumber of the SLRs, q_s/a^* , as a function of temperature for $x = 0.48$, eye-guided by the dash line. (E) Resistivity measurement as a function of temperature, for $x = 0.48$, upon cooling at zero field (top line) and under a magnetic field of 10 kOe (bottom line).

based on the model we proposed above that these nanoclusters occupy roughly 40% in this bulk material (see Fig. S3 for details and the real space distribution of the nanoclusters using superlattice reflection only in dark field images, shown in Fig. S4). It should be mentioned that the structurally modified nanoclusters could be suppressed by magnetic fields greater than 10 kOe (24), although small magnetic fields below 200 Oe are unlikely to change the density of such nanoclusters but realign their spin directions.

The model depicted in Fig. 3 *A* and *B* has another important outcome on the physical properties of the structurally modified nanoclusters—i.e., in their FM state, these clusters are conductive. The zero-field resistivity sharply increases upon cooling below T_2 (see Fig. 2*E*), which has to arise from a sudden modification of the transport properties within the structurally modified nanoclusters (i.e., the electrical conductivity of the FM

nanoclusters is much larger than that of the AFM nanoclusters). Moreover, the conductivity of the FM nanoclusters is likely comparable to the conducting property of the FM submicron domains, which are metallic at temperatures between T^* and T_2 (otherwise the resistivity in the temperature range below T^* would be determined by the predominant metallic submicron domains and the metal-insulator transition at T_2 would be hardly noticeable). The conductivity of the FM submicron domains continuously increases as the temperature decreases and it further lowers the bulk resistivity at temperatures below T_2 . A synopsis of the phase transitions and coexistence at $x = 0.48$ is depicted in Fig. 3C. We note that the small temperature interval between T_1 and T^* (*ca.* 10 K) is insignificantly reflected in the property measurements at $x = 0.48$ (Fig. 1 and Fig. 2E). However, the separation of these two temperatures is evidently observed in the resistivity measurements in LCMO in other doping levels

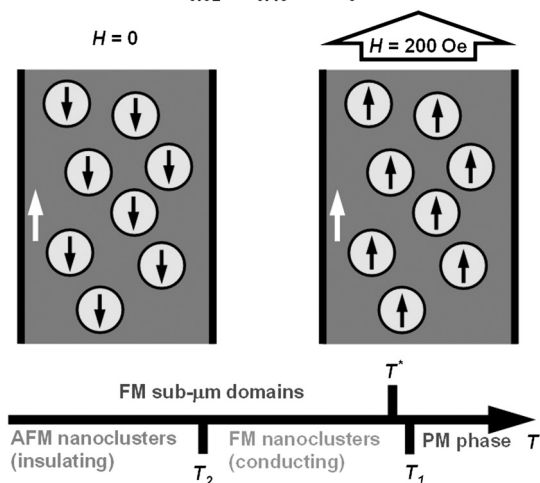
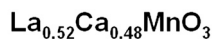


Fig. 3. Interpretation of the results obtained for $x = 0.48$. (A) FM nanoclusters (with superstructure) embedded in a FM submicron domain (without superstructure). At zero field, the spin directions of the FM nanoclusters are opposite to those in the FM matrix; (B) The spin directions of the FM nanoclusters are aligned with the submicron FM matrix under the applied magnetic field of $H = 200$ Oe. (C) A summary of the phase separation through the phase transitions for LCMO $x = 0.48$.

at $0.4 \leq x \leq 0.45$, which will be elaborated below. The observation of T_1 and T^* demonstrates that the structurally modified component and nonmodified component of this material have different transitions, although the origin for the two transition temperatures being close, but not exactly the same, is not yet understood.

In order to reveal doping dependence in other CMR LCMO, in Fig. 4 *A–D*, we show the data obtained for $x = 0.45$ (Fig. S5), demonstrating essentially identical results for $x = 0.39$, including the bulk property measurements and the TEM observations). Fig. 4*A* shows the similar FM submicron domain formation as that for $x = 0.48$, with a swift formation temperature $T^* \sim 230$ K for $x = 0.45$. We note that these domains form or melt within a temperature range of 1–2° upon cooling or warming, as observed from our Lorentz images as well as those reported in ref. 25 using electron holography with higher spatial resolution on LCMO.

Transport measurements (Fig. 4B) indicate that the resistivity peaks at $T_1 \sim 253$ K (clearly above T^*), where the FM submicron domains are yet to form over the sample. CMR has been measured as the suppression of this resistivity peak by application of a magnetic field. Therefore, the explanation of the resistivity drop at intermediate temperatures at zero-field is as important as the understanding of the behavior of the resistivity peak under applied magnetic field in the CMR mechanism. Clearly in contrast with some previous results in other CMR manganites (10–12), our data support the conclusion that growth and percolation of FM submicron domains are not at the root of the resistivity drop at zero field in LCMO for $0.4 \leq x < 0.5$. The observed formation of the FM submicron domains here has features of a typical second-order phase transition, thus dynamic FM fluctuations are expected at temperatures above T^* during the transition of the matrix without superstructure. The behavior of these fluctuations, however, is beyond the scope of the paper.

We further note that the structurally modified nanoclusters could play a significant role in the resistivity drop at the zero field. Unlike the constant volume fraction (*ca.* 40%) of the nanoclusters below T_1 for $x = 0.48$, the structurally modified nanoclusters have maximum density at T_1 where the CMR occurs for $x = 0.45$ and 0.39 , and the density quickly decreases at low temperatures (see Fig. S1). For example, the volume fraction of these nanoclusters is approximately 20% at $T_1 \sim 253$ K and approximately 5% at 160 K for $x = 0.45$ (8). Therefore, if the structurally modified nanoclusters in $x = 0.45$ and 0.39 still have magnetic transition from intermediate temperature to low temperature upon cooling, that transition has much less influence in the bulk magnetization than the case for $x = 0.48$. However, the observed anomaly and reversed thermal hysteresis behavior in magnetization allows us to infer the magnetic property of these nanoclusters shown in Fig. 4C. Because the FM submicron domains were observed to have second-order PM-FM phase transition without hysteresis (see the left part in the inset of Fig. 4C), reversed thermal hysteresis in the magnetization can only be attributed to the structurally modified nanoclusters, suggesting FM component in these nanoclusters at intermediate temperatures. More evidently, such conclusion is supported by the direct observation of the FM nanoclusters using Lorentz imaging, shown in Fig. 5. At CMR temperature $T = 253$ K when the structurally modified nanoclusters already exist, while the FM submicron domains are yet to form upon cooling, static nanoclusters with

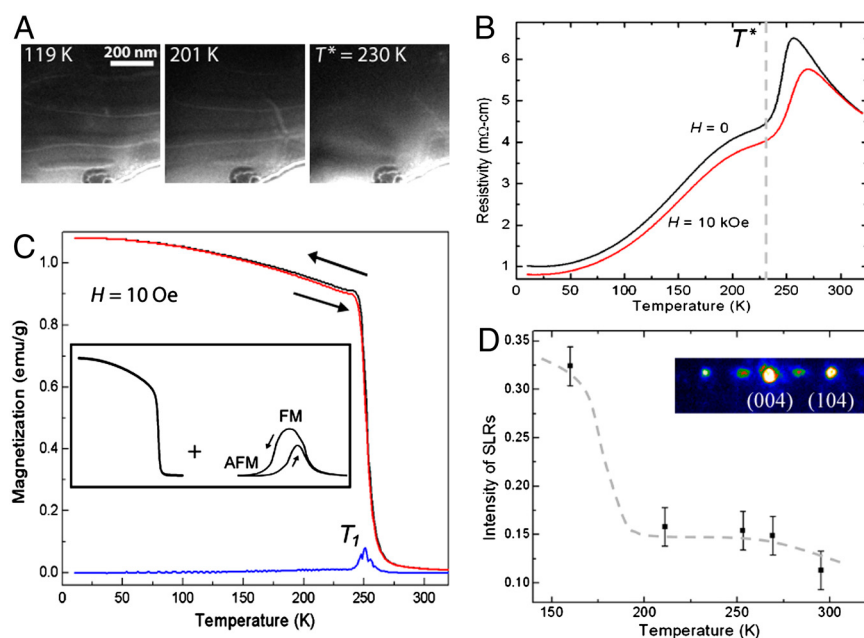


Fig. 4. Structural and property measurements of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.45$, see Fig. S5 for results obtained at $x = 0.39$). (A) A series of Lorenz Fresnel images showing the evolution of the FM submicron domains (without superstructure) upon cooling (from right to left) for LCMO $x = 0.45$. The FM submicron domains have a sharp formation temperature $T^* \sim 230$ K. (B) Resistivity measurement as a function of temperature for $x = 0.45$. The formation temperature T^* of the FM submicron domains is clearly below the peak, being more related to a kink in the curve. (C) Magnetization as a function of temperature upon cooling (black) and warming (red) for $x = 0.45$ under magnetic field $H = 10$ Oe. The difference is plotted at the bottom. The inset implies the total magnetization is a superposition of contribution from the matrix of the FM submicron domain (Left) and the FM nanoclusters (Right). (D) The intensity of the SLRs surrounding the (004) reflections (normalized to the fundamental reflections) in electron nanodiffraction patterns (with one example showing as an inset) as a function of temperature, obtained from individual structurally modified nanoclusters for $x = 0.45$. It clearly shows a drastic increase of the intensity of the SLRs at the temperature around 170 K (eye-guided by the dash line), suggesting a structural transition of the superstructure inside the nanoclusters.

direct observations in real space (8), which can now be explained by the fact that the superstructures of nanoclusters substantially differ from that of the long-range phase at varied temperature ranges.

The precise origin of the structurally modified nanoclusters is still lacking theoretically. Monte Carlo calculations have shown that the AFM nanoclusters with the superstructure would be prominent in systems (7), and FM characteristics can result in the appropriate region of the parameters space (electron-phonon coupling and t_{2g} -spins exchange) (33). Other studies suggested that short-range phases with structural modulations have versatile transport properties (34, 35). Although our findings strongly propose that the structurally modified nanoclusters are FM, the direction of the FM component inside the nanoclusters cannot be exclusively determined by the TEM data showing here. The in-plane FM component of the nanoclusters were observed at both [100] and [001] zone, suggesting the spin direction with components normal to a and c axes in the $Pnma$ notation for the crystal orientation. Moreover, the magnet-field effect on the nanoclusters is not fully understood. With those open questions, the observed temperature and dopant dependence of the structural modified nanoclusters will stimulate theoretical studies that require significant computational efforts focusing on the basic microscopic interactions in manganites. In addition, we note that the competition between the FM nanoclusters and large FM domains was observed to play an important role in other strongly correlated systems, such as doped cobaltite (36). Therefore, we anticipate that our findings will guide a pathway to a deeper un-

derstanding of the nature of the CMR phenomenon and the competing degree of freedom in strongly correlated functional oxides.

Materials and Methods

High-quality polycrystalline bulk $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.4 \leq x \leq 0.5$) were synthesized using the procedure in ref. 37. TEM experiments were carried out in numerous locations of the samples with various preparation procedures (by ion milling and crashing) to ensure the results presented here are indeed representative and can be correlated to the bulk properties. In particular, the Lorentz imaging of the FM submicron domains and the electron diffraction of the nanoclusters obtained from samples prepared by ion milling and crashing are the same. The scanning electron nanodiffraction (SEND), the dark-field imaging of the nanoclusters, and Lorentz imaging of the FM nanoclusters were performed on the samples prepared by ion milling in order to find thin areas. The SEND and the dark-field imaging were done in a conventional TEM (JEOL 2010F and JEOL 3000F) with a magnetic field ca. 2–3 T in the sample space. The Lorentz imaging of FM domains and FM nanoclusters were done in a dedicated Lorentz microscope (JEOL 2100F-LM) with a magnetic field ca. 4 Oe in the sample space (22). The spatial distribution of the CO nanoclusters was observed to be homogeneous for $x = 0.39$ and 0.45 in the crystal domains using scanning electron nanodiffraction and dark-field images.

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