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Magnetic-field-induced collapse of charge-ordered nanoclusters and the colossal magnetoresistance effect in $Nd_{0.7}Sr_{0.3}MnO_3$

T. Y. Koo,[1] V. Kiryukhin,[1] P. A. Sharma,[1] J. P. Hill,[2] and S-W. Cheong[1,3]
[1]*Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854*
[2]*Department of Physics, Brookhaven National Laboratory, Upton, New York 11973*
[3]*Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*
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We report synchrotron x-ray scattering studies of charge/orbitally ordered (COO) nanoclusters in $Nd_{0.7}Sr_{0.3}MnO_3$. We find that the COO nanoclusters are strongly suppressed in an applied magnetic field, and that their decreasing concentration follows the field-induced decrease of the sample electrical resistivity. The COO nanoclusters, however, do not completely disappear in the conducting state, suggesting that this state is inhomogeneous and contains an admixture of an insulating phase. Similar results were also obtained for the zero-field insulator-metal transition that occurs as temperature is reduced. These observations suggest that these correlated lattice distortions play a key role in the colossal magnetoresistance effect in this prototypical manganite.

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Manganite perovskites of the chemical formula $A_{1-x}B_xMnO_3$ (where A is a rare-earth, and B is an alkali-earth atom) have recently attracted considerable attention because they exhibit a number of interesting electronic properties.[1] Perhaps the most dramatic of these is the magnetic-field-induced insulator-metal transition, often referred to as the colossal magnetoresistance (CMR) effect. In its most widely studied form, the CMR effect is a transition from a paramagnetic insulating (PI) to a ferromagnetic metallic (FM) phase. The very large difference between the electrical resistivities of the PI and FM phases lies at the core of the CMR effect, and considerable efforts have been spent in order to explain this difference.[1] The metallic nature of the FM phase was first explained in the 1950s in the framework of the double-exchange mechanism.[2] In this model, itinerant e_g electrons have their spins aligned with the localized t_{2g} core spins of the Mn atoms by virtue of a strong Hund coupling, and the e_g electrons can therefore hop easily between the ferromagnetically aligned Mn atoms. Conversely, the motion of the e_g electrons is suppressed in the disordered paramagnetic environment, and the PI phase should, therefore, exhibit larger resistivity.

However, in the 1990s it was pointed out that the change in resistivity was far too large to be explained by the double-exchange model.[3] Theoretical[3,4] and experimental[5–7] work has suggested that the high resistivity of the PI phase results in part from the presence of the lattice polarons that form when an e_g electron localizes on a Mn^{3+} site, inducing a Jahn-Teller distortion of the MnO_6 octahedron.

At low temperatures, the CMR manganites exhibit a variety of charge and orbitally ordered phases. Further, charge and orbital correlations are in many cases found even in the samples which do not show the corresponding long-range order, often giving rise to microscopically inhomogeneous states.[8–11] In fact, short-range structural correlations were recently observed in the PI phase in $La_{1-x}Ca_xMnO_3$, $La_{2-2x}Sr_{1+2x}Mn_2O_7$, and $Pr_{1-x}Ca_xMnO_3$ manganites.[10,11,7] These correlations are interpreted as arising from nanoscale regions possessing charge and orbital order and associated Jahn-Teller lattice distortions. The latter distortions form a periodic lattice modulation in the ordered regions, making it possible to detect these regions using x-ray and neutron scattering techniques. Because the characteristic correlation length of these regions is typically 10–20 Å, we refer to them as charge/orbitally ordered (COO) nanoclusters. The electrical resistivity has been shown to increase with the concentration of these correlated regions,[7,10] indicating that they are insulating. Thus, in addition to the single polarons discussed above, correlated regions can contribute to the high resistivity of the PI phase.

The exact role of the COO nanoclusters in the magnetic-field-induced insulator-metal transition (the CMR effect) is, however, currently not clear. In this work, we study the effects of a magnetic field on these structural correlations in a single crystal of $Nd_{0.7}Sr_{0.3}MnO_3$ using x-ray diffraction. We find that as the sample undergoes a magnetic-field-induced insulator-metal transition, the structural correlations due to the COO nanoclusters are strongly suppressed. The COO nanoclusters, however, do not disappear completely in the conducting state, suggesting that this state consists of a mixture of metallic and insulating regions. Similar results were also obtained for the insulator-metal transition that occurs as the temperature is reduced in zero magnetic field. These observations suggest that the correlated lattice distortions play a key role in insulator-metal transitions in this prototypical manganite.

Single crystals of $Nd_{0.7}Sr_{0.3}MnO_3$ were grown using the standard floating zone technique. The x-ray diffraction measurements were carried out at beamlines X22B and X22C at the National Synchrotron Light Source. The x-ray beam was focused by a mirror, monochromatized by a Ge (111) monochromator, scattered from the sample, and analyzed with a pyrolytic graphite crystal. The sample was mounted either in a closed-cycle refrigerator ($T=10-450$ K), or in a 13 T superconducting magnet. In the former case, the x-ray energy was 10 keV and a vertical scattering geometry was em-

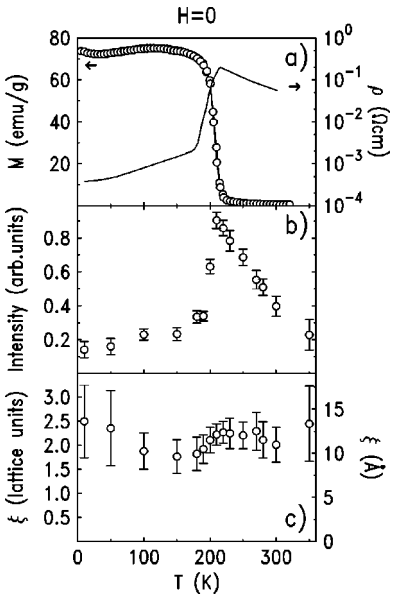

FIG. 1. (a) Temperature dependence of the zero-field electrical resistivity (solid line) and the magnetization (open circles) in a magnetic field of 2000 Oe of $Nd_{0.7}Sr_{0.3}MnO_3$. (b) The intensity of the (4, 4.5, 0) peak due to the correlated structural distortions. The single-polaron background is subtracted as discussed in the text. (c) The correlation length of the ordered regions.

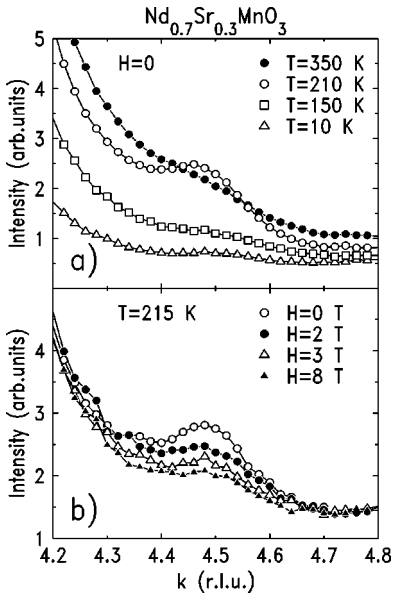

FIG. 2. X-ray scans along the (4, k, 0) direction taken in (a) zero-magnetic field and various temperatures, and (b) $T=215$ K and various fields.

ployed, while in the latter 7.8 keV x rays and a horizontal scattering geometry were utilized. In this paper, Bragg peaks are indexed in the orthorhombic *Pbnm* notation in which the longest lattice constant is *c*. The scattering vectors (*h*,*k*,*l*) are given in reciprocal lattice units.

Before presenting the field-dependent data, we first discuss the zero-field behavior of $Nd_{0.7}Sr_{0.3}MnO_3$. This compound is a paramagnetic insulator at high temperatures. With decreasing temperature, it undergoes a transition to a ferromagnetic metallic state at $T_c \approx 210$ K, see Fig. 1(a). The properties of this compound are, therefore, similar to those of $La_{0.7}Ca_{0.3}MnO_3$. In the latter compound, the PI state was found to exhibit short-range structural correlations with the reduced wave vector of $(h,k,l)=(0,0.5,0)$ and a correlation length of several lattice constants.[10,11] We find that $Nd_{0.7}Sr_{0.3}MnO_3$ exhibits the same kind of structural correlations. Figure 2(a) shows scans along the (4,*k*,0) direction in the reciprocal space. A clear peak is seen at $k=4.5$ at $T=210$ K, just above T_c. The peak is observed on a sloping background which is attributed to the scattering due to single polarons,[7] also known as Huang scattering, and to thermal-diffuse scattering. Similar data were taken at a number of temperatures. The results were fitted to a sum of a peak with the Lorentzian-square line shape, and a monotonically sloping background, the latter described by a power-law function. The intensity of the peak is proportional to both the concentration of the correlated regions and to the square of the magnitude of the lattice distortion in these regions. However, neutron measurements of the pair-distribution function (PDF) in related samples indicate that the magnitude of the lattice distortion does not change with temperature.[6] Therefore, we interpret the temperature dependence of this peak as being simply proportional to the temperature dependence of the concentration of the correlated regions in the sample. The width of the peak is inversely proportional to the correlation length of these regions.

Figure 1(b) shows the intensity of the (4, 4.5, 0) peak as a function of temperature. As observed in $La_{0.7}Ca_{0.3}MnO_3$,[10] this intensity always decreases with decreasing resistivity [Fig. 1(a)]. This behavior is consistent with a picture in which the e_g electrons in the correlated regions are localized: as the nanoclusters disappear, the resistivity decreases. Interestingly, the data of Fig. 1(b) show that the lattice correlations do not disappear even at the lowest temperatures, deep in the FM phase. The FM phase, therefore, must be inhomogeneous, always containing insulating COO nanoclusters. Hence, it appears that the insulator-metal transition in this compound is a complex process in which the insulating phase gradually disappears as the volume fraction of the metallic phase grows. One possible description of this process can be given in terms of percolative two-fluid model discussed in Ref. 12. Similar descriptions based on the results of small-angle neutron scattering and tunneling spectroscopy measurements were also proposed in Refs. 13 and 14. Our observations are also consistent with the results of the neutron PDF measurements in related samples.[6] The latter measurements showed that local Jahn-Teller lattice distortions, albeit at a small concentration, are present in the FM phase. Our data demonstrate that at least some of these distortions stem from the COO nanoclusters.

Figure 1(c) shows the correlation length of the ordered nanoclusters, which is defined as the inverse half width at half maximum of the (4, 4.5, 0) peak. This correlation length is between two and three lattice constants and does not depend on temperature, to within errors. The above definition would give the correct correlation length for exponentially decaying correlations and a Lorentzian line shape. Note,

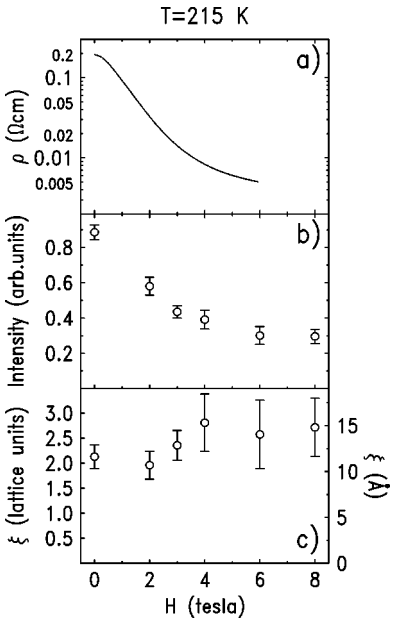

FIG. 3. Magnetic field dependence of (a) the electrical resistivity, (b) the intensity of the (4, 4.5, 0) peak due to the correlated distortions, and (c) the correlation length of the ordered regions. All the data were taken at $T=215$ K.

however, the actual size of the correlated regions depends on the precise form of the correlation function—which is currently unknown. For example, simple calculations of the structure factor for perfectly ordered clusters of a finite size show that in such a case the correlation length, as defined above, would underestimate the cluster size by as much as a factor of 2.

We now turn to the main question of this paper—the role of the COO nanoclusters in the CMR phenomenon. To study the effects of a magnetic field on the nanoclusters, x-ray experiments were carried out in a magnetic field at $T=215$ K, just above the Curie temperature. Figure 3(a) illustrates that at $T=215$ K, the application of a magnetic field results in a substantial drop of the electrical resistivity. X-ray scans at the (4, 4.5, 0) peak position taken at this temperature in various magnetic fields are shown in Fig. 2(b). The intensity of the correlated peak arising from the COO nanoclusters clearly diminishes with increasing field. However, the correlations remain present in the material even at the highest fields, deep in the metallic phase, as was also the case at low temperatures in the FM phase in zero field. Therefore, as in the latter case, the magnetic-field-induced conducting state is inhomogeneous, and the field-induced insulator-metal transition may proceed via a complex process involving coexistence of conducting and insulating phases.

The data of Fig. 2(b) were analyzed in the same manner as the temperature-dependent data. The fitted intensity of the correlated peak and the correlation length of the ordered nanoclusters are shown in Figs. 3(b), and 3(c), respectively. The correlated regions exhibit a correlation length of 2–3 lattice constants, and their concentration, which is proportional to the amplitude of the (4, 4.5, 0) peak, decreases with the increasing field, tracing the behavior of the resistivity. Interestingly, the size of the correlated regions does not change as the magnetic field is varied, to within errors. As discussed above, this size also does not depend on temperature in zero magnetic field. Further, this same cluster size was previously obtained for $La_{0.7}Ca_{0.3}MnO_3$ samples.[11] These observations suggest that there is an intrinsic mechanism defining the size of the nanoclusters common to all these materials.

To explain the effect of the magnetic field on the correlated lattice distortions, we first need to understand crystallographic and magnetic structure of the COO nanoclusters. Several possible model structures describing the observed lattice correlations have been proposed. In one model,[15,10,11] the correlated domains are described as small regions possessing the CE-type charge and orbital ordering with its checker-board-type charge order and the characteristic orbital ordering.[1] This picture is based on the observed lattice modulation wave vector, which is the same for the long-range ordered CE-type structure and for the short-range correlations in $La_{0.7}Ca_{0.3}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$. In addition, in $Pr_{0.7}Ca_{0.3}MnO_3$ these correlations were observed to directly evolve into large regions possessing the CE-type order. A uniform magnetic field is known to destroy CE-type order,[1] and hence such a model is consistent with our measurements. Other descriptions of the correlated regions, such as correlated polarons, and a bipolaron model, have also been proposed.[10,11] In addition, in layered manganites, short-range structural correlations were observed at a different wave vector. These correlations were described as a charge density wave arising from nesting properties of the Fermi surface.[16] We are currently unaware of any predictions for the effect of a magnetic field in these models.

The data of Figs. 1–3 show that the COO nanoclusters are suppressed in the ferromagnetic metallic phase independent of whether the insulator-metal transition is induced with a magnetic field or by changing the temperature. Together with the observed correlation between the concentration of the nanoclusters and the electrical resistivity, these data strongly suggest that the nanoclusters play a key role in insulator-metal transitions in $Nd_{0.7}Sr_{0.3}MnO_3$.

Finally, we note that, in contrast to the intensity of the (4, 4.5, 0) peak, the intensity of the sloping background in Fig. 2(b) does not show any significant change as a function of applied magnetic field ($\Delta I/I<5\%$). As discussed above, this sloping background is attributed to the scattering due to single polarons,[7] and to thermal-diffuse scattering. A quantitative estimate of the thermal-diffuse contribution requires a full calculation of the lattice dynamics that is beyond the scope of this paper. Without this, we cannot make an accurate estimate of the changes in the single polaron concentration in the applied field. However, the data of Fig. 2(b) suggest that the change in the concentration of single polarons in the applied field is not significant, which in turn implies that single polarons play a less important role in the CMR effect than the COO nanoclusters. Further experimental and theoretical work is needed to put this suggestion on a quantitative basis.

In conclusion, we report x-ray diffraction studies of the

temperature- and magnetic-field-dependent behavior of charge/orbitally ordered nanoclusters in a single crystal of $Nd_{0.7}Sr_{0.3}MnO_3$. We find that the field-induced insulator-metal transition (the CMR effect) in this compound, which is a typical CMR manganite, is accompanied by the destruction of the COO nanoclusters. The COO nanoclusters, however, do not completely disappear in the conducting state, suggesting that this state is inhomogeneous and always contains an admixture of the insulating phase. We argue that these observations point to the important role of correlated lattice distortions in the CMR effect.

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