

Structural Correlations and the Colossal Magnetoresistance Effect

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Perovskite manganites are a class of materials that have attracted enormous attention recently, in large part because they exhibit the so-called colossal magnetoresistance (CMR) effect [1]. That is, these materials display dramatic changes in their electrical resistance in an applied magnetic field. The changes are so large that the material can in fact change from an insulator to a metal—a phenomenon that is both fascinating and replete with potential applications. At high temperatures, these materials are paramagnetic insulators, while at low temperatures, they exhibit a number of phases including ferromagnetic metallic and antiferromagnetic insulating. Understanding the paramagnetic insulating (PI) phase, which has properties that remain largely unexplained, is central to unraveling the mystery of the CMR effect.

Recently, evidence of structural correlations in the PI phases of a number of manganites [2,3,4,5] has been reported. These correlations appear as broad—but well-resolved—peaks in the scattering. Interestingly, these peaks were found to disappear as the samples were cooled into the metallic phase, which suggests a connection between the transport behavior and the correlations. Stimulated by these results, we have carried out studies of a number of perovskite manganite systems. We first studied three contrasting manganites and observed essentially identical correlations in each case—regardless of the respective low-temperature properties. Next, studies carried out in a magnetic field demonstrated the important result that these correlations are intimately connected with the CMR effect. Finally, investigations of the doping dependence show that the modulation wavevector of the correlations varies in the simplest possible manner with the doping. Taken together, these results present a picture of common and very stable structural correlations, and suggest that they are responsible for the insulating nature of the high temperature phase and are intimately connected with the CMR effect.

Contrasting Perovskite Manganites

Three $x = 0.3$ -doped single-crystals were studied on beamlines X22C and X20C at the National Synchrotron Light Source: $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (PCMO), $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO), and $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (NSMO). At room temperature, all samples exhibit PI phases,

and have low-temperature transitions to insulating (PCMO, $T_{\text{co}} = 200$ K) or metallic (LCMO, $T_p = 252$ K and NSMO, $T_p = 210$ K) phases, where T_{co} is the charge and orbital order transition temperature and T_p is the metal-insulator transition temperature. Structural correlations were observed in each sample in its PI phase. As an example, Figure 1 [6] displays a reciprocal space mesh scan taken around the (440) Bragg peak in NSMO at 230 K. The orange lobes centered at (4.5 4 0) and (4 4.5 0) are due to the presence of structural correlations in the PI phase. Importantly, in all three samples, similar structural correlations were observed, with an identical wavevector of $(0.5\ 0\ 0)/(0\ 0.5\ 0)$, and the same correlation length of ~ 10 Å.

In PCMO and LCMO, the only difference between the two materials is the trivalent cation size. Despite this, PCMO and LCMO exhibit completely different low-temperature phases—charge and orbitally ordered insulating and ferromagnetic metallic, respectively. This is believed to be the result of the slightly smaller Pr radius, which results in a larger distortion of the Mn-O-

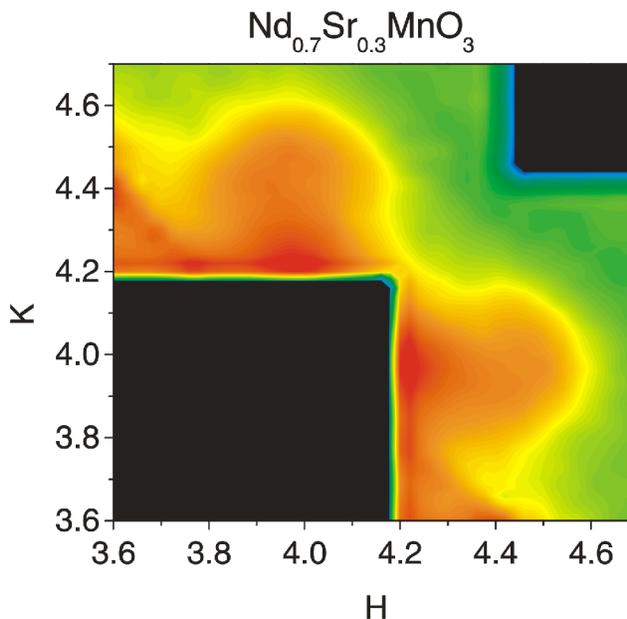


Figure 1. Reciprocal space mesh scan around the (440) Bragg peak in $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, measured at a temperature of 230 K.

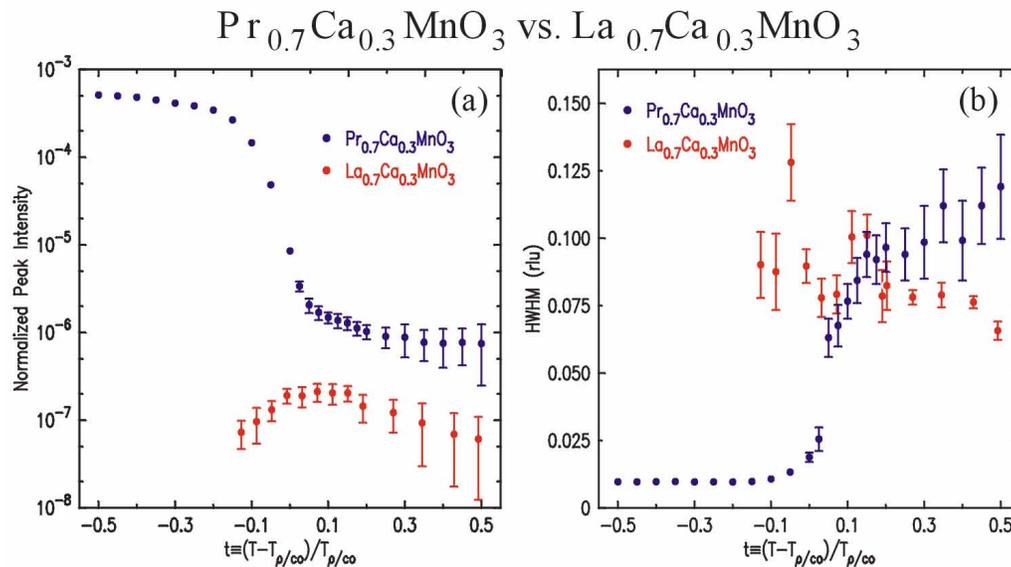


Figure 2. (a) Fitted peak intensity—normalized to the (220) Bragg peak intensity at 220 K ($\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$) and 100 K ($\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$)—as a function of reduced temperature $t = (T - T_{\rho/\text{co}}) / T_{\rho/\text{co}}$. (b) Fitted half-widths of the peaks as a function of reduced temperature $t = (T - T_{\rho/\text{co}}) / T_{\rho/\text{co}}$.

Mn bond angles in PCMO. This change in the distortion affects the relative strength of the electron-phonon coupling—a key ingredient for modeling the transport behavior of CMR materials [7,8]—and it is this same coupling that gives rise to the lattice distortions in the PI phase. Therefore temperature dependent studies of the structural correlations are of interest in order to help elucidate the role of this coupling. Intriguingly, as shown in Figure 2 [9], the structural correlations are found to behave similarly in the PI phases of PCMO and LCMO. In both cases, the intensities decrease gradually with increasing temperature and the correlation lengths remain on the order of ~ 10 Å. These results suggest that the structural correlations are in fact robust with respect to changes in the strength of the electron-phonon coupling, in sharp contrast to the sensitivity of the low-temperature ground state.

Field Dependence

The field-driven insulator-metal transition is central to the CMR effect. In light of this, an obvious question to ask is: what is the effect of a magnetic field on the structural correlations? To address this, we have carried out studies at X22B in an applied magnetic field. Figure 3 [10] shows the results for NSMO ($x=0.3$). Several key facts emerge from this work. First, the intensity arising from the correlations drops dramatically on entering the field-induced metallic phase, following the

field-dependence of the resistivity. In contrast, the intensity of the diffuse (uncorrelated) scattering appears to be unchanged. This result demonstrates that the structural correlations are intimately connected with the CMR phenomenon—and the insulating nature of the PI phase. Intriguingly, the structural correlations do not disappear completely in the metallic phase, suggesting that this phase is inhomogeneous. Similar results were observed in the zero-field insulator-metal transition that occurs as the temperature is reduced. Second, Figure 3 [10] shows that the correlation length of the structural distortions is unchanged as a function of field—again pointing to the stability of these correlations and suggesting that the size of those regions is determined by a mechanism that is insensitive to an applied field.

Doping Dependence

In the studies described above, the structural correlations were always observed to have the same modulation wavevector and correlation length, irrespective of applied field, temperature or manganite system. This immediately poses the question as to what determines the observed structure. A natural parameter to vary in order to address this question is the doping. This parameter controls the occupancy of the more delocalized e_g levels, which decreases linearly with x , and manganite systems are extremely sensitive to this

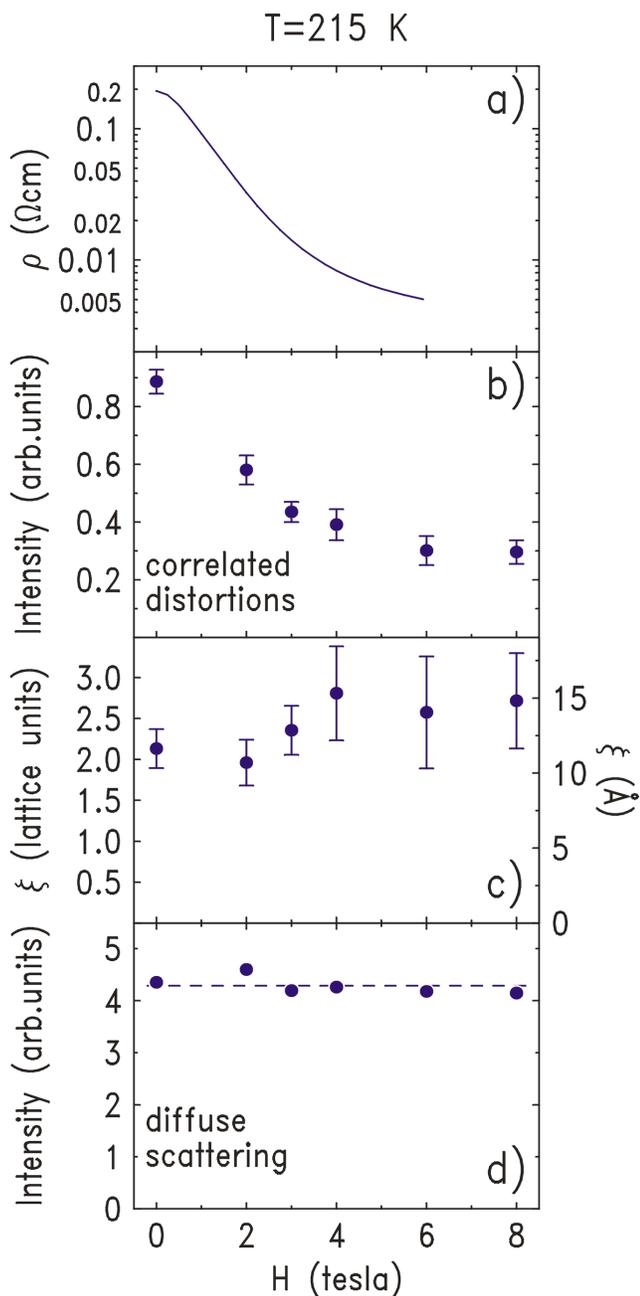


Figure 3. In $\text{Nd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, the magnetic field dependence of (a) the electrical resistivity, (b) the intensity of the $(4\ 4.5\ 0)$ peak due to structural correlations, (c) the correlation length of the ordered regions, and (d) the diffuse scattering due to uncorrelated distortions and TDS. All data were collected at a temperature of 215 K

doping—displaying a wide variety of different low temperature properties as a function of x . In order to investigate the doping dependence of the correlations, single-crystals of $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, $x = 0.3, 0.45$, and 0.5 , were studied on beamlines X22C and X20C. The three samples have transitions from the PI phase to the ferromagnetic metallic phase at temperatures of 210, 280, and 250 K for $x = 0.3, 0.45$ and 0.5 , respectively. Scans carried out near Bragg peaks, such as those shown in Figure 4 [6], indicated the presence of structural correlations in the PI phases of each sample. Interestingly, while the correlation lengths of the ordered regions are similar, the wavevectors are found to vary with x . The magnitude of the wavevector in the $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ system, in fact, varies linearly with x in exactly the same way as in other manganites with ferromagnetic metallic low-temperature ground states (see Figure 5 [6]). This result suggests that doping is the key parameter that defines the structure of the correlated regions in perovskite manganites.

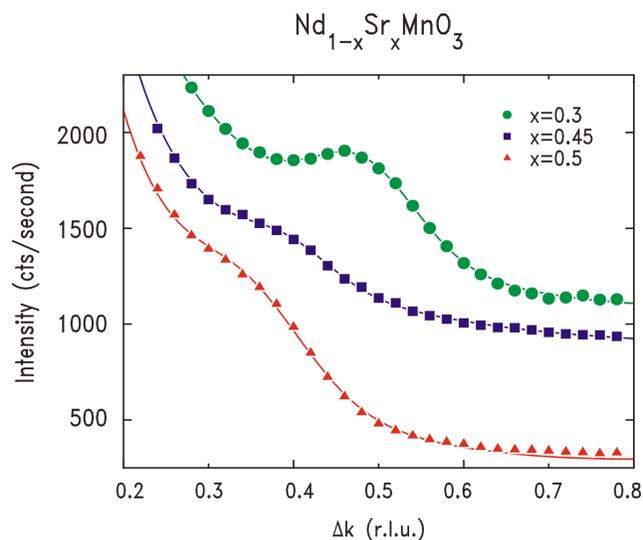


Figure 4. In $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, scans along $(4\ 6+\Delta k\ 0)$ for $x = 0.45$ and 0.5 , and along $(4\ 4+\Delta k\ 0)$ for $x = 0.3$. The temperatures at which data were collected are 210, 275, and 260 K for the $x = 0.3, 0.45$ and 0.5 samples, respectively. The solid lines are the results of fits, and for clarity, $x = 0.3$ and 0.45 data are shifted up by 750 cts/second.

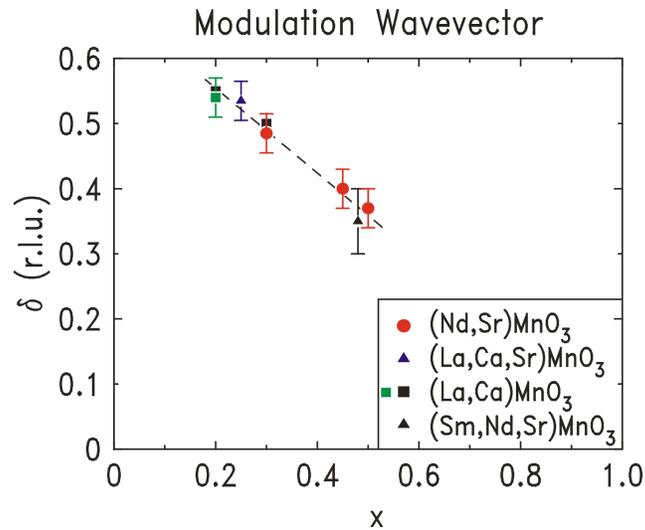


Figure 5. The wavevector, δ , of the lattice modulation in the correlated regions as a function of doping, x . Colored symbols represent data reported in [6], while the data shown with black symbols are taken from [2-5,9].

Conclusion

In summary, we have observed very similar structural correlations in the PI phase of a variety of doped manganites. The correlations appear to be intimately connected with the insulating nature of the PI phase and the CMR effect: i.e., the scattering intensity is greatly reduced on entering a metallic phase either as a result of cooling or in an applied magnetic field. In each case, the structural correlations are strikingly similar, exhibiting a temperature-, doping-, and field-independent correlation length of $\sim 10\text{\AA}$. Further, in all systems with a low-temperature ferromagnetic metallic state studied to date, the modulation wavevector is found to vary linearly with the doping, x , suggesting that the structure of these correlated regions is determined by this single parameter. Future studies will be required to determine the precise nature of the robust structural correlations, but the results of the present work suggest that this would be a worthwhile exercise and that these correlations will lie at the heart of any understanding of the fascinating phenomenon of CMR.

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