Percolative phase transition on ferromagnetic insulator manganites: uncorrelated to correlated polaron clusters

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(Dated: June 30, 2018)

In this work, we report an atomic scale study on the ferromagnetic insulator manganite LaMnO$_3$ using $\gamma-\gamma$ PAC spectroscopy. Data analysis reveals a nanoscopic transition from an undistorted to a Jahn–Teller–distorted local environment upon cooling. The percolation thresholds of the two local environments enclose a macroscopic structural transition (Rhombohedral–Orthorhombic). Two distinct regimes of JT–distortions were found: a high temperature regime where uncorrelated polaron clusters with severe distortions of the Mn$_3^{3+}$O$_6$ octahedra survive up to $T \approx 800$ K and a low temperature regime where correlated regions have a weaker JT–distorted symmetry.

PACS numbers: 75.47.Lx, 76.80.+y, 64.60.Ak, 31.30.Gs

Intense experimental and theoretical work has been devoted to manganite systems due to their colossal magnetoresistance (CMR), polaron dynamics and charge/orbital ordering phenomena. The undoped manganites (AMnO$_3$ where A is a trivalent ion of La, Pr, . . .) typically show antiferromagnetic insulator behavior and cooperative Jahn-Teller (JT) distortion of MnO$_6$ octahedra. Oxygen excess or the presence of divalent ions at A–sites reduce the static JT–distortion by the creation of Mn$^{4+}$ ions. This effect favors the ferromagnetic interaction via dynamic electron transfer between Mn$^{3+}$ and Mn$^{4+}$, the so called double-exchange (DE) interaction. Although DE interaction explains qualitatively the CMR, it does not fully account for the large resistivity of the paramagnetic and ferromagnetic insulator phases. Polaron formation must certainly play an important role in this respect. Polaron clusters survive in the undistorted $R$ phase up to temperatures as high as 766 K. These distortions are as strong as those observed in the orbital ordered LaMnO$_3$. Lowering $T$, the clusters continuously expand until a microscopic transition takes place at $T_c \approx 170$ K. Below the transition, the distortions are accommodated into a weaker JT–distorted phase.

LaMnO$_3+\Delta$ polycrystalline samples ($\Delta = 0$, 0.08 and 0.12) were produced by the solid state reaction method. Powder x-ray diffraction measurements show that the samples are chemically homogeneous. In agreement with Refs. 11, 12, we find an antiferromagnetic insulator ground state for the orthorhombic JT–distorted $\Delta = 0$ compound ($T_N \approx 139$ K), a ferromagnetic insulator behavior for the weakly distorted $\Delta = 0.08$ sample ($T_c \approx 150$ K) and a ferromagnetic insulator state for the compound with $\Delta = 0.12$ ($T_c \approx 145$ K). This latter system presents as well an $O$–$R$ phase transition around room temperature. As shown in Refs. 11, 13, the oxygen excess $\Delta$ results in equivalent amounts of La and Mn vacancies, with the fraction of Mn$^{4+}$ equal to 2$\Delta$. $\gamma-\gamma$ PAC measurements were performed using a high-efficiency 6-BaF$_2$ detector spectrometer 14. PAC samples (one per measurement) were implanted at room temperature with $^{111}$In$^{111}$Cd to a homogeneous low dose of $10^{12}$ cm$^{-2}$ at 60 keV in the ISOLDE/CERN facility. Re-
remaining point defects created during implantation were eliminated by annealing at 700 °C under O₂ controlled atmosphere for 20 minutes. The peak density of probing Cd only attains 1 ppm of the La concentration. Consequently, the implanted Cd atoms are simply incorporated into La vacancies. The perovskite A (La) site is specially appropriate to detect lattice distortions in the surrounding MnO₆ octahedra since slight changes in the charge geometry will significantly alter the EFG parameters.

The ¹¹¹ᵐCd probes decay to ¹¹¹Cd through an intermediate state by the emission of two consecutive γ rays. The half life for the ¹¹¹ᵐCd isomeric state is T¹/₂ = 48 min, while for the intermediate state is T¹/₂ = 84 ns. The angular correlation between the two γ rays can be perturbed by both the EFG and the Magnetic Hyperfine Field (MHF). These fields respectively couple to the nuclear electric quadrupole (Q) and the magnetic dipole (µ) moments of the intermediate nuclear state. The Hamiltonian for such static interactions, in the proper reference frame of the EFG tensor Vᵢⱼ with |Vᵢⱼ| ≥ |Vᵧᵧ| ≥ |Vₓₓ|, reads

\begin{equation}
\mathcal{H} = \frac{e \alpha}{6} \left[ 3 I_x^2 - I (I + 1) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right] + \mu \cdot \vec{B}_hf,
\end{equation}

where \( \omega_0 = 3 e Q V_{zz}/(2 I (2 I - 1) \hbar) \) is the fundamental precession frequency, I represents the nuclear spin of the probe intermediate state (I = 5/2 for ¹¹¹Cd), \( \eta = (V_{xx} - V_{yy})/V_{zz} \) is the EFG asymmetry parameter and \( \vec{B}_hf \) is the magnetic hyperfine field. The perturbation of the γ − γ directional correlation is described by the experimental R(t) function, where t is the time spent by the nucleus in the ¹¹¹Cd intermediate state. For a hyperfine interaction, R(t) may be expanded as

\[ R(t) = \sum A_{kk} G_{kk}(t) \]

with \( A_{kk} \) being the angular correlation coefficients. The perturbation factor \( G_{kk}(t) \) is the signature of the fields interacting with the probes: MHF and a EFG in the ferromagnetic phase and EFG alone for \( T > T_c \). Below \( T_c \), in the presence of the two fields, we apply combined interaction theory to obtain the MHF and EFG parameters. Above \( T_c \), on the other hand, \( G_{kk}(t) \) may be expressed as

\[ G_{kk}(t) = S_{k₀} + \sum S_{kn} \cos (\omega_n t) e^{-\omega_n \delta t} \]  \hspace{1cm} (2)

considering only pure electric quadrupole interactions. The frequencies \( \omega_n \) and amplitudes \( S_{kn} \) are determined by \( \mathcal{H} \) diagonalization. For spin \( I = 5/2 \), three frequencies are observable that are function of \( \omega_0 \) and \( \eta \) \[ ¹⁶ \]. The exponential term in equation (2) accounts for an attenuation of the R(t) function that appears in all spectra. This effect is due to randomly distributed intrinsic vacancies and defects that produce a Lorentzian distribution of static EFGs with central value \( \omega_0 \) and relative width \( \delta \). Independently, in manganites, short-range charge diffusion coupled to lattice distortions (polarons) can lead to EFG fluctuations. These fluctuations contribute to further attenuate R(t) when their time scale is comparable to the life time of the PAC probe intermediate state. When the characteristic fluctuation time (\( \tau \)) is shorter than the nuclear spin precession time (2 \( \pi/\omega_0 \)), the R(t) function can be satisfactorily approximated by a single exponential damping term \( e^{-\lambda t} \) multiplying the static expression \[ ¹⁶ \] with \( \lambda \propto \omega_0^2 \tau \).

Some experimental R(t) curves are displayed in Fig. 1 for the compound with \( \Delta = 0.12 \). We find in the temperature range from 10 K to 766 K the coexistence of three main local environments (\( u, d, r \)), i.e. three fractions of probes (\( f_u, f_d, f_r \)) interacting with different local EFG distributions. The environment \( r \) is detected by a low residual fraction of the Cd probes (5%), which is temperature independent. Its EFG parameters are approximately \( V_{zz} ≈ 102 \text{ V/Å}^2 \) and \( \eta_r ≈ 0.9 \) at room temperature. These values suggest a very asymmetric local charge distribution. The origin of this environment might be related to probes located at the vicinity of Mn/La vacancies and/or other defects. Actually, assuming that the positions of the vacancies are not correlated, the probability that a Cd sitting in a La vacancy has in its surrounding a Mn or next shell La vacancies is roughly 2%.

In Fig. 2, the temperature dependence of the EFG asymmetry parameter \( \eta \) (top) and principal component \( V_{zz} \) (bottom) for the u and d environments is displayed. For comparison, the EFG parameters found in \( \Delta = 0.08 \) and \( \Delta = 0 \) samples are also included in the same figure. The u environment that is dominant at high \( T \) shows an almost axially symmetric EFG (\( \eta_u ≈ 0 \)). This value characterizes an EFG with an axis of threefold or higher rotational symmetry, which is compatible with the Rhombohedral lattice structure observed at high tem-
temperature. The MnO$_6$ octahedra in the $R$ structure are constrained by symmetry to be JT–undistorted (equal Mn–O bond lengths), thus we will name this local environment undistorted. In contrast, the $d$ (distorted) environment is characterized by a weaker $V_{zz}$ and highly asymmetric EFG ($\eta_d > 0.45$). At high $T$, the values of $\eta_d$ and $V_{zz}^d$ coincide with the ones observed for the undoped fully JT–distorted Orthorhombic system, $\Delta = 0$, (full circles in Fig. 2). Consequently, at high temperatures, the $d$ local environment must be characterized by a distortion involving several (minimum eight) Mn$^{3+}$O$_6$ octahedra similar to the collective JT-distorted lattice of the orbital ordered LaMnO$_3$ [19]. Lowering $T$ below 300 K, the asymmetry parameter $\eta_d$ decreases stabilizing at a value close to that observed for the $\Delta = 0.08$ sample (solid stars in Fig. 2). This behavior suggests that the JT-distortions are weakening till they reach a similar degree as in the $\Delta = 0.08$ sample. The EFG principal components $V_{zz}^d$ and $V_{zz}^u$ slightly increase with decreasing temperature. This is a typical feature of pervoskite and related systems [20]. Below $T_s \approx 145$ K both $d$ and $u$ local environments experience increasing magnetic hyperfine fields upon decreasing temperature (inset of Fig. 2), presenting at 10K values of $B_{zz}^d = 3.8(2)T$ and $B_{zz}^u = 4.0(3)T$ compatible with a full ferromagnetic environment of the surrounding Mn ions [21, 22].

Further insight in the behavior of $d$ and $u$ environments may be achieved by studying the $T$ dependence of the volume fractions $f_u$ and $f_d$. As may be seen in Fig. 3, the $u$ environment is dominant at very high temperatures ($f_u \approx 86\%$ at $T = 766$ K), though $d$ regions survive up to that $T$ ($f_d \approx 9\%$). This confirms the high stability of the inhomogeneous phase-segregated state. Our data, at high $T$, are compatible with a scenario where random distributed JT–distorted nanoclusters are embedded in a undistorted matrix as predicted by [24]. At very low $T$, the fraction of $u$ environment reaches a remanent value ($f_u \approx 10\%$), which is typically observed in CMR manganites [25] and is a signature of the ferromagnetic-metallic (FMM) and FMI phase coexistence. When the temperature changes, $f_u$ (symmetrically $f_d$) suffers a smooth variation leading from an undistorted to a JT–distorted dominant microscopic environment. If we assume that this variation is a continuous phase transition, the order parameter would be $f_u - f_u^c$ and must follow a power law behavior $f_u - f_u^c \sim (T - T_c)^{\beta}$ when the critical temperature $T_c$ is approached from above. To check this possibility, we display $f_u$ in a log-log plot in Fig. 3 (inset). The data adjust pretty well to a power law with $T_c \approx 170 \pm 10 K$ (relatively close to $T_c$) and $\beta \approx 0.42 \pm 0.02$. Associated to the transition, there must also exist a correlation length, correlation of the $d$ spatial distribution, that must diverge at $T_s$. As may be seen in Fig. 2, when $T$ decreases $\eta_d$ starts to fall as the $d$ component percolates (at $f_d \approx 31.16\%$ [26]) and only stabilizes around $T_s$. Macroscopically, on the other hand, x–rays measurements detect a structural transition ($R$–$O$) that lies exactly between the temperatures corresponding to the percolation thresholds of the two main nanoscopic components. These are precisely the temperatures in which the minority invading cluster suffers a sudden size divergence becoming macroscopically observable.

The temperature dependence of the attenuation of $R(t)$ provides additional information about the dynamics of the $u$ and $d$ environments. A complete sketch of the dynamic and static attenuation for $R(t)$ in both environments is depicted in Fig. 4. The best fit to the $R(t)$

![FIG. 2: Asymmetry parameter $\eta$ (top) and EFG principal component $V_{zz}$ (bottom) for LaMnO$_3$ as a function of $T$. EFG parameters for $\Delta = 0.08$ and $\Delta = 0$ are also showed. Inset: $T$ dependence of the MHF for the $d$ environment.](image)

![FIG. 3: Temperature dependence of the probe volume fractions $f_u$, $f_d$ and $f_r$. Triangles: orthorhombic phase percentage from x-ray diffraction. The shadowed region is limited by the temperatures where the percolation thresholds occur. Inset: log-log plot of $(f_u - f_u^c)$ vs $(T - T_c)$.](image)
s spectra discards the presence of time dependent interactions for the \( u \) environment (\( \delta_u \approx 4\% \) independently of \( T \) and \( \lambda_u = 0 \)). Thus, in all temperature range, the charge transfer between \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \) (activated hopping) in this environment should occur with a frequency higher than we can probe. For the \( d \) environment, on the other side, the best fits were obtained admitting a fluctuating EFG (\( \lambda_d \neq 0 \) and \( \delta_d = 2\% \)) in the temperature region spanning from \( T = 266 \, K \) to \( T = 350 \, K \). Notice that these time dependent effects cannot be attributed to Cd/O and/or defects diffusion since they would be detected in both fractions. The temperature dependence of the dynamic attenuation parameter, \( \lambda_d \), allows us to estimate an activation energy \( E_a \). This energy is obtained from \( \lambda_d = \lambda_{\infty} e^{E_a/kT} \), and was found to be \( E_a \approx 0.31 \, eV \) (see inset Fig. 4), close to the polaron binding energy reported in the literature for low doped manganites (see inset Fig. 4), close to the polaron binding energy reported in the literature for low doped manganites. We identify such EFG fluctuations with polaron diffusion related to charge (hole) transport. The EFG fluctuation time (\( \tau \)) can be estimated from the maximum of \( \lambda_d(T) \) (see inset Fig. 4). Considering that a carrier (hole) can hop to any of the 8 octahedra around a La site (8 possible EFG states), we find \( \tau \approx 0.5 \, \mu s \) at \( T = 266 \, K \) corresponding to ultra–slow polaron diffusion. Similar polaron residence times have been recently reported in Ref. 21, although the \( E_a \) measured there was smaller possibly due to the intense magnetic field (\( 7 \, T \)) needed to perform NMR measurements. The competition of the distinct dynamics of the \( u \) (fast hopping) and \( d \) (related to polaronic conduction) environments is responsible for the macroscopic ferromagnetic insulator behavior observed in these systems. Below \( T_c \), both local environments become ferromagnetic and a phase coexistence between metallic (\( u \)) and insulator (\( d \)) regions exists. However, the majority fraction (\( d \)) is characterized by ultra–slow diffusion of charge carriers imposing an overall insulator behavior.

In conclusion, we report an extensive study on the ferromagnetic insulator manganite LaMnO\(_{3.12}\) using \( \gamma - \gamma \) PAC spectroscopy. We analyze in detail the evolution and stability of polaron clusters in an extremely wide range of \( T \) that includes a structural transition between \( R \) and \( O \) phases. PAC measurements reveal a continuous transition between two different dominant local atomic environments (one JT–distorted (\( d \)) and another undistorted (\( u \))). Information is also obtained on the local structure, the dynamics and the correlations of these two environments. The macroscopic transition arises as a consequence of the microscopic changes, since it occurs between the percolation thresholds of the two local components. The \( d \) environment survives up to very high \( T \) where it can be identified with uncorrelated polaron clusters. The correlation of \( d \) clusters increases for \( T \) below the \( d \) percolation threshold diverging at \( T_c \). These results provide further insight in the understanding of the nature/evolution of polaronic distortions and FMM-FMI phase competition responsible for the insulator behavior of these systems.

The authors gratefully thank W. Troeger, U. Wahl, J.M. López, R. Valiente, J. Vieira and R. Catherall for fruitful discussions. This work was funded by the Portuguese Research Foundation (FCT), FEDER (projects POCTI/FN/FNU/50183/03, PDCT/FP/FNU/50145/2003), and EU (Large Scale Facility contract HPRI-CT-1999-00018). J.J.R. received partial funding from the NSF under grant 0312510. A.M.L.L. and E.R. acknowledge their grants to FCT.

References

1. C. Zener et al., Phys. Rev. 82, 403 (1951).
2. A.J. Millis et al., Phys. Rev. Lett. 74, 5144 (1995).
3. S.J.L. Billinge et al., Phys. Rev. Lett. 77, 715 (1996).
4. G. Zhao et al., Nature 381, 676 (1996).
5. D. Louca et al., Phys. Rev. B 56, R8475 (1997).
6. V. Kryukhin et al., Phys. Rev. B 67, 064421 (2003).
7. L. Martín-Carrón et al., Phys. Rev. B 66, 174303 (2002).
8. N. Mannella et al., Phys. Rev. Lett. 92, 166401 (2004).
9. V. Kryukhin et al., Phys. Rev. B 70, 214424 (2004).
10. E. Dagotto, New J. of Physics 7, 67 (2005).
11. C. Ritter et al., Phys. Rev. B 56, 8902 (1997).
12. F. Prado et al., J. Sol. Sta. Chem. 146, 418 (1999).
13. J.A.M. van Roosmalen and E.H.P. Cordfunke, J. Solid State Chem. 110, 109 (1994).
14. T. Butz et al., Nucl. Instr. Meth. A 284, 417 (1989).
15. G. Schatz and A. Weidinger, Nuclear Condensed Matter Physics, John Wiley & Sons England (1996).
16. T. Butz et al., Hyp. Int. 189, 52 (1989).
17. A. Baudry and P. Boyer, Hyp. Int. 35, 803 (1987).
18. Note that the fact that \( V_{zz}^d < V_{zz}^u \) alone is not proof enough of a higher symmetry. It has been experimentally observed a sudden decrease in the \( V_{zz}^d \) and increase in \( \eta \) related to a change from a \( R \) to an \( O \) structure in stoichiometric LaCrO\(_3\) and LaFeO\(_3\) perovskites.
When the Sternheimer corrections are taken into account, our values for the EFG parameters agree with the results reported in the literature on the undoped compound using NMR and from ab-initio FLAPW theoretical calculations.

R. Dogra et al. Phys. Rev. B 63, 224104 (2001).
G. Allodi et al. Phys. Rev. Lett. 87, 127206 (2001).
P. Ravindran, private communication.
M. K. Gubkin et al., J. Mag. Mag. Mat. 154, 351 (1996).
E. Dagotto et al. Phys. Reports 344, 1-153 (2001).

M.M. Savosta and P. Novak, Phys. Rev. Lett. 87, 137204 (2001).
D. Stauffer and A. Aharony, Introduction to percolation theory, Taylor & Francis (1992).
A. Weisse et al., Phys. Rev. B 68, 024402 (2003).
J.S. Zhou and J.B. Goodenough, Phys. Rev. B 68, 144406 (2003).
H. Winkler and E. Gerdau, Z. Physik 262, 363 (1973).