Phonon-Metamorphosis in Ferromagnetic Manganite Films:
Probing the Evolution of an Inhomogeneous State

Ch. Hartinger, F. Mayr, and A. Loidl

EP V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany

T. Kopp

EP VI, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany
(Dated: October 25, 2018)

The analysis of phonon anomalies provides valuable information about the cooperative dynamics of lattice, spin and charge degrees of freedom. Significant is the anomalous temperature dependence of the external modes observed in La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) films. The two external modes merge close to the ferromagnetic to paramagnetic transition at $T_C$ and, moreover, two new modes evolve in this temperature range with strong resonances at slightly higher frequencies. We propose that this observed phonon metamorphosis probes the inhomogeneous Jahn-Teller distortion, manifest on the temperature scale $T_C$. The analysis is based on the first observation of all eight phonon modes in the metallic phase of LSMO and on susceptibility measurements which identify a Griffiths-like phase.

PACS numbers: 75.47.Lx, 72.80.-r, 78.20.-e, 75.40.Cx, 75.10.Nr

The colossal magnetoresistance (CMR) in the manganites is a paradigm of the cooperative dynamics of charge, spin and lattice degrees of freedom (DOF). Whereas the interplay of charge and spin DOF was realized early on with the discovery of the double exchange mechanism (DE), the role of the lattice DOF was appreciated only recently: Millis et al. argued that the DE alone cannot explain the resistivity data of investigations are: scanning tunnelling spectroscopy [8,9] which examine the local Jahn-Teller (JT) distortions related to a microscopic charge distribution.

Most of the previous research focussed on La$_{1-x}$Ca$_x$MnO$_3$, as the CMR effect is strongest in the Ca-doped compounds, at $x \simeq 1/3$. However, since for these compounds the ferromagnetic to paramagnetic transition ($T_C$) nearly coincides with the metal-insulator transition ($T_{MIT}$), it is of particular relevance to investigate La$_{1-x}$Sr$_x$MnO$_3$ where the two temperature scales are different. In this work, we address the observability of the inhomogeneous bulk state through far infrared (FIR) optical spectroscopy in La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) films. We associate phonon anomalies with the formation of the inhomogeneous state. To our knowledge, anomalies of the phononic excitations in LSMO have not been analyzed in the vicinity of the magnetic transition. Probing the inhomogeneous state with phonons should provide insight into the temperature-dependent evolution of electronic correlations which couple to the local lattice structure.

The origin of phononic anomalies may be traced (i) to a strong coupling of phonon modes with an electronic continuum but also (ii) to a modification of the local symmetry, e.g., due to an alteration of the JT distortion. Mechanism (i), which leads to an asymmetric “Fano lineshape” of distinct phonons, is observed in La$_{2/3}$Ca$_{1/3}$MnO$_3$ films [11]. In LSMO films the electron-phonon coupling is much weaker, as evidenced by the polaronic excitations [12], and correspondingly the asymmetry of the phonon absorption lines is too small to be observable. However, the latter effect (ii), which we denote as “metamorphosis of phonons”, is seen in our LSMO films. The metamorphosis not only includes a temperature dependent frequency shift but, more notably, the merging of phonon lines and the evolution of new resonances. We observe a transfer of spectral weight from the pronounced phonon modes at low temperature into the “new modes” at high temperature. This metamorphosis is controlled by the magnetic temperature scale $T_C$.

The study of thin films is indispensable in order to resolve the full set of phonon modes even in the metallic low-temperature phase. Enhanced screening in the single crys-
tals suppresses the phonon resonances wherefore there are no reports on the infrared active phonons in La$_{2/3}$Sr$_{1/3}$MnO$_3$ available in the literature. Apart from rendering the phonons observable, thin films also serve the purpose of extending the inhomogeneous state to a wider temperature range as lattice strain and imperfections support the Griffiths-like phase.

Measurements were performed on a single crystal and two thin films of La$_{2/3}$Sr$_{1/3}$MnO$_3$, which were grown onto (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_5$)$_{0.7}$. The film thickness was 300 nm for LSMO #1 and 400 nm for LSMO #2. X-ray analysis revealed a rhombohedral structure for all samples. The reflectivity measurements were carried out between 50 cm$^{-1}$ and 40000 cm$^{-1}$, using the Fourier transform spectrometers Bruker IFS 113v and IFS 66v/S. Careful determination of the optical conductivity $\sigma$ was achieved by using results of a submillimeter interferometer for the low-energy range in the optical conductivity.

At low temperature long-range ferromagnetic ordering induces the metallic state. With increasing temperature the FIR optical conductivity $\sigma$ diminishes up to the metal-insulator transition at $T_{\text{MIT}}$. Figure 1 displays $\sigma$ in the energy range of the phononic excitation for LSMO #2 (lines) and LSMO #1 (open circles). We identify eight peaks of active transverse-optical (TO) phonon modes, corresponding to all IR active vibrations from R$3$-symmetry. In Tab. II we present a comparison between the experimental values of the infrared-active phonon frequencies of LSMO #2 at $T = 405$ K and the calculated frequencies for pure rhombohedral LaMnO$_3$ by Abra- shev et al. 13. The calculated positions for the undoped compound should be taken as a rough estimate for LSMO since the lattice constants and atomic positions are modified by doping. Several eigenfrequencies are known from neutron scattering measurements, which are in good agreement with our data 14.

A particular temperature dependence of the mode frequency is observed for the external modes. With increasing temperature the two external modes approach each other and the merged modes shift to lower frequency above $T_C \approx 345$ K (cf. Fig. 1). A degeneracy of modes corresponds to a higher lattice symmetry. Moreover, at approximately room temperature, two new modes appear, pointing to a lower lattice symmetry. The new modes gain weight for temperatures close to $T_C$ so that they dominate the group of external modes above $T_C$. This phenomenon of phonon metamorphosis is observable in both films, in LSMO #2 as well as LSMO #1 (cf. open circles in Fig. 1). The groups of stretching and bending modes are weakly affected by the FM-PM transition except for the torsional mode which is shifted to higher frequencies.

The external group on an enlarged scale is displayed in Fig. 2. The two new modes at approximately 169 and 186 cm$^{-1}$ are referred to as $\nu_3$ and $\nu_4$, respectively. The selected temperatures fully cover the interval in which both, the magnetic and metal-to-insulator transitions, take place ($T_C \approx 345$ K and $T_{\text{MIT}} \approx 401$ K). The presumption that the evolution of these modes is controlled by the spin DOF is substantiated by the temperature analysis of the mode frequencies. The temperature dependence of the splitting of the low frequency pair of modes $\Delta \nu$ is presented in Fig. 3 (left panel, full circles). The solid line is the normalized magnetization ($M(T)/M(0)$), displayed in this left panel. Although no theoretical modelling is available to relate magnetization and mode splitting quantitatively, the observation that $M$ and $\Delta \nu$ drop on the same temperature scale $T_C$ to zero suggests a correlation between spin polarization and these phonon modes. The same observation is true for the temperature dependence of the mode frequencies $\nu_3$ and $\nu_4$. The temperature scale is clearly $T_C$, and not $T_{\text{MIT}}$, as shown for $\nu_3(T)$ in the right panel of Fig. 3. Neutron scattering measurements show that the structural distortion does not change at $T_C$ and thereby confirm that neither the lattice structure nor

### Table I: Correspondence between calculated and measured phonon modes (LSMO #2) for the space group R$3$-c (in cm$^{-1}$) at $T = 405$ K, and the values in parenthesis to neutron scattering with La$_{0.3}$Sr$_{0.7}$MnO$_3$ samples.

| Calculated | Measured | Assignment |
|------------|----------|------------|
| $A_{2u}$   | $E_u$    | $A_{2u}$   | $E_u$ |
| 317        | 373      | vibration (Mn) | 373 |
| 162        | 180      | external     | 150 |
| 310        | 357      | bending      | 338 (336) |
| 641        | 642      | stretching   | 580 (576) |
| 240        | 285      | torsional    | 285 |
FIG. 2: Metamorphosis of phonon modes: optical conductivity $\sigma$ of the external modes and the new modes ($\nu_1$, $\nu_2$). The latter modes are absent at low temperature. With increasing temperature, spectral weight is transferred from the low-energy external group to the new modes.

The thermal expansion of the lattice can be attributed to the temperature behavior of the external modes in the vicinity of $T_C$. It is suggestive to relate the observed phonon metamorphosis to the formation of an inhomogeneous state, as this state may support two types of external modes.

An inhomogeneous magnetic state may be identified from susceptibility measurements in low magnetic fields. Salaam and Chun [17] could not detect the onset of a Griffiths-like phase for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ single crystals. However, thin films are intrinsically more inhomogeneous and the question arises if they display Griffiths singularities. In fact, our measurements of the susceptibility $\chi$ in LSMO #2 (400 nm film) and LSMO #1 (300 nm film) in Fig. 3 support such a scenario. Whereas the single crystal with the same Sr-concentration shows the conventional Curie-Weiss behavior with an effective magnetic moment $p_{\text{eff}} = 5.1 \mu_B$ (open circles), the films display a sharp downturn in $\chi^{-1}(T)$ at a temperature scale $T^* \sim 370$ K above their respective Curie temperatures $T_C^{#1} = 310$ K and $T_C^{#2} = 345$ K. The onset $T^*$ is identical for both films and corresponds to the Curie temperature $T_C \sim 370$ K of the single crystal. Such a behavior may be interpreted in terms of a Griffiths-like phase, where the enhanced disorder in the films, in comparison to the single crystal, accounts for the reduced $T_C$ and the formation of inhomogeneous magnetic states at $T^* \sim T_C^{sc}$ [4].

Whereas the non-Curie-Weiss behavior of the susceptibility points to the existence of spin clusters in the films, it does not predict the temperature at which an inhomogeneous state first develops. Probably “electronic phase separation between phases with different densities on a nano scale” [4] is established before the disorder-induced Griffiths-like phase for the spin system sets in. Even if the underlying model were known, it would be difficult to make conclusive predictions as the phase separation in these systems seems to be dynamic [13]. For a better characterization of the bulk inhomogeneous state in the full temperature range up to the FM-PM transition we propose to analyze the evolution of the considered phonon modes in more detail, specifically their magnetic field dependence should be addressed in future work. We conclude the paper with a discussion of the origin of the new modes.

We suggest that the observed phonon metamorphosis is to be understood in the context of a $T$-dependent, inhomogeneous dynamical Jahn-Teller distortion (IDJT). The IDJT is probed by distinct phonon excitations which “sense” the inhomogeneities as soon as the charge carriers slow down with increasing temperature and the lattice DOF experience
a crossover from adiabatic to nonadiabatic behavior.

Louca and Egami [10] investigated deviations of the local structure from the average crystal structure in La$_{1-x}$Sr$_x$MnO$_3$ by pulsed neutron scattering with pair distribution function analysis (PDF) and Shibata et al. [20] with x-ray absorption fine structure (XAFS). Although their findings differ for the metallic phase quantitatively, both groups identify a temperature-dependent, inhomogeneous local lattice distortion. Louca and Egami introduced the notation of an “anti-JT distortion” for the undistorted sites (with Mn$^{4+}$) where the holes, i.e. the charge carriers, reside at high temperature. Correspondingly, the splitting of the resonances decreases because sites without anti-polarons (Mn$^{3+}$) experience a strong JT-distortion and support external modes at a higher frequency (as is well known from the undoped systems [21, 22, 23]). These “new modes at higher frequency” act on the average charge carrier concentration, not on the instantaneous hole positions. In this regime, only a weak JT-distortion is observed and the external modes are split as seen for the 6 K line shape of the inset of Fig. 1. For increasing temperature, the charge carrier dynamics is faster with respect to the lattice around the slower holes (Mn$^{3+}$) is locally less JT-distorted. A finite-size polaron emerges which is, according to Louca and Egami, rather an anti-polaron where the JT distortion is less effective due to fluctuations in the $t_{2g}$ spin directions, and the overall picture becomes more local. A finite-size polaron emerges which is, according to Louca and Egami, rather an anti-polaron where the lattice around the slower holes (Mn$^{4+}$ sites) is locally less and less JT-distorted. Correspondingly, the splitting of the external modes is reduced. The weight of these phonon resonances decreases because sites without anti-polarons (Mn$^{3+}$ sites) experience a strong JT-distortion and support external modes at a higher frequency (as is well known from the undoped or weakly doped systems [21, 22, 23]). These “new external modes” at higher frequency also experience a larger splitting, again consistent with the observations in undoped or weakly doped systems [21, 22, 23]. These “new modes at a higher frequency” act on the average charge carrier concentration, not on the instantaneous hole positions. In this regime, only a weak JT-distortion is observed and the external modes are split as seen for the 6 K line shape of the inset of Fig. 1. For increasing temperature, the charge carrier dynamics is faster with respect to the lattice around the slower holes (Mn$^{3+}$ sites) is locally less JT-distorted. A finite-size polaron emerges which is, according to Louca and Egami, rather an anti-polaron where the JT distortion is less effective due to fluctuations in the $t_{2g}$ spin directions, and the overall picture becomes more local. A finite-size polaron emerges which is, according to Louca and Egami, rather an anti-polaron where the lattice around the slower holes (Mn$^{4+}$ sites) is locally less and less JT-distorted. Correspondingly, the splitting of the external modes is reduced. The weight of these phonon resonances decreases because sites without anti-polarons (Mn$^{3+}$ sites) experience a strong JT-distortion and support external modes at a higher frequency (as is well known from the undoped or weakly doped systems [21, 22, 23]). These “new external modes” at higher frequency also experience a larger splitting, again consistent with the observations in undoped or weakly doped systems. For even higher temperatures, close to $T_C$, the anti-polaron is reduced to a JT undistorted lattice site and the dynamics of this hole is diffusive. The higher symmetry of these sites supports only one external mode frequency whereas the Mn$^{3+}$ sites with a full JT distortion now support two external mode vibrations with higher spectral weight according to their larger relative number. We refer to this situation as the temperature dependent IDJT. The phase transition scenario [24] supports the IDJT. The basis for the observation of the IDJT is a crossover from adiabatic to nonadiabatic behavior of the lattice dynamics.

To conclude, we want to emphasize the particular importance of the external modes as an excellent phononic “tool” to investigate this cooperative behavior of the lattice with spin and charge DOF. These phonons have a weak dispersion which allows them to probe local distortions. Moreover, the frequency shift of the external modes is strong with Sr-doping because these modes correspond to a vibration of the La-Sr cage with respect to the Mn-O octahedra. For this reason the low-energy modes of the external group are well separated from the new modes at high temperature. The disentanglement of the external modes in the electronic inhomogeneous state is the prerequisite of the observed phonon metamorphism.

We acknowledge stimulating discussions with J. Deisenhofer and R. Hackl. The research was supported in part by BMBF (13N6917A, 13N6918A) and by the DFG via SFB 484 (Augsburg).

[1] A.J. Millis, P.B. Littlewood and B.I. Shraiman, Phys. Rev. Lett. 74, 5144 (1995).
[2] M. Uehara, S. Mori, C.H. Chen, and S.-W. Cheong, Nature 399, 560 (1999).
[3] A. Moreo, S. Yunoki, and E. Dagotto, Science 283, 2034 (1999).
[4] E. Dagotto, T. Hotta and A. Moreo, Phys. Rep. 344, 1 (2001).
[5] M.B. Salamon, P. Lin, and S.H. Chun, Phys. Rev. Lett. 88, 197203 (2002).
[6] R.B. Griffiths, Phys. Rev. Lett. 23, 17 (1969).
[7] E. Dagotto, Nanoscale Phase Separation and Colossal Magnetoresistance (Springer, Berlin 2002).
[8] M. Fäth et al., Science 285, 1540 (1999).
[9] T. Becker et al., Phys. Rev. Lett. 89, 237203 (2002).
[10] D. Louca and T. Egami, Phys. Rev. B. 59, 6193 (1999).
[11] Ch. Hartinger et al., unpublished
[12] Ch. Hartinger et al., Phys. Rev. B. 69, 100403(R) (2004).
[13] M. V. Abrashev et al., Phys. Rev. B 59, 4146 (1999).
[14] W. Reichardt and M. Braden, Physica B 263B, 416 (1999).
[15] M. C. Martin et al., Phys. Rev. B 53, 14285 (1996).
[16] A. Mellergård, R.L. McGreevy and S.G. Eriksson, J. Phys.: Condens. Matter 12, 4975 (2000).
[17] M.B. Salamon and S.H. Chun, Phys. Rev. B 68, 014411 (2003).
[18] As a consequence of the imprecise mass determination of thin films the scale of $\chi^{-1}(T)$ is subject to some uncertainty.
[19] R.H. Heffner et al., Phys. Rev. Lett. 85, 3285 (2000).
[20] T. Shibata, B.A. Bunker and J.F. Mitchell, Phys. Rev. B 68, 24103 (2003).
[21] A. Paolone et al., Phys. Rev. B 61, 11255 (2000).
[22] V.B. Podobedov et al., Phys. Rev. B. 58, 43 (1998).
[23] In La$_{0.95}$Sr$_{0.05}$MnO$_3$ the resonances of the external modes are at 169 and 180 cm$^{-1}$ for room temperature.