Cooperative dynamics in doped manganite films: phonon anomalies in the ferromagnetic state

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We present optical measurements of phononic excitations in La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) and La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) thin films covering the full temperature range from the metallic ferromagnetic to the insulating paramagnetic phase. All eight phonons expected for the R$3c$ symmetry in LSMO and 17 out of the expected 25 phonons for the Pnma symmetry in LCMO have been determined. Close to the ferromagnetic-to-paramagnetic transition both compounds reveal an anomalous behavior but with different characteristics. Anomalies in the phononic spectra are a manifestation of the coupling of lattice degrees of freedom (DOF) to electronic DOF. Specifically, the low-frequency external group proves to be an indicator for lattice modifications induced by electronic correlations. The enhanced electron-phonon coupling in LCMO is responsible for Fano-like interference effects of distinct phonon modes with electronic continuum excitations: we observe asymmetric phonon line shapes, mode splitting and spectral weight transfer between modes.

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I. INTRODUCTION

With the enormous progress of research on colossal magnetoresistance (CMR) manganites over the last decade it has been realized that besides charge and spin also lattice degrees of freedom play a significant role in the formation of the CMR and the metal-insulator transition (MIT). Special attention focused on the optimal doped manganites, characterized by the largest CMR effects—in particular, La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO). As the temperature range in which the CMR effect and the MIT are observed is close to room temperature, these compounds have become potential candidates for technical applications.

The phonon excitation spectrum has been studied in detail for undoped LaMnO$_3$ which is, below approximately 750 K, in a Jahn-Teller (JT) distorted orthorhombic (Pnma) structure. A theoretical analysis of the complete set of phonon modes in the doped compounds is still missing. LCMO has an orthorhombic symmetry whereas the Sr-doped compound, La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO), is rhombohedrally distorted. The infrared-active phonons of undoped rhombohedral (R3c) LaMnO$_3$ were identified however these zero-doping investigations cannot make up for experiments at finite doping. In fact, the local Mn-O geometry depends strongly on the size of the ions and doping concentration which accounts for the structural differences between LCMO and LSMO.

Experimental studies of two single crystals, undoped and with $\sim$ 8% Sr-doping, were performed by Paolone et al. They discussed the assignment of all infrared active phonon modes in LaMnO$_3$ at low temperature. However, to the best of our knowledge, there are no reports on phonon modes in the metallic phase of LSMO. For bulk samples of LCMO, three sets of broad phonon bands are observed which reveal external-, bending- and stretching-type lattice vibrations, as classified in the cubic symmetry.

Apart from providing a fingerprint of the lattice structure, phononic spectra can indicate the relevance of electronic correlations. The dominant effect of mobile electrons on the lattice vibrations is generally a suppression of phononic resonances due to screening. For metals, this may render the phonons unobservable in far-infrared (FIR) optical spectroscopy. However, since the polycrystalline samples are poor metals, and even more so the investigated thin films, phonon resonances are still clearly resolved even in the conducting low-temperature ferromagnetic phase.

In LCMO a significant shift of the stretching mode near the MIT was found and associated with a reduced screening through charge carriers close to the MIT. Although the observed shifts of phonons in LCMO are evidently related to electronic correlations since they come along with the MIT it is not obvious that they are explained exclusively by a reduced screening. In particular, not all phonon modes display the shift and, furthermore, in LSMO we observe phononic shifts which are tied to the ferromagnetic-to-paramagnetic (FM-PM) transition, not the MIT (see Sec. IIIC). In LCMO the FM-PM transition and the MIT coincide whereas in LSMO they are well separated. A comparative study of LCMO and LSMO should address and illuminate the fundamental question if the phononic excitations couple to spin degrees of freedom.

Since the phonon resonances are well pronounced in the optical spectroscopy measurements of the metallic manganite films they provide a unique opportunity to analyze the consequences of a coupling of lattice degrees of freedom (DOF) with spin and charge. Correlation of lattice DOF with charge DOF has to be in an weak (LSMO) to strong coupling range (LCMO) as, for example, the polaronic excitations in the mid-infrared (MIR) evidence a coupling in this range. Also neutron diffraction measurements for LCMO revealed an anomalous volume thermal expansion at the paramagnetic-to-ferromagnetic MIT which has to originate from a sufficiently strong coupling. We will elaborate further on the consequences of a strong phonon-electron coupling for the
phononic resonances in this paper and we will identify the characteristics in the FIR spectra signifying cooperative dynamics not only of lattice and electronic charge but also of lattice and spin degrees of freedom.

The paper is organized as follows: Sec. II deals with the experimental details, sample characterization and data analysis. In Sec. III A we present reflectivity measurements of the infrared active phonons in thin films of LSMO and LCMO at temperatures ranging from the insulating paramagnetic (PM) to the metallic ferromagnetic (FM) phase. In Sec. III B we give a comprehensive analysis of phonons from the respective optical data. The spectra confirm the anticipated mode structure for the respective symmetry of the lattice and prove the high quality of the thin films. In Sec. III C we elaborate on the close relation between lattice and spin degrees of freedom by studying the temperature dependent shift of phonon modes across the ferromagnetic transition. In Sec. IV we discuss Fano-like modifications of the line shape of distinct phonon modes in LCMO which testify a significant coupling of the lattice excitations to the electronic continuum in the Ca-doped manganite films. The interference of nearly degenerate modes in LCMO which testify a significant coupling of the electronic excitations may result in spectral weight transfer and level repulsion which we discuss within a phenomenological approach for coupled phononic and electronic modes. A summary of our findings and conclusions are presented in the last section, Sec. V.

II. EXPERIMENTAL DETAILS AND SAMPLE CHARACTERIZATION

The films for this investigation have been prepared using a standard pulsed laser deposition technique. LCMO was grown to a thickness of 200 nm onto NdGaO$_3$ single crystalline substrates. LSMO #1 with a thickness of $d = 300$ nm and LSMO #2 with $d = 400$ nm were deposited on (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_5$)$_{0.7}$. X-ray diffraction of LCMO revealed an orthorhombic structure with a preferred growth along the [110] axis while LSMO was confirmed to be in a rhombohedral structure with preferred growth along the [100] axis.

The infrared reflectivities of the sample and the pure substrate were measured using a combination of Fourier transform spectrometers, Bruker IFS 113v and IFS 66 v/S, to cover the frequency range from 50 to 40 000 cm$^{-1}$. Temperature dependent measurements from 6 to 295 K were performed with a He-cryostat. Higher temperatures were measured in a home made oven in which the sample was exposed to a continuous flow of heated nitrogen gas. To obtain the optical conductivity $\sigma$ a Kramers-Kronig (KK) analysis was performed which included the results from submillimeter spectroscopy between 5 and 30 cm$^{-1}$. Applying the Fresnel optical formulas for the complex reflectance coefficient of the substrate-film system, the optical conductivity for the films was calculated.

Magnetization measurements were carried out between 2 and 400 K by using a commercial Quantum Design SQUID magnetometer. The dc resistance measurements were performed by a standard four-probe method. The temperature dependence of the ac resistance was done in a Mach-Zehnder interferometer arrangement, which allows the measurements of both, transmission and phase shift. Applying the Fresnel formulas, the ac resistance was determined directly without any approximations.

Frequently, manganite films exhibit FM transition temperatures $T_C$ lower than those reported for the bulk materials with the same nominal composition. The differences can be attributed to grain boundaries, strain, microstructure depending on the details of the growth process and on the lattice parameters of the substrate. They all result in a variation of the strength of the lattice distortion, which determines the structure and, accordingly, the electrical and magnetic behavior. It is well known, that differences between bulk samples and thin films can occur, depending on the quality of the films. However, we observe that the overall optical characteristics of the films are in good agreement with bulk properties.

To probe the electrical and magnetic properties of the different films we determined the characteristic transition temperatures. We define $T_C$ as the magnetic Curie temperature, $T_C^r$ as the inflection point and $T_{MIT}$ is taken from the maximum in the dc and ac resistivity curve. We summarize the results of the transition temperatures for both compounds in Tab. I. Since $T_C^r$ and $T_{MIT}$ are relatively similar, we will use the notation $T_C^r$ for either one if not stated otherwise. To identify

| $T_{MIT}$ (K) | $T_C^r$ (K) | $T_C^c$ (K) | sample |
|--------------|-------------|-------------|--------|
| LCMO ($d=200$ nm) | 245 | 243 | 242 | LCMO |
| LSMO ($d=300$ nm) | 338 | 287 | 300 | LSMO #1 |
| LSMO ($d=400$ nm) | 401 | 328 | 345 | LSMO #2 |

FIG. 1: Upper panel (LSMO): Temperature dependence of the magnetization at $H = 100$ Oe (left scale) and DC-resistivity (right scale). Lower panel (LCMO): Magnetization at $H = 10$ Oe (left scale); DC- and AC-resistivity at $\nu = 600$ GHz (right scale).
the MIT and FM-PM transition of the thin film samples, we display magnetization and dc as well as ac resistivity in Fig. 1. As expected, $T_C$ nearly coincides with $T_{\text{MIT}}$ for LCMO.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Temperature dependence of the reflectivity

The frequency-dependent reflectivity of LCMO is presented in Fig. 2 for temperatures in the metallic FM (dotted lines) and in the insulating PM (solid lines) phase. Above the MIT (245 K) the shape and intensity of $R$ is temperature independent. With the temperature increasing from 6 K to 295 K, the weight of several phonon modes gradually increases and a typical insulating behavior with an energy gap of about 680 cm$^{-1}$ develops. Variations in position and intensity of some characteristic phonon modes are apparent.

The overall distinction between the reflectivity spectra of LCMO and LSMO is striking (compare Figs. 2 and 3). The less complex structure of the phonon spectrum of LSMO, see Fig. 3, is evidence for the higher symmetry of the unit cell. Above 400 K the spectra hardly change. The reflectivity in LCMO #1 is slightly lower than in LSMO #2, otherwise the spectra are essentially identical.

In addition, the LCMO spectra display phonon anomalies at $T_C$, a feature which is entirely missing in LSMO. X-ray and neutron powder diffraction studies demonstrate an anomalous volume thermal expansion for the Ca-doped compound at the MIT, and neutron powder diffraction studies demonstrate an anomalous temperature dependence of some characteristic phonon modes are apparent.

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the IR active phonon frequencies of LSMO #2 at $T = 250$ K and the calculated frequencies. The calculated positions for the undoped compound can only be taken as a rough estimate for LSMO since the lattice constants and atomic positions are modified by Sr-doping. Also the assumption of equal Mn-O bond lengths in the MnO$_6$ octahedra is not strictly valid for the doped compounds, since the JT effect breaks the symmetry dynamically and thereby affects the groups of bending and stretching modes. Finally, the unequal masses of the (La/Sr)-ions should influence the external mode.

In Fig. 5 the optical conductivity of LCMO at 250 K is plotted jointly with labels for the phonon eigenfrequencies. The latter result from a fit with noninteracting harmonic oscillators. From the series of observed sharp peaks below $\sim 600$ cm$^{-1}$ we can clearly identify 17 phonon modes. The theoretical studies for the Pnma symmetry performed by Fedorov et al. and Smirnova were evaluated for the undoped case. Both sets of theoretical frequencies are remarkably different from the experimental data reported in detail by Paolone et al. for LaMnO$_3$.

In Tab. III the phonon frequencies for LCMO at 6 K and 250 K are listed and compared with published data on the infrared spectra of undoped LaMnO$_3$. At 6 K we can identify 15 and at 250 K 17 phonon modes. With increasing doping concentration weak phonon modes become broader and disappear in the background. Therefore not all 25 infrared active modes can be resolved. Remarkably, no phonon frequency

**TABLE II**: Correspondence between calculated and measured phonon modes for the space group R3c. The measured frequencies (in cm$^{-1}$) refer to LSMO #2 at $T = 250$ K, and the values in parenthesis to neutron scattering with aLa$_{0.7}$Sr$_{0.3}$MnO$_3$ sample.

| Osc. Nr. | A$_{2u}$ | E$_u$ | assignment | A$_{2u}$ | E$_u$ |
|----------|----------|-------|-------------|----------|------|
| 1        | 317      | 379   | vibration (Mn) | 379      |      |
| 2        | 162      | 180   | external     | 149      | 155  |
| 3        | 310      | 357   | bending      | 340 (336)| 441 (424)|
| 4        | 641      | 642   | stretching   | 585 (576)| 662  |
| 5        | 240      |       | torsional   | 265      |      |
larger than 600 cm\(^{-1}\) have been observed in LCMO. The deviations of the resonance frequencies in pure LaMnO\(_3\) from those in Ca-doped films are a consequence of a less distorted structure but enhanced disorder.

C. Phononic resonances across the FM-PM transition

The spectral resolution of phononic excitations in the films is superior to that in bulk LCMO samples and we can resolve even both stretching modes in the Pnma symmetry. Only the high-frequency stretching mode (see inset of Fig. 6) exhibits a significant shift to lower energy with increasing temperature. This observation is to be related to the previously reported IR spectra of a polycrystalline LCMO sample by Kim et al.\(^{10}\) The authors observed only three broad modes of which the stretching mode displays a notable frequency shift around \(T_C\). This shift on approaching the MIT was attributed to a reduction of screening through mobile charge carriers\(^{32}\) and, thereby, the authors depreciated a magneto-elastic effect. One argument against this interpretation is the observation that only one mode of the stretching group would be “sizeably less screened”\(^{22}\) and we will see in Fig. 7 for the external modes that again only one mode shifts appreciably close to the MIT.

Some representative spectra of the phonon modes are seen in Fig. 6. Remarkably, at low temperatures a sharply resolved phononic structure remains which indicates that screening effects by mobile charge carriers play only a minor role. Consequently, we propose that the frequency shift of the high-frequency stretching mode (see inset of Fig. 6) has a different origin. In this regard, the importance of spin-lattice correlations has been pointed out by Podobedov et al.\(^{24}\) who observed similar temperature effects of the phonon modes through polarized Raman spectra in an undoped sample (i.e. metallic screening is absent)\(^{32}\). Their assignment of the shift to spin-lattice correlations is in agreement with x-ray absorption fine-structure measurements for La\(_{1-x}\)Ca\(_x\)MnO\(_3\) by Booth et al.\(^{25}\) In the following we will further elucidate the correlation between the anomalous shift and the magnetization.

An intriguing example of a mode which exhibits the addressed anomaly in LCMO is the external mode (see the reflectivity in the inset of Fig. 2 and the optical conductivity in Fig. 7 left panel). The lowering of the symmetry from purely cubic to orthorhombic or rhombohedral implies a diversification of the three main phonon modes (external, bending and stretching) with the result that also the external mode depends on the Mn-O geometry\(^{24}\).

As a consequence of the anharmonicity of the lattice an increase of the phonon resonance frequencies with decreasing temperature is expected.\(^{31}\) However, the considered phonon modes show an irregular temperature dependence (see Fig. 7 for the external modes, and the inset of Fig. 6 for the stretching modes). The shifts are controlled by the phase transition at 245 K. In the left panel of Fig. 7 the positions of both external modes of LCMO are displayed for various temperatures. The lower mode exhibits only slight variations whereas the higher mode shows a clear anomaly which sets in at about 160 K.

The observation that the magnetization (solid line in Fig. 8) scales with the frequency shift of the higher external mode (solid circles) below \(T_C\), suggests a correlation between spin polarization and this external mode. In comparison, the frequency shift of the high-energy stretching mode in the inset of Fig. 6 is seven times larger. As expected, the external mode is only slightly affected by the local, correlation-induced dis-
tortion of the Mn-O octaedra. We point out that a link between magnetic correlations and phononic frequency shifts was realized before and it was applied successfully to explain the behavior of phonon modes in a ferromagnetic spinel.

The right panel of Fig. 7 presents the two external modes of LSMO. While the low-energy mode shows a softening with decreasing $T$, the higher mode displays the previously discussed hardening. Overall, the modes approach each other, and at $T_C$ hardly two modes are resolvable. We infer from this observation that the temperature scale of the mode evolution is in fact the magnetic temperature scale $T_C$.

Contrary to their behavior in LSMO, the two external modes in LCMO do not become degenerate when $T_C$ is approached. However in the next section, we will understand that electron-phonon coupling is much stronger in LCMO with consequences for the mode structure. In fact, interference of nearby modes is pronounced in LCMO (see Fig. 8).

We will discuss this observation within a phenomenological approach although, without a detailed microscopic analysis, it is not feasible to fix position and weight of the considered phononic resonances conclusively. The formation of the different phononic resonances is strongly influenced by the details of electronic correlations and their coupling to the phonons. Nevertheless, we will see that for some of the modes, which strongly interact with the electronic correlations, a considerable amount of their weight may have its origin in a transfer of spectral weight from the electronic degrees of freedom (cf. the “bare” mode-amplitude $A_2$ in Tab. IV with the resulting amplitude in Fig. 8 for the lower external mode at about 170 cm$^{-1}$). It is conceivable that differences in the phononic mode structure of LSMO and LCMO—the shape and especially the relative weights of the phononic resonances—are, to a large extent, controlled by electron-phonon coupling.

IV. FANO LINESHAPES IN LCMO

The lineshape of the phonon spectrum evidences the strength of the electron-lattice correlations as the coupling of lattice vibrations to excitations of the electronic system may lead either to destructive or constructive interference. The Lorentzian resonant shape of the phonon mode is thereby de-
where
\[ \hat{A} = (A_1, \ldots, A_n, A_{sp}, A_e, A_d) \] (2)
is a vector of \( n \) matrix elements \( (A_j) \) for optical dipole transitions of phonon modes, for the small polaron \( (A_{sp}) \), for an incoherent \( (A_e) \) and for a Drude contribution \( (A_d) \). \( \hat{G} \) is the Green function matrix of the electron-phonon system. Thereby \( A_{sp} \) is calculated by applying the \( f \)-sum rule to the SP component
\[ A_{sp} = \sqrt{\frac{1}{\varepsilon_0 2\pi^2 c} \int_0^\infty d\nu \Re \sigma_{sp}(\nu)} \] (3)
where \( \varepsilon_0 \) is the vacuum permittivity and \( c \) is the speed of light. The SP optical conductivity is\textsuperscript{42,43}
\[ \Re \sigma_{sp}(\nu, T) = \sigma_0(T) \frac{\sinh(4E_b\nu/\Delta^2)}{4E_b\nu/\Delta^2} e^{-\nu^2/\Delta^2} \] (4)
Here \( \sigma_0(T) \) is the dc-conductivity, \( E_b \) is the SP binding energy, \( \Delta = 2\sqrt{2E_bE_{\text{vib}}} \), and \( E_{\text{vib}} \) is the characteristic vibrational energy which is the thermal energy \( T \) in the high-temperature regime and \( \nu_{ph}/2 \) at low temperatures \( (k_B T < \hbar 2\pi \nu_{ph}) \). The dimension of \( \nu \) and all other energy scales is cm\(^{-1}\).

We assume that not only the phonon modes approximately decouple but also the electronic modes, which generate the SP resonance, the Drude contribution and the resonance in the FIR range. The inverse Green function matrix is in this phenomenological scheme
\[ \hat{G}^{-1} = \begin{pmatrix} G_1^{-1} & 0 & \ldots & g_1 & k_1 & 0 \\ 0 & G_2^{-1} & \ldots & g_2 & k_2 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ g_1 & g_2 & g_3 & \ldots & G_{sp}^{-1} & 0 \\ k_1 & k_2 & k_3 & \ldots & 0 & G_e^{-1} \\ 0 & 0 & 0 & \ldots & 0 & 0 \end{pmatrix} G_d^{-1} \] (5)
with the respective Green functions of the phonon modes, the small polaron, incoherent and the Drude background:
\[ G_j(\nu) = \frac{\nu}{\nu_j^2 - \nu^2 - i\nu\gamma_j} \] (6)
\[ G_{sp}(\nu) = \frac{i \Re \sigma_{sp}(\nu) - \Im \sigma_{sp}(\nu)}{\varepsilon_0 2\pi c A_{sp}^2} \] (7)
\[ G_e(\nu) = \frac{\nu}{\nu_e^2 - \nu^2 - i\nu\gamma_e} \] (8)
\[ G_d(\nu) = \frac{1}{\nu + i\nu\gamma_d} \] (9)
\( \gamma_j \) and \( \nu_j \) are the width and the frequency of the \( j \)th phonon mode, \( \gamma_e \) and \( \nu_e \) of the electronic oscillator, and \( \gamma_d \) parameterizes the Drude contribution. The imaginary part of \( \sigma_{sp} \) is obtained from a Kramers-Kronig relation. The strengths of the polaron-phonon \( (g_j) \) and electron-phonon \( (k_j) \) coupling parameters determine the asymmetric line shape while the sign controls at which side of the phonon mode the dip will appear. For \( g_j = k_j = 0 \) a Lorentzian shape is recovered for the \( j \)th phonon. In relation (5) we set the coupling of the Drude-phonon coupling to zero as its effect on the resonant lineshapes is small for the considered temperature range below the MIT and we thereby avoid a larger number of fitting parameters. Moreover the Drude contribution is absent above the MIT but the lineshapes are still similar to those below the MIT, an observation which excludes a priori a dominant role of the Drude term.

The fit procedure consists of the following three steps: First, the polaron parameters are fixed through the fit of the mid-infrared polaron resonance.\textsuperscript{12} Then the background in the FIR range is parameterized through \( G_e \) and \( G_d \). Finally, the frequencies and widths of the phonon resonances are determined, the coupling constants are extracted from fitting their respective shape, and the frequencies and widths are readjusted in order to gain the optimal fit.

In Fig.\textsuperscript{9} we show experimental and theoretical data for the low-frequency phonon group measured at different temperatures. We now analyze in detail the most distinctive asymmetric mode in LCMO at about 114 cm\(^{-1}\) and include the two adjacent phonon modes for the interpretation. This group is well separated from other phonon excitations, which allows us to neglect the coupling to the remaining modes. In Tab.\textsuperscript{14} the interaction parameters on the basis of our approach are pre-
sented for the 114 cm$^{-1}$ phonon for different temperatures $T$.

All line shapes of the first phonon mode in Fig. 9 exhibit a dip on the high-energy side, a consequence of the negative sign of the coupling parameters. The coupling constant is proportional to the effective mass. In manganites the carriers have hole character. The associated inverse sign of the effective mass may be responsible for a negative value of $g_j$ and $k_j$. It turns out that neither a coupling to the Drude nor to the incoherent contribution can induce the nearly perfect antisymmetric shape of the 114 cm$^{-1}$ peak-dip structure. Only a sufficiently strong coupling to the polaronic excitations supports this antisymmetric Fano shape. The increase of coupling strength $g_1$ with temperature is significant. It results from the fact that the line shape keeps its antisymmetric form up to the highest temperature (295 K) while the electronic background is reduced by a factor 8 from 160 K to 295 K. Since the line shape of the phonon is controlled by a product of the coupling constant and the strength of the polaronic background ($\sigma_0$), the coupling constant has to increase correspondingly to keep

**TABLE IV:** Parameters of the Fano-like fit for the 114 cm$^{-1}$ phonon of LCMO at different $T$ using the approach of Eqs. (1)–(9).

| $T$ (K) | 160 | 200 | 220 | 295 |
|--------|-----|-----|-----|-----|
| $A_1$ (cm$^{-1}$) | 150 | 148 | 143 | 140 |
| $\gamma_1$ (cm$^{-1}$) | 4.1 | 4.1 | 4.1 | 3.9 |
| $\nu_1$ (cm$^{-1}$) | 118.0 | 117.2 | 116.9 | 116.4 |
| $g_1$ (cm$^{-1}$) | -12 | -10 | -11 | -15 |
| $k_1$ (cm$^{-1}$) | -3 | -8 | -9 | -16 |
| $A_{sp}$ (cm$^{-1}$) | 16502 | 15251 | 15958 | 15495 |
| $\sigma_0$ (Ω$^{-1}$ cm$^{-1}$) | 890 | 460 | 350 | 108 |
| $E_b$ (cm$^{-1}$) | 1990 | 2000 | 2520 | 3300 |
| $\nu_{ph}$ (cm$^{-1}$) | 350 | 261 | 310 | 300 |
| $A_2$ (cm$^{-1}$) | 1350 | 1350 | 1350 | – |
| $\gamma_2$ (cm$^{-1}$) | 140 | 150 | 350 | – |
| $A_3$ (cm$^{-1}$) | 3500 | 3370 | 2800 | 1600 |
| $\gamma_3$ (cm$^{-1}$) | 370 | 340 | 280 | 250 |
| $\nu_3$ (cm$^{-1}$) | 276 | 320 | 340 | 345 |

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**FIG. 10:** Fits of the low frequency phonon group with and without electron-phonon (e-ph) coupling for data at room temperature.

the observed shape.

The line shapes of the two modes at about 170 cm$^{-1}$ do not deviate strongly from Lorentzians which is consistent with rather small couplings $g_2$ and $g_3$ (cf. Tab. IV). However, in order to reproduce the “hump” in between the phonon at 114 cm$^{-1}$ and the nearly degenerate external modes at about 170 cm$^{-1}$ one needs a sufficiently strong electron-phonon coupling $k_2$ to the electronic resonance at about 300 cm$^{-1}$. These electron-phonon couplings, $k_2$ and $k_3$, affect the position and the spectral weight of the resonances at $\nu_2$ and $\nu_3$ considerably. The three coupled modes ($\nu_2$, $\nu_3$, $\nu_e$) constitute a “triad” with a bonding (lowest), non-bonding (intermediate) and anti-bonding state. The bonding and anti-bonding modes always experience level repulsion so that the bare frequencies $\nu_2$ and $\nu_3$ can be both at 171 cm$^{-1}$ (degenerate modes, cf. Tab. IV) but the two resonances are still well separated at 295 K (at 167 cm$^{-1}$ and at 171 cm$^{-1}$, cf. Fig. 9 and Tab. III). The level repulsion is accompanied by a transfer of spectral weight: according to Tab. IV and Fig. 9 the lowest mode of the triad takes nearly all its weight from the electronic mode at 295 K. This observation may explain why the two-mode structure at 170 cm$^{-1}$ in LCMO is still intense at or above the MIT whereas in LSMO the mode at about 170 cm$^{-1}$ is weak (cf. Fig. 7 right panel). In Fig. 10 we display the “bare modes”, with parameters of Tabs. IV and V joined with the interaction-dominated mode spectrum in order to summarize visually the effects of the strong electron-coupling on the external mode group in LCMO.

In contrast to LCMO, the phonon spectra for LSMO exhibit no asymmetric shape and can be described by Lorentzian oscillators. In the latter compound the electron-phonon coupling is smaller, as is confirmed by shape, position and temperature dependence of the polaronic mid-infrared (MIR) resonance.

**V. CONCLUSIONS**

Manganite thin films provide an excellent opportunity to study the phononic excitations of LSMO and LCMO in their
metallic phases. The films allow for a well-resolved, distinct phonon spectrum in infrared spectroscopy, even for temperatures well below the MIT. In LSMO we identified each of the eight infrared-active phonons expected for the R3c symmetry and in LCMO we were able to resolve 18 out of 25 phonons expected for the Pnma-symmetry.

The phonon spectra reveal a number of anomalies which result from a finite electron-lattice coupling and which confirm the importance of cooperative effects of microscopic degrees of freedom when approaching the ferromagnetic-to-paramagnetic and the metal-insulator transition.

First and most apparent, we observe that the FIR spectra change substantially up to the MIT (see Figs. 2 and 3) but then, above the MIT, temperature dependent modifications are negligible. This overall T-dependence of the spectra up to the MIT is related to a strongly reduced screening of the phononic excitations, due to localization or diffusive motion of electronic charges. However also a coupling of lattice and spin degrees of freedom is evidenced by the phononic excitation spectrum: temperature dependent shifts of several phonon modes, which vary on the same temperature scale as the magnetization, confirm the correlation of these degrees of freedom (see Figs. 6–8).

In LCMO the pronounced asymmetric line shapes, observed for several phonons (see Figs. 5 and 9), are a manifestation of the strong electron-phonon coupling. We analyzed the Fano line shapes of the external group within a phenomenological approach. We find that the mode splitting of the 170 cm$^{-1}$ resonance and its considerable spectral weight at high temperature (above the MIT) is induced by the electronic continuum. This observation may explain the discrepancy with LSMO where these two external modes are degenerate at high temperature since LSMO is characterized by a weaker electron-phonon coupling where Fano-like line shapes are entirely missing. A microscopic evaluation is mandatory in order to assign unambiguously these anomalous characteristics of the phononic spectra to the interference with specific electronic excitations. The preliminary identification within the phenomenological approach has provided ample motivation for such an effort.

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Moreover, a full evaluation of screening would have to include the diffusive nature of the charge transport which results in a retarded screening dynamics with a less prominent signature. Near the magnetic transition an irregular shift at 609 cm$^{-1}$ was attributed to spin-lattice interaction due to the observed variations of the lattice parameters and sublattice magnetization.

The origin of the mode degeneracy in LSMO and its relation to the evolution of the spin degrees of freedom will be investigated in a subsequent publication (Hartinger et al., unpublished).

Although the scheme with a pure triad of bonding, non-bonding and anti-bonding modes is oversimplified, it visualizes sufficiently the expected modifications of mode positions and spectral weight with increasing coupling. Certainly, the higher-energy external mode at about 172 cm$^{-1}$ has not a pure non-bonding character and it also experiences a small level shift and modifications of its spectral shape through its interaction with the other modes.