Orbiton-mediated multi-phonon scattering in La$_{1-x}$Sr$_x$MnO$_3$

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We report on Raman scattering measurements of single crystalline La$_{1-x}$Sr$_x$MnO$_3$ ($x=0$, 0.06, 0.09 and 0.125), focusing on the high frequency regime. We observe multi-phonon scattering processes up to fourth-order which show distinct features: (i) anomalies in peak energy and its relative intensity and (ii) a pronounced temperature-, polarization-, and doping-dependence. These features suggest a mixed orbiton-phonon nature of the observed multi-phonon Raman spectra.

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I. INTRODUCTION

Recently, there has been a debate about the underlying nature of the experimentally reported orbitons observed by Raman spectroscopy in orbital ordered LaMnO$_3$. Despite pronounced temperature- and symmetry-dependent properties of the modes, the assignment has been confronted with criticism and alternative concepts. For instance, multi-phonon scattering has been theoretically predicted to arise from the Franck-Condon (FC) process via self-trapped orbitons. Interestingly, in spite of mutually exclusive selection rules an infrared absorption study shows similar features as Raman scattering measurements at about 125 meV (1000 cm$^{-1}$), 145 meV (1160 cm$^{-1}$), and 160 meV (1280 cm$^{-1}$). This was attributed to multi-phonon scattering instead of orbital excitations. On the other hand, orbiton-phonon mixed modes are predicted to appear as satellite structures in the phonon spectrum due to electron-phonon coupling.

LaMnO$_3$ shows $d_{3z^2-r^2}/d_{3y^2-r^2}$ orbital ordering below $T_{JT} = 780$ K accompanied by a cooperative Jahn-Teller (JT) distortion. Two different contributions to this antiferro-orbital ordering, which support each other, have been suggested. The first mechanism relies on the cooperative JT effect. In this case, orbiton excitations accompany lattice distortions and vice versa. Their energy, determined by the strength of electron-phonon coupling, is between 0.7 and 2 eV. The second mechanism is based on superexchange interaction. Within this mechanism orbitons are collective excitations and their energy is expected at much lower energies of 160 meV because of strong on-site Coulomb repulsion. Thus, the determination of the respective contribution to orbital ordering and its energy scale are closely related to the nature of orbital excitations.

Quite recently, resonant Raman scattering measurements have shown a symmetry-dependent resonance of the one- and two-phonon signal around the JT gap at 2 eV, suggesting a phononic origin of the assigned orbitons due to the FC mechanism. However, a detailed temperature- and symmetry-dependence is still lacking which is significant in addressing a coupling of phonons to orbital ordering. Thus, a careful examination on the higher energy regime of the Raman spectrum above 1300 cm$^{-1}$ is indispensable to uncover all aspects of orbital dynamics. Furthermore, their doping dependence can give further clues because the orbital ordering undergoes a transition while crossing the phase boundary between the canted antiferromagnetic insulating (CAF) and ferromagnetic insulating (FMI) state.

In this paper we report on Raman scattering measurements of single crystalline La$_{1-x}$Sr$_x$MnO$_3$ ($x=0$, 0.06, 0.09 and 0.125), focusing on the higher energy regime. For $x = 0$ we observe multi-phonon scattering up to fourth order of the one-phonon modes at frequencies between 490 and 640 cm$^{-1}$. The distinct symmetry-, temperature-, and doping-dependencies of this scattering contribution unveil the insufficiency of the FC mechanism in describing the observed multi-phonon scattering. This points to a orbiton-phonon mixed nature of the observed multi-phonon scattering.

II. EXPERIMENTAL DETAILS

Single crystals of La$_{1-x}$Sr$_x$MnO$_3$ ($x=0$, 0.06, 0.09, and 0.125) were grown by using the floating zone method. These samples are twinned. As a result, some crystallographic axes cannot be discriminated. Raman scattering measurements were performed in a quasi-backscattering geometry with the excitation line $\lambda = 514.5$ nm (2.34 eV) of an Ar$^+$ laser. The small incident power of 8 mW avoids significant heating and irradiation effects. Raman spectra were collected by a DILOR-XY triple spectrometer.
TABLE I: Peak frequencies of multi-phonon scattering of different orders. Multiples of first order scattering frequencies are given in parentheses. The multi-phonon scattering peaks are grouped according to their overtones of the 493-, 602-, and 641-cm\(^{-1}\) modes. Two different frequencies which belong to the same group are attributed to different polarizations.

| 1\(^{st}\) polarization | 2\(^{nd}\) | 3\(^{rd}\) | 4\(^{th}\) |
|-------------------------|---------|---------|---------|
| \((xx)\)                | 985 (986) | 1485 (1488) | - (1972) |
| \((x'x')\)               | 1017 | 1539 | 2096 |
| \((xx)\)                | 1137 | 1653 | 2297 |
| \((x'x')\)               | 1173 (1604) | 1781 (1806) | 2418 (2408) |
| \((xx,x'x')\)            | 1281 (1282) | 1911 (1923) | 2542 (2564) |

and a nitrogen cooled CCD (charge-coupled device) detector. The high temperature measurements from 300 K to 640 K were carried out using a heating stage under vacuum.

III. EXPERIMENTAL RESULTS

Figure 1(a) displays polarized Raman spectra of \(\text{LaMnO}_3\) at 5 K. The incident and scattered light are parallel and perpendicular to the quasicubic surface of the perovskitelike crystals. For such scattering geometries, Raman spectra are expected in the \((xx, x'x', xy, \text{ and } x'y')\) polarizations where \(x, y, x', \text{ and } y'\) correspond to the respective quasicubic [100], [010], [110], and [110] directions. Since the studied samples are twinned, the parallel configuration contains \((xx)\) and \((x'x')\) polarizations while the crossed one consists of \((xy)\) and \((x'y')\) polarizations. Due to different selection rules the Raman spectra of the parallel and crossed polarizations show a slightly different behavior in the total number of phonon modes and their relative intensity.

Below 650 cm\(^{-1}\) we observe 17 phonon modes as first-order scattering out of 24 symmetry-allowed modes for the \(Pnma\) crystal structure. The number and sharpness of the observed modes guarantees a high quality of the single crystal. The modes below 330 cm\(^{-1}\) are due to vibrations of \((\text{La/Sr})\) cations and rotations of the MnO\(_6\) octahedra. The modes above 400 cm\(^{-1}\) arise from bending and stretching vibrations of the octahedra.\(^{11}\) The atomic displacement of the respective normal modes has been provided by M. N. Iliev et al. \(^{[12]}\). For the detailed physics of the one-phonon modes we refer to our previous work.\(^{13}\) Hereafter, we will focus on the high frequency regime covering the reported orbitons. Our results reproduce well the three features at about 1000, 1160, and 1280 cm\(^{-1}\) which were assigned to orbitons.\(^1\) Moreover, at much higher energies even additional maxima show up. All maxima between 1485 and 1911 cm\(^{-1}\) as well as between 2096 and 2542 cm\(^{-1}\) appear close to periodically [see Figs. 1(b) and (c)]. This suggests a common origin based on the one-phonon modes between 493 and 641 cm\(^{-1}\). Thus, the claimed orbitons should not be considered as pure orbital waves. In principle, a collective or-bital wave might be also observable besides multi-phonon scattering. However, we did not find evidence for this collective state below 3000 cm\(^{-1}\) (\(\approx 360\) meV). If present, this might be due to a negligible scattering cross section caused by the strong JT distortion. This implies that the orbital ordering in \(\text{LaMnO}_3\) is predominantly determined by the JT mechanism. A closer look at the higher-energy maxima reveals a fine structure. This is due to a twinning of the single crystal and the polarization-dependence of the multi-phonon frequency. The latter feature is unusual in conventional multi-phonon scattering and allows us to assign the symmetry of the maxima by comparison to the Raman study of an untwinned single crystal.\(^1\)

The measured frequencies of the high-energy excitations are listed in Table I together with calculated integer multiples of one-phonon modes. Here note that the assignment of two-phonon peaks to specific one-phonon modes is not straightforward since two-phonon scattering arises predominantly from regions of the Brillouin zone where the phonon density of states is largest. Nonetheless, as a starting point we will assign them to simple multiples of one-phonon peaks. This is because the FC mechanism is asserted to be mainly responsible for the
The overtones of the 641-cm$^{-1}$ ($x'x'$) and 602-cm$^{-1}$ ($xx$) modes show a linear behavior up to third-order. A deviation from such a feature is seen at fourth-order. (b) The integrated intensity of higher-order phonon spectra. Especially, the 641-cm$^{-1}$ mode shows a strong decrease of scattering intensity with increasing order.

FIG. 2: (online color) (a) The individual energy differences between $n$-phonon scattering and integer multiples of one-phonon peaks as a function of order. The energy difference is not equal to zero. In particular, the overtones of the 493-cm$^{-1}$ ($xx$) and 602-cm$^{-1}$ ($xx$) modes show a linear behavior up to third-order. A deviation from such a feature is seen at fourth-order. (b) The integrated intensity of higher-order phonon spectra. Especially, the 641-cm$^{-1}$ mode shows a strong decrease of scattering intensity with increasing order.

Observation of multi-phonon scattering.$^{9,14}$ In this local mechanism, higher-order scattering usually shows up at integer multiples of one-phonon peak energy, as the FC process results from a displacement of the intermediate electronic state from the initial one rather than a simultaneous emission of $n$-phonons. Thus, this feature enables us to check the validity of the FC mechanism.

The 985- and 1485-cm$^{-1}$ peaks correspond to the overtones of the 493-cm$^{-1}$ mode in $xx$ polarization. The 1017-, 1539-, and 2096-cm$^{-1}$ peaks might also be related to higher-order scattering of the 493-cm$^{-1}$ mode in $x'x'$ polarization. Similarly, the 1137 (1173)-, 1653 (1781)-, and 2297 (2418)-cm$^{-1}$ modes are assigned to the overtones of the 602-cm$^{-1}$ mode in $xx$ ($x'x'$) polarization. The 1281-, 1911-, and 2542-cm$^{-1}$ modes correspond to the overtones of the 641-cm$^{-1}$ mode. Several distinct features show up. The second order scattering at 1281 cm$^{-1}$ is much more intense than the first order one at 641 cm$^{-1}$. Furthermore, as Fig. 2(a) displays, there are the energy differences between multi-phonon scattering and integer multiples of one-phonon peaks. For example, the overtones of the 602-cm$^{-1}$ mode in $xx$ polarization shift to higher energy up to third order and then show a decrease at fourth order. In contrast, those of the 493-cm$^{-1}$ mode in $x'x'$ polarization shift to lower energy with increasing order. The overtones of the 641-cm$^{-1}$ mode show no substantial anomaly in frequency. Instead, its scattering intensity as a function of order does not parallel to other modes contrary to the FC picture. As a consequence of a strong decrease of scattering intensity at fourth order it becomes weaker than that of the 602-cm$^{-1}$ mode in $x'x'$ polarization [see Fig. 1(c) and Fig. 2(b)]. This demonstrates that the FC mechanism cannot capture the full aspect of the observed multi-phonon scattering. Further note that even if one considers a combination of first-order peaks, one cannot produce consistently all higher-order peaks.$^{15}$

We turn now to the temperature dependence of the higher-order Raman spectra. As Fig. 3 shows, upon heating the second order maxima undergo a broadening and softening. The third and fourth order signal (not shown here) can be detected up to 350 K and 150 K, respectively. Their behavior parallels that of the second order signal within the measured temperature interval. The main features are summarized in Fig. 4. First, with increasing temperature the normalized intensity of the one-phonon mode as well as of their overtones falls off like an order parameter [see Fig. 4(a) for a typical behavior at 493 cm$^{-1}$]. Second, the second order mode softens by 40 cm$^{-1}$ upon heating from 5 K to 640 K. The representative example at 1281 cm$^{-1}$ is shown in Fig. 4(a). This is contrasted by a small frequency shift of the corresponding one-phonon mode by $\sim$ 6 cm$^{-1}$. Noticeably, its temperature dependence agrees well with that of the phonon intensity. Third, the ratio of a second- to first-order integrated phonon intensity, $I_2/I_1$, decreases gradually with increasing temperature as Fig. 4(b) shows.

FIG. 3: (online color) Polarized Raman spectra of LaMnO$_3$ as a function of temperature. The spectra are shifted for clarity.
mode. This symmetry dependence reproduces partially
the intensity of the 639-cm$^{-1}$ mode. (b) The ratio of second- and first-order
scattering at 1163 cm$^{-1}$ as a function of temperature.

FIG. 4: (a) Temperature dependence of the normalized in-
tensity of the 493-cm$^{-1}$ mode as well as the peak energy of
the 1281-cm$^{-1}$ mode. (b) The ratio of second- and first-order
scattering at 1163 cm$^{-1}$ as a function of temperature.

FIG. 5: (online color) Second-order Raman spectra of
La$_{1-x}$Sr$_x$MnO$_3$ at 5 K as a function of doping ($x = 0$, 0.06,
0.09, and 0.125)

In Fig. 6(a) we provide a polarization dependence of
the $x = 0.06$ sample owing to the discrimination between
$xy$ plane and $z$ axis. Remarkably, in $zz$ polarization we
observe solely the 1281-cm$^{-1}$ mode. This is quite unusual
when taking into account that the intensity of the 639-
cm$^{-1}$ mode is much weaker than that of the 494-cm$^{-1}$
mode. This symmetry dependence reproduces partially
the result reported in Ref.[1] and can hardly be under-
stood within a conventional multi-phonon picture. Fig-
ures 6 (b) and (c) display the temperature dependence
for $x = 0.09$ and 0.125. The $x = 0.09$ shows a moder-
ate decrease of the second-order maxima upon heating
from 5 K to room temperature. In contrast, the FMI
sample ($x = 0.125$) exhibits a rather strong suppression
of the second-order signal through the metal-insulator
transition at $T_C = 185$ K where the rearrangement of or-
bital ordering takes place. This suggests a relationship
between the observed multi-phonon scattering and the
change of an orbital ordering form through the CAF/FMI
phase boundary (see below).

IV. DISCUSSIONS

In the following we will examine the origin of the
anomalous multi-phonon scattering.

Usually, anharmonic electron-phonon interactions can
lead to multi-phonon scattering in transition metal ox-
ides. The simultaneous emission of $n$ phonons occurs due
to lattice anharmonicity. Since this mechanism is a sim-
ple extension of a first-order process to higher order, the
intensity of $n$-phonon scattering decays as $g^{2n}$, where $g$
is the electron-phonon coupling constant. In addition, the
intensity ratio of a second- to first-order scattering, that
is $I_2/I_1$, would be independent of temperature since the respective intensity has the same resonant dependence on incident photon energy.\textsuperscript{17} Obviously, these considerations cannot account for (i) the larger intensity of the second-order peak at 1281 cm$^{-1}$ compared to that of the first-order peak at 641 cm$^{-1}$ ($I_2/I_1 \sim 20$ at 5K), (ii) the anomalous evolution of peak energies in higher-order scattering (see Table I and Fig. 2), and (iii) the temperature-dependent ratio of $I_2/I_1$ [see Fig. 4(b)].

Another effective mechanism is based on resonance scattering. In this process multi-phonons are created by a first-order electron-lattice interaction together with a virtual electron excitation.\textsuperscript{17} When the incident photon energy is in resonance with localized electronic excitations, multi-phonon scattering becomes enhanced. Very recently, resonant Raman scattering measurements of LaMnO$_3$ reveal a sharp resonance around 2 eV via the creation of orbiton excitons.\textsuperscript{9} Since in our experiment the incident light energy of 2.34 eV lies in the window of resonance (0.65 eV), the observed multi-phonon scattering is also governed by resonant scattering caused by orbitons. Significantly, orbital excitations in the JT ordered state are governed by resonant scattering caused by orbitons.

In the JT ordered state, orbiton induced satellites are intrinsically coupled to phonons under electron-phonon coupling. Theoretically, orbiton induced satellites are predicted to develop at higher frequencies of the phonon spectrum.\textsuperscript{4} In this scenario, the dominant energy scale of orbiton satellites is determined by the strength of electron-phonon coupling. Noticeably, the anomalous increase of the peak energy is observed at fourth-order scattering between 2096 and 2542 cm$^{-1}$ [see Figs. 1 and 2]. If this anomaly is considered to be a result of the influence of orbiton satellites on multi-phonon scattering, one can obtain strong electron-phonon coupling of $g \sim 1$.\textsuperscript{4} However, orbiton satellites do not show up as separate peaks. Rather, a orbiton-phonon mixed character is reflected in diverse anomalies of the observed multi-phonon modes.

This scenario can well explain the observed giant softening of the two-phonon modes by 40 cm$^{-1}$ as a function of temperature [see Fig. 4(a)]. Upon heating, the JT distortions become weaker as demonstrated by the order-parameter-like fall-off of the intensity of the Mn-O bond stretching mode in Fig. 4(a). The weakening of electron-phonon coupling will lead to a shift of the orbital excitation energy to lower energies.\textsuperscript{4} Further evidence is provided by the temperature-dependent ratio of $I_2/I_1$. With increasing temperature the local JT oxygen displacement caused by the FC process will fade away. Consequently, the FC contribution to multi-phonon scattering gradually decreases while reducing the orbiton-phonon mixed character of multi-phonon scattering. Then, a crossover of the FC mechanism to a conventional one results in the reduced lifetime of the orbital exciton seen in Fig. 4(b).

Also the drastic change of the two-phonon modes through the CAF/FMI phase boundary supports our interpretation. The three features of the CAF samples turn into a broadened maximum around 1000 cm$^{-1}$ in the $x = 0.125$ sample. The comparison between the Sr- and oxygen-doped samples\textsuperscript{16} unveils that the broadened maximum around 1000 cm$^{-1}$ at $x = 0.125$ results from a softening of the maxima centered around 1300 cm$^{-1}$ at $x = 0.09$. Such a giant shift of the two-phonon mode as a function of doping is quite unusual and cannot be understood without considering the orbital degrees of freedom. In the CAF phase a $d_{3z^2-r^2}/d_{3y^2-r^2}$ type of an orbital ordering is stabilized mainly by the cooperative JT distortions, leading to the JT gap of 2 eV. When the incident light energy is within the window of resonance (0.65 eV), Raman scattering process takes place through an orbital flip from a $d_{3z^2-r^2}/d_{3y^2-r^2}$ orbital ordered state.\textsuperscript{9} In this resonant Raman process, the energy and shape of multi-phonon scattering are largely determined by a matrix element of orbiton excitons. Thus, the three-peak feature of the observed two-phonon scattering and their polarization dependence should be attributed to the specific orbital ordering pattern of LaMnO$_3$. In the FMI phase a new type of orbital state evolves from the LaMnO$_3$-type orbital state upon cooling below $T_C \approx 185$ K while suppressing the JT distortions.\textsuperscript{10} Although its exact form is not known, there exists evidence that orbital polarons are an essential part of a new orbital ordered state.\textsuperscript{10,13} Most probably, thus, the orbital ordering of the FMI phase will be given as a combination of an orbital polaron and a $d_{3z^2-r^2}/d_{3y^2-r^2}$ orbital. Noticeably, the binding energy of orbital polarons, $\Delta_p = 0.6$ eV, is much smaller than the JT gap of 2 eV.\textsuperscript{20} As a result, Raman scattering process will be mainly governed by an off-resonance one. This leads to a smearing of the features arising from orbitons. Actually, the three-peak feature changes into the unstructured maximum. In par-
ticular, this is related to a fluctuation of the underlying orbitals in the FMI phase.\textsuperscript{10,13} The weakening of orbiton-phonon coupling can account for a giant softening of the two-phonon frequency. Therefore, we come to the conclusion that the multiphonon scattering in LaMnO\textsubscript{3} relies strongly on the orbital ordered pattern. Furthermore, the intrinsic orbiton-phonon couplings are responsible for the observed anomalous behaviors in intensity and frequency.

\section*{V. SUMMARY}

In summary, we have reported a detailed study of the higher-order Raman scattering in the manganites La\textsubscript{1−x}Sr\textsubscript{x}MnO\textsubscript{3} as a function of temperature and doping. For the first time, we are able to probe and analyze phonon scattering up to forth-order using Raman spectroscopy. Doping dependence of two-phonon scattering together with the frequency shift of several higher order modes indicates several anomalies which cannot be understood within the canonical FC mechanism. The full understanding of the multi-phonon scattering in the orbital-ordered LaMnO\textsubscript{3} system can be achieved by considering the orbiton-phonon mixed character. Our study suggests that in orbital ordered systems multi-phonon scattering can serve as a valuable probe of the orbital dynamics.

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