Correlation between lattice vibrations with charge, orbital, and spin ordering in the layered manganite Pr$_{0.5}$Ca$_{1.5}$MnO$_4$

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A Raman spectroscopy study on the half-doped single-layer manganite Pr$_{0.5}$Ca$_{1.5}$MnO$_4$ has been performed in combination with x-ray diffraction, resistivity, magnetization, and specific heat measurements. The results provide insight into the underlying mechanisms of phenomena that arise from correlations between lattice, charge, orbital, and spin degrees of freedom. The appearance of a new Raman mode at 366 cm$^{-1}$, a visible jump in the resistivity, and a doubling of the unit cell signify the onset of charge/orbital ordering at 320 K. This transition is also marked by a sharp peak in the magnetic susceptibility and specific heat, suggesting strong spin-charge coupling. Our structural analysis suggests that the charge disproportionation below 320 K is small. Orbital fluctuations below 320 K are evidenced by the evolution with temperature of the Jahn-Teller Raman mode (situated at 533 cm$^{-1}$ at 320 K). A coincidence between the onset of two-dimensional short-range antiferromagnetic order at 215 K and anomalies in both the temperature dependence of the Jahn-Teller mode and the Mn-O bonding pattern in the $ab$ plane indicate that the short-range magnetic order plays a role in stabilizing the orbital fluctuations. Below the Néel temperature of 127 K, the softening of both the 366 cm$^{-1}$ mode and an octahedral tilting mode at 214 cm$^{-1}$ mark the onset of three-dimensional antiferromagnetic ordering. The estimated spin-phonon coupling constants for these two modes are 2.6 and 6.8 cm$^{-1}$, respectively. This study highlights the remarkable coupling of charge, orbital, and spin degrees of freedom to the lattice in single-layer Pr$_{0.5}$Ca$_{1.5}$MnO$_4$.

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I. INTRODUCTION

The mixed valence manganites show a complex phase diagram arising from the interplay between various degrees of freedom, leading to a variety of lattice, spin, charge, and/or orbitally ordered states. The rich variety of physical properties arising from these states can be controlled by chemical substitution, temperature, pressure, and external fields. As proposed by Goodenough [1], it is generally considered that charge ordering (CO) of the Mn$^{3+}$ and Mn$^{4+}$ sites is accompanied by orbital ordering (OO), where the occupied 3$d_{x^2-r^2}$ orbitals of the Mn$^{3+}$ ions are oriented in a zigzag fashion to form chains in the $ab$ plane. This OO plays an important role in determining the optical, electronic, and magnetic properties.

In the half-doped system, the CO-OO order is followed at lower temperature by an antiferromagnetic (AFM) spin ordering (SO), where the manganese 3$d$ spins are aligned ferromagnetically (FM) along the zigzag chains and antiferromagnetically between adjacent chains (CE-type AFM order). In this conventional model, both the magnetic orbitals and the spin orientations are confined in the $ab$ plane, and the orbital and spin interactions along the $c$ axis are considered to be weak. This model has been challenged by several experiments which showed that the orbital occupation and spin alignment are not always confined to the $ab$ plane [2,3]. Furthermore, there are indications that the long-range CO is not always accompanied by a long-range ordering of the orbital occupation [4]. In addition to the site-centered CO model [1,5], a Zener polaron, bond-centered model has also been proposed based on x-ray synchrotron and neutron diffraction data, which suggests that the CO involves the formation of dimers of mixed valence manganese and shifts of the oxygen ions [6,7].

Even though they have been widely studied, there are several intriguing properties of manganites that require further investigation, in particular, the dimensionality of the MnO$_6$ coordination which is known to have a significant influence on the physical properties. The single-layered $A_2$MnO$_4$ system has a higher CO-OO transition temperature than the $A$MnO$_3$ perovskite analog. Unlike the conventional OO model of the perovskite, the hybridization of $3d_{x^2-r^2}$ and $3d_{x^2-y^2}$ orbitals has been reported for the single-layered system [2,3]. The electrons are then distributed among nearly degenerate orbitals and a well-ordered orbital state is reached at a temperature lower than the CO transition. This has important consequences, including the existence of orbital fluctuations and their coupling to other degrees of freedom.

The interplay of charge and orbital order with lattice dynamics in single-layer manganites has been investigated previously in a Raman spectroscopy study on La$_{0.5}$Sr$_{1.5}$MnO$_4$ [8]. The activation of several phonons, originating from the lattice distortions at the CO-OO transition, was observed and their evolution with temperature was followed in order to probe charge/orbital fluctuations. The temperature evolution of the Jahn-Teller (JT) mode was reported to clearly mark the CO transition. In addition, the existence of orbital fluctuations was suggested, based on the temperature evolution of the diffuse scattering. Orbital ordering was proposed to partially set in.
below the CO transition with the fully ordered state being reached around $T_{Kr}$. A decrease of the Raman mode intensity along the $c$ direction was also observed and interpreted as an indication of the decrease of interplane coupling below the CO transition.

In this study of the half-doped single-layer system $\text{Pr}_0.5\text{Ca}_{1.5}\text{MnO}_4$ (PCMO), we discuss the correlation between a rotational MnO$_6$ octahedral mode and the charge ordering, possible orbital fluctuations, and the effect of two-dimensional short-range AFM order on these orbital fluctuations. We also discuss the coupling of the lattice system, in particular, changes in the Mn-O bonding pattern, to the charge, orbital, and spin degrees of freedom. To that end, we perform Raman spectroscopy measurements in combination with powder x-ray diffraction, magnetization, resistivity, and specific heat measurements. In $\text{Pr}_0.5\text{Ca}_{1.5}\text{MnO}_4$, the Mn$^{3+}$ and Mn$^{4+}$ cations, which have different Mn-O bond lengths, are supposed to be nominally equal in concentration. Furthermore, both FM and AFM coupling coexist in addition to the competition between CO and itinerant electrons. Possessing a relatively small average Pr/Ca radius of 1.18 Å and a small variance of $2 \times 10^{-3}$ Å $^2$ [9], this compound exhibits a large octahedral distortion and the quenched disorder is largely suppressed. This situation leads to a complex phase diagram. Thus far, a CO-OO phase transition at 320 K has been observed [9–12], followed by the onset of two-dimensional (2D) short-range AFM order at 200 K [13], and three-dimensional (3D) long-range AFM order at 127 K [9,12,13].

In our current study, the CO ordering is clearly signified by an abrupt jump of the magnetic susceptibility, a visible change in the resistivity, a sharp jump in the specific heat, a clear change in the Mn-O bonding pattern, and a crystallographic transition from the $\text{Bmab}$ to the $\text{Pnma}$ space group. In contrast to $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, where the CO transition is accompanied by a change in lattice symmetry from tetragonal to orthorhombic, a transition from tetragonal to orthorhombic symmetry occurs in $\text{Pr}_0.5\text{Ca}_{1.5}\text{MnO}_4$ at 470 K [14], well above the CO-OO transition at 320 K. Our current study differs from that of Yamamoto et al. [8], which focused on the JT mode and diffuse scattering, in that our Raman study also includes analysis of the rotational mode at 366 cm$^{-1}$ which has order-parameter-like features and marks the CO-OO transition, as well as the tilting mode which is sensitive to charge and spin orderings. In addition, we estimate the magnitude of the charge-lattice coupling and spin-lattice coupling. Overall, our study gives a comprehensive picture of the relationships between lattice dynamics, Mn-O bonding, magnetic susceptibility, specific heat, and resistivity in half-doped single-layer manganites. Using several different experimental techniques, we show that charge, orbital, and spin order in $\text{Pr}_0.5\text{Ca}_{1.5}\text{MnO}_4$ does not occur in a straightforward fashion.

II. EXPERIMENTS

Crystal platelets were cut from a single-crystal rod grown using the floating zone technique. Single-crystal x-ray diffraction (XRD) was performed in the temperature range 100–350 K on a crystal fragment of approximate dimensions $0.2 \times 0.1 \times 0.05$ mm using a Bruker D8 Venture four-circle diffractometer operating with Mo $K\alpha$ radiation and equipped with a Triumph monochromator and a Photon100 area detector. Powder XRD was performed on a pulverized single crystal. Diffraction patterns were collected between 298 and 343 K using a Bruker D8 Advance diffractometer operating with Cu $K\alpha$ radiation. Low-temperature diffraction patterns ranging from 300 to 40 K were measured using a Huber G670 diffractometer, also with Cu $K\alpha$ radiation. The temperature dependence of the magnetization was measured using a Quantum Design magnetic property measurement system (MPMS) XL superconducting quantum interference device (SQUID) magnetometer. A 40 mg sample was placed in a gelatin capsule filled with cotton to avoid sample rotation during the measurement. Magnetization measurements were performed on warming in both zero field cooled (ZFC) and field cooled (FC) modes from 5 to 340 K, in applied external magnetic fields of 0.1 T along the $a$, $b$, and $c$ axes. The temperature dependence of the electrical resistivity was measured using a four-probe method in which platinum wires were contacted to the sample using $\approx 1$ mm$^2$ silver paste droplets deposited at 1 mm intervals along the $a$ axis. The wires were connected to the terminals of a chip carrier which was mounted on the cold finger of a He flow cryostat. The temperature was varied from 340 to 100 K. $I$-$V$ curves were measured using a Keithley 237 source-measure unit. The resistivity measurements were performed by varying the voltage and measuring the current, and taking the slope of the $I$-$V$ curves. The temperature dependence of the heat capacity was measured using a Quantum Design 9T physical properties measurement system (PPMS). The sample was mounted on the microcalorimeter platform using Apiezon N grease. The temperature was varied from 5 up to 340 K with intervals of 5 K.

Raman spectroscopy measurements were performed on the $ab$ plane of a naturally cleaved single-crystal PCMO sample. A continuous wave laser (532 nm) with a power density of 0.5 W/cm$^2$ was used as the excitation source. Polarized Raman spectra were recorded at different temperatures using a Jobin Yvon T64000 micro-Raman spectrometer; the sample was mounted in a cold finger Oxford microstat. Considering the largest distortions of the Mn-O bonds below the CO-OO temperature (see the XRD results below), measurements were performed in back scattering mode with the $c(aa)c$ and $c(ba)c$ configurations in the range 35–615 cm$^{-1}$. Different features of the Raman spectra in these two different configurations are expected to be observed as a consequence of symmetry lowering upon charge ordering.

III. STRUCTURAL, MAGNETIC, AND THERMODYNAMIC PROPERTIES

Figure 1 shows the temperature dependence of the powder XRD patterns between 343 and 303 K, as well as at 40 K, in order to provide a general description of the structural changes. In the inset, the splitting of the 020 and 200 peaks below 320 K indicates an increase in the degree of orthorhombicity below the CO-OO transition. The patterns were fitted using the GSAS software package with the EXPGUI interface [15] and the lattice parameters were $a = 5.376(3)$ Å, $b = 5.411(6)$ Å, and $c = 11.830(9)$ Å at room temperature.

Figure 2(a) shows the temperature dependence of the lattice constants, where pronounced changes are apparent across the CO-OO transition. The degree of orthorhombicity is largest...
around 200 K. A nonmonotonic change also occurs at $T_N$, indicating a coupling of the spins to the lattice. The lattice constants showed a similar trend as in a previous neutron diffraction study [13]. In the inset, the ratio between the $c$ lattice constant and the sum of the $a$ and $b$ lattice constants is shown. A remarkable change in this ratio is apparent in the range $320 \text{ K} < T < 200 \text{ K}$. A kink is visible close to $T_N$ of 127 K.

Figure 2(b) shows the magnetic susceptibility as a function of temperature. There are three main features: (1) a rather sharp maximum at $320 \text{ K}$, (2) a broad maximum around 200 K, and (3) a sudden drop below $T_N = 127 \text{ K}$ for the $a$- and $b$-axis susceptibility. The susceptibility measured along the $c$ axis instead shows an increase below $T_N$. These features are more apparent in the derivative of the magnetic susceptibility [inset to Fig. 2(b)], where a small anomaly at 127 K is also observed for the $c$ axis. The specific heat as a function of temperature is presented in Fig. 2(c). The phase transition from the disordered to the CO-OO state leads to a sharp peak at 320 K, indicating the entropy release accompanying this transition. The specific heat in the low-temperature regime appears to be dominated by phonon contributions without any observable anomaly at $T_N = 127 \text{ K}$. The formation of short-range AFM order at higher temperatures has been proposed as the reason for this absence [17]. In the inset of Fig. 2(c) a small jump of the electrical resistivity at 320 K coincides with the onset of the CO-OO insulating state.

A more detailed structural investigation was performed using single-crystal XRD. Pseudomerohedral twinning in which two domains are formed by a 90° rotation around the $c$ axis was taken into account in the data analysis at all temperatures. Superstructure reflections appeared below 321 K, corresponding to a doubling of the $b$ axis. The space group symmetry changed from $Bmeb$ to $Pnma$, consistent with a previous XRD study of Pr$_{0.5}$Ca$_{1.5}$MnO$_4$ [18] and the same symmetry as the orbital-ordered state of Eu$_{0.5}$Ca$_{1.5}$MnO$_4$ [19]. In the $Pnma$ supercell Mn is situated on 4$a$ and 4$c$ sites, and Ca/Pr is located on a pair of 4$c$ sites and an 8$d$ site. As shown in Fig. 3, the Mn-O bonding pattern is different for the two sites; given that charge ordering is expected in the $Pnma$ phase, bond valence sums (BVSs) were calculated assuming that Mn$^{3+}$ and Mn$^{4+}$ occupy the octahedra with shorter and longer average Mn-O lengths, respectively. Excess specific heat at $\sim 280 \text{ K}$ [indicated by * in (c)] originates from the Apiezon N grease [16].
of significance here is the JT distortion mode in BVS is much larger. These data suggest that the charge disproportionation below 320 K is small; we will hereafter refer to the 4a site as Mn\textsuperscript{3.5−δ}+ and the 4c site as Mn\textsuperscript{3.5+δ}+. A similar degree of charge disproportionation was previously reported for Eu\textsubscript{0.5}Ca\textsubscript{1.5}MnO\textsubscript{4} [19].

Some further selected structural parameters are plotted in Fig. 4. Of significance here is the JT distortion mode \(Q2\), which quantifies the relative difference between the short (s) and long (l) Mn-O bonds in the \(ab\) plane and is defined as \(Q2 = (l - s) / \sqrt{2}\). Similar to the BVS, an anomaly in the temperature evolution of \(Q2\) for the Mn\textsuperscript{3.5−δ}+ octahedron is observed at 200 K. A similar feature is seen in the evolution of \(\Delta_d\), which is a measure of the overall octahedral distortion and is defined as \(\Delta_d = \frac{1}{6} \sum_i [(\text{MnO}_{i}) - \text{MnO}_{\text{average}}]/\text{MnO}_{\text{average}})^2\). In perovskites the A-site cations will tend to shift with temperature as the degree of JT distortion and/or octahedral tilting/rotation develops [21]. Here, all the Ca/Pr atomic coordinates stay fixed within error bars over the measured temperature range, except for the \(x\) coordinate of one of the two 4c Ca/Pr atoms, which moves steadily along the \(a\) axis with temperature, as shown in Fig. 3. The shift of this atom temporarily “slows down” close to \(≈200\) K, which coincides with the anomaly in BVS and the local minimum in the \(Q2\) mode for Mn\textsuperscript{3.5−δ}+.

### IV. VIBRATIONAL PROPERTIES

Figure 5 shows the temperature dependence of the Raman spectra between 100 and 350 K. For the \(c(aa)\) configuration, a broad mode centered at 533 cm\(^{-1}\) is observed above the CO-OO phase transition, as well as weaker features at 70, 180, and 212 cm\(^{-1}\). For the \(c(ba)\) configuration, the broad mode centered at 533 cm\(^{-1}\) is also observed above the CO-OO phase transition, together with four weak peaks at 80, 120, 180, and 205 cm\(^{-1}\). Upon lowering the temperature, the intensity of the 533 cm\(^{-1}\) mode increases, it shifts to higher frequency, and the linewidth narrows. Several new peaks at 443, 408, 366, 314, 100, and 57 cm\(^{-1}\) are observed for the \(c(aa)\) configuration while new modes at 448, 405, 366, 309, 212, 99, and 76 cm\(^{-1}\) are observed for the \(c(ba)\) configuration.

For the \(Bmnb\) space group, 24 Raman modes are expected, which are decomposed into \(7A_g + 5B_{1g} + 4B_{2g} + 8B_{3g}\). Among those, only the \(A_g\) and \(B_{2g}\) modes are accessible in our experiment: The \(A_g\) modes are active in the \(c(aa)\) configuration, while the \(B_{2g}\) modes are active in the \(c(ba)\) configuration. The other modes are only accessible in configurations which include a polarization along the \(c\) axis, which is not the case in our experiment. The number

![FIG. 3. (Color online) Mn-O bonding pattern in the \(Bmnb\) phase at 325 K and in the \(Pnma\) phase at 275 K with bond lengths in Å. The solid black line indicates the unit cell in each case. The green arrows in the 275 K structure indicate shifts of Pr/Ca atoms compared to the 325 K structure.](image)

![FIG. 4. (Color online) Temperature dependence of (a) \(Q2\), (b) \(\Delta_d\), (c) bond valence sum, and (d) Ca/Pr \(x\) coordinate. Red and blue data points correspond to Mn\textsuperscript{3.5−δ}+ and Mn\textsuperscript{3.5+δ}+ octahedra, respectively. The inset in (d) shows the two crystallographically distinct Mn-O-Mn angles in the \(ab\) plane.](image)

![FIG. 5. (Color online) Raman spectra of Pr\textsubscript{0.5}Ca\textsubscript{1.5}MnO\textsubscript{4} at different temperatures in (a) the \(c(aa)\) configuration and (b) the \(c(ba)\) configuration. The inset shows Raman spectra measured at 100 K for the frequency range from 170 up to 1200 cm\(^{-1}\). For clarity, the spectra have been shifted vertically and are presented on a logarithmic scale.](image)
of observed Raman modes above \( T_{COOO} \) is consistent with that expected for the \( Bmeb \) space group. Below \( T_{COOO} \), the number of active Raman modes increases such that we observe nine \( A_g \) modes in the \( c(\alpha\alpha)c \) configuration and ten \( B_{2g} \) modes in the \( e(\nu\nu)c \) configuration. This clearly indicates a lowering of the crystal symmetry below \( T_{COOO} \), in line with our single-crystal XRD analysis and the work of Okuyama et al. on \( Eu_0.5Ca_1.5MnO_4 \) [19], who also observed the change of space group from \( Bmeb \) into \( Pnma \). For the \( Pnma \) space group, the Raman active modes below \( T_{COOO} \) can be classified as \( 29A_g + 22B_{1g} + 29B_{2g} + 22B_{3g} \) [22]. This represents many more than the number of observed Raman active modes in our experiment, which is most likely due to accidental degeneracies and/or weak mode intensities.

In order to obtain quantitative information on the temperature dependence of the Raman modes, our experimental data were fitted using the Lorentzian response functions

\[
I(\omega) = \sum_i \frac{\sigma_i}{(\omega - \omega_i)^2 + (\Gamma_i/2)^2}
\]

Before fitting, we subtracted a constant background from our data and performed a Bose-Einstein thermal factor correction. For each mode \( i \) we obtained the scattering strength \( a_i \), the mode frequency \( \omega_i \), and the linewidth \( \sigma_i \) [\( 2\sigma \) is the full width at half maximum (FWHM)]. Assuming that the phonons decay via an anharmonic process, the changes in frequency and linewidth with temperature were further analyzed using an anharmonic model [23,24] in which one phonon decays into two or three identical phonons. Here, we focus on the modes at 533, 366, and 212 cm\(^{-1}\), which show obvious changes at the CO-OO and spin ordering transitions. In single-layer systems, modes in this range have generally been associated with the oxygen vibrations [8,25,26]. In particular, the 533 cm\(^{-1}\) mode was previously assigned to a JT distortion in the \( ab \) plane [8]. To the best of our knowledge, no specific assignment of the mode at 366 cm\(^{-1}\) has yet been made for single-layer compounds. However, in \( LaSrMnO_4 \), a peak at 356 cm\(^{-1}\) was associated with a magnetically activated mode [26]. Considering its sensitivity to the CO-OO and spin ordering, we associate our 366 cm\(^{-1}\) peak with the rotation of MnO\(_6\) octahedra around the \( x \) axis, as previously suggested for the perovskite systems [27]. In Ref. [8], modes close to 212 and 180 cm\(^{-1}\) were associated with the motion of rare earth ions. In our experiment, those two modes are strongly correlated with each other and are sensitive to the spin ordering. Therefore, we associate them with tilting of the MnO\(_6\) octahedra around the \( y \) axis, as previously suggested in Ref. [28] for the perovskite systems.

The temperature dependence of the frequency, linewidth, and amplitude of the JT mode are shown in Fig. 6. The frequency shows a small anomaly at 215 K that separates two different temperature regimes. The three-phonon anharmonic process, in which one phonon decays into two identical phonons, can only be fitted to the low-temperature data (100 K < \( T < 215 \) K) whereas the four-phonon process, in which one phonon decays into three identical phonons, can only be fitted to the high-temperature data (215 K < \( T < 360 \) K), as shown in Fig. 6(a). The intersection of these low- and high-temperature regimes at 215 K coincides with the broad maximum in magnetic susceptibility, suggesting that the onset of 2D short-range AFM order changes the phonon decay channels. The linewidth of the JT mode is also not well fitted by a single anharmonic model, as shown in Fig. 6(b).

FIG. 6. (Color online) Temperature dependence of (a) the frequency and (b) the linewidth of the JT mode, extracted from Fig. 5(b). A change in trend of the frequency shift is observed at 215 K. The dashed blue and red lines are fits assuming three- and four-phonon decay processes, respectively, and the green line in (b) represents the sum of three- and four-phonon contributions over the whole temperature regime. The inset shows the amplitude of the JT mode as a function of temperature.

Again, a combination of three- and four-phonon processes is required in order to fit the experimental data over the entire temperature range. A gradual increase in amplitude is observed with decreasing temperature. The amplitude increases more rapidly below 215 K, suggesting the stability of the JT mode.

Figure 7(a) shows the temperature evolution of the octahedral rotational mode at 366 cm\(^{-1}\) in the \( c(\alpha\alpha)c \) configuration. This mode appears below 320 K and its intensity increases with decreasing temperature. As shown in Fig. 7(b), a “mean field” approximation of \( G(1 - T/T_{COOO})^{0.5} \) fits the integrated intensity below the CO-OO transition well, with a charge-lattice coupling \( G \) of 0.58 cm\(^{-1}\). The experimental data start to deviate from the mean field approximation below 200 K, suggesting that the presence of a magnetic degree of freedom induces an additional type of fluctuations.

The temperature dependence of the frequency and linewidth of the octahedral rotational mode are shown in Figs. 8(a) and 8(b).
The increasing intensity on cooling is accompanied by an upward shift in the frequency and a narrowing of the linewidth. The Raman frequency hardens by up to 4 cm$^{-1}$ as $T_N$ is approached. It is interesting to note that upon cooling below $T_N$, the frequency softens again by 2 cm$^{-1}$. The anharmonic model fits to the data assuming predominantly three-phonon decay processes are shown by the red lines in Fig. 8. In order to study the effect of the magnetic transition, the anharmonic model fit was subtracted from the temperature dependence of the frequency below 140 K, as shown in the inset of Fig. 8. A fit using $\Delta \omega(T)_{\text{spin-phonon}} \approx F[1 - T/T_N]^\nu$ yields a spin-lattice coupling $F$ of 2.6 cm$^{-1}$ and a critical exponent $\nu$ of 0.5.

Figure 9 shows the temperature dependence of the two octahedral tilting modes, labeled $A$ and $B$, observed in the $c(ba)c$ configuration. These modes evolve differently with temperature. In order to clearly describe the relation between these modes, the ratio of the integrated intensities $I_A/I_B$ is shown in Fig. 9(b). The data show the presence of two distinct phase transitions: An abrupt change in slope of $I_A/I_B$ occurs at $T_{\text{CO-OO}}$ and a small change in slope occurs at $T_N$. These features reflect the structural changes associated with the onset of CO-OO and 3D spin ordering.

Figure 10 shows the temperature dependence of the frequency and linewidth of mode $B$. The frequency of mode $B$ shows obvious anomalies both at the CO-OO and AFM phase transitions. However, the linewidth decreases linearly with temperature down to 250 K and remains constant upon further cooling. The red lines are fits of the anharmonic model to the experimental data. The softening of the frequency below the AFM transition indicates the influence of magnetic ordering on this phonon, whereas the relatively constant linewidth below 250 K might indicate the suppression of charge and orbital fluctuations before the 3D AFM order appears. In order to accentuate the role of spin-phonon coupling, the inset of Fig. 10(a) shows the deviation of the frequency of mode $B$ below 140 K from the anharmonic fit. This deviation, expressed as $\Delta \omega(T)_{\text{spin-phonon}} \approx F[1 - T/T_N]^\nu$, is well fitted to the data using a spin-phonon coupling $F = 6.8$ cm$^{-1}$ and a critical exponent $\nu = 0.57$.

V. DISCUSSION

Our temperature-dependent Raman data reveal a number of characteristic changes at the CO-OO transition of 320 K that represent strong indications of orbital fluctuations and 2D AFM short-range ordering in the intermediate state 320 K < $T < 127$ K, whereas 3D AFM ordering is stabilized below 127 K. Compared to the previously reported Raman data in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$ [8], where the evolution of the JT mode at 533 cm$^{-1}$ was identified as a signature of the CO transition and diffuse scattering as an indication of orbital fluctuations, we observe the evolution of the JT mode as an indication of orbital fluctuations and the evolution of the rotational mode at 366 cm$^{-1}$ as a signature of charge ordering. To support this interpretation of the Raman data, we also report on the evolution of the Mn-O bonding pattern in the $ab$ plane ($Q_2$).
as well as magnetic susceptibility, resistivity, and specific heat data.

The intensity of the JT mode shows a gradual temperature evolution only, in contrast to the order-parameter-like behavior observed in \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4 \) \[8\]. This might be due to the absence of a change in lattice symmetry from tetragonal to orthorhombic at \( T_{\text{CO-OO}} \) since that structural change occurs at the much higher temperature of 470 K in \( \text{Pr}_{0.3}\text{Ca}_{1.5}\text{MnO}_4 \). The CO-OO transition in \( \text{Pr}_{0.3}\text{Ca}_{1.5}\text{MnO}_4 \) is signified by the appearance of the octahedral rotational mode \( (366 \text{ cm}^{-1}) \), the intensity of which shows order-parameter-like behavior. The analysis of this mode using a mean field model is consistent with order-parameter-like behavior with a critical exponent of \( \nu = 0.5 \). The \( T_{\text{CO-OO}} \) is also characterized by the onset of a continuously shifting frequency for octahedral tilting mode \( B \) below the transition and by a more rapid transfer of intensity to tilting mode \( A \) on heating above the transition. The latter observation implies a correspondingly rapid symmetry lowering. Indeed, these Raman signals are closely correlated with the XRD data, which reveal an abrupt change in the lattice constants and an increase in the degree of orthorhombicity at this transition. Further analysis using single-crystal Raman data shows that the \( Q^2 \) distortion exhibits a remarkable change at \( T_{\text{CO-OO}} \). As presented in Figs. 3 and 4(a), the Mn-O bonds become unequal in length below the \( T_{\text{CO-OO}} \), depending on the valence of the manganese ions. The effect of the symmetry breaking from \( \text{Mn}^{3+} \)–O–\( \text{Mn}^{3+} \) bonds to \( \text{Mn}^{(3.5+\delta)+} \)–O–\( \text{Mn}^{(3.5–\delta)+} \) bonds and the gradual decrease of the Mn-O-Mn bond angles in the \( ab \) plane with decreasing temperature \[inset to Fig. 4(d)\] in turn leads to the observed changes in the rotation and tilting modes. Our analysis of the rotation mode intensity suggests that fluctuations of this mode accompanying the CO-OO transition are small enough to justify a mean field model. This finding is in agreement with previous studies on PCMO, where the CO below the transition could be approximately described by a mean field model \[29\]. Based on this observation, we propose that one of the physical phenomena behind the charge and orbital order in \( \text{Pr}_{0.3}\text{Ca}_{1.5}\text{MnO}_4 \) is the change in Mn-O bond lengths. Our observation clearly indicates a strong coupling between charge ordering and the lattice in this system. A sharp jump in the magnetic susceptibility at 320 K suggests that there is also a strong correlation between CO-OO ordering, the lattice, and the spin system. This issue has been also discussed in Ref. \[13\]. In addition, a large release of entropy is shown by the sharp peak in specific heat, which marks the transition from a disordered to an ordered charge system.

In contrast with the previous study of Yamamoto et al. \[8\], which connected the diffuse scattering with orbital fluctuations, we analyze the possible orbital fluctuations by following the evolution of the JT mode. Our analysis in Fig. 6 shows that the evolution of the frequency with temperature cannot be simply fitted with an anharmonic model for a three-phonon process. A four-phonon model is necessary to fit the data above 215 K. These observations show that the phonon frequency decays into different channels above 215 K. The disappearance of short-range AFM above 215 K apparently activates a new decay channel of nonmagnetic origin. We propose that this is related to the presence of orbital fluctuations below the CO-OO transition that induce lattice instability. Even though neutron scattering data clearly suggest the onset of orbital order at \( T_{\text{CO-OO}} \) \[14\], the possibility of orbital fluctuations has been discussed in several previous studies \[30,31\]. In our experimental results, the anomaly in the JT Raman mode frequency at 215 K coincides with the anomaly in \( Q^2 \), which reflects changes in the short and long Mn-O bond lengths in the \( ab \) plane for the \( \text{Mn}^{(3.5–\delta)+} \) site and has the same symmetry as the JT Raman mode \[8\]. In our case, the \( 3d_{x^2–y^2} \) and \( 3d_{2–y^2} \) orbitals might be nearly degenerate such that the \( e_g \)-orbital occupation would be strongly temperature dependent. This would in turn change the Mn-O bonding pattern with temperature and appear as an anomaly in the evolution of the JT Raman mode. This finding is in agreement with a previous study of Mn-O bonds in \( \text{La}_{1–x}\text{Sr}_x\text{MnO}_4 \), which suggested that the structure is very sensitive to the occupation of \( e_g \) orbitals \[32,33\]. We also note that a recent optical conductivity study of \( \text{Pr}_{0.3}\text{Ca}_{1.5}\text{MnO}_4 \) suggests that the oxygen \( p \)-orbital orientation changes in each temperature regime \[29\]. A change in oxygen \( p \)-orbital orientation will influence the manganese \( e_g \)-orbital orientation because the oxygen ions are displaced along the directions of the Mn-O-Mn bonds. The oxygen ions are also involved in magnetic ordering, connecting the manganese ions via double-exchange or superexchange interactions. Any change in the oxygen or manganese orbital orientation will thus affect the magnetic ordering. Figures 2(b), 4(a), and 6(a) show the coincidence between the broad maximum in magnetic susceptibility, the anomaly of \( Q^2 \), and the anomaly in the JT mode frequency at 215 K, which implies that the 2D short-range AFM ordering is closely coupled to the JT and orbital fluctuations in \( \text{Pr}_{0.3}\text{Ca}_{1.5}\text{MnO}_4 \). This coincidence might suggest that the presence of 2D AFM short-range ordering stabilizes the orbital fluctuations.

The linewidth of the JT mode above 215 K is relatively broad and requires a four-phonon mode model to fit the experimental data. In Ref. \[31\], this type of linewidth broadening is discussed in terms of the local melting of orbital order which begins below the OO transition. In contrast to a system with JT distortion, where a sharp JT phonon mode with finite lifetime is expected to be observed below the JT transition temperature, a monotonous change of the phonon linewidth below the JT transition temperature is observed in our system, implying that the JT distortion is progressively changing below \( T_{\text{CO-OO}} \), as also evidenced by the temperature dependence of \( Q^2 \) in Fig. 4(a). Considering the relation between the JT distortion and the \( e_g \) orbitals of \( \text{Mn}^{(3.5–\delta)+} \), the large broadening of this phonon mode with increasing temperature might be explained in terms of a noncoherent distribution of \( \text{Mn}^{(3.5–\delta)+} \) and \( \text{Mn}^{(3.5+\delta)+} \) \[30\], which leads to a lattice instability and a local rearrangement of the half-filled \( \text{Mn}^{(3.5–\delta)+} e_g \) orbital. This phenomenon has been previously observed in \( \text{LaMnO}_3 \) when the temperature approached the CO-OO transition and was interpreted as a signature of orbital fluctuation \[30\].

The magnetization data in Fig. 2(b) show that the onset of 3D long-range AFM order occurs at 127 K. This transition is also marked by changes of the lattice constants, which indicates a strong spin-lattice coupling. This coupling leads to a softening of the octahedral rotational mode, as shown in Fig. 8. A spin-phonon coupling of 2.6 cm\(^{-1}\) is obtained from the rotational mode analysis. A larger softening is observed for octahedral tilting mode \( B \), as shown in Fig. 10, where
a spin-phonon coupling of 6.8 cm\(^{-1}\) is obtained, showing a strong relation between the AFM order and the Mn-O-Mn bond angles. It should be noted that the onset of phonon softening is observed at 140 K, which is about 13 K higher than the AFM phase transition, indicating that spin-lattice coupling is present in the short-range AFM ordering regime. An anomaly in the evolution of the Mn-O-Mn angle [in the inset of Fig. 4(d)] is also observed, but at a higher temperature of 150 K, which might also support our interpretation of the effect of short-range AFM ordering on the lattice system.

We also notice a transfer of intensity with temperature between octahedral tilting modes A and B, as shown in Fig. 9. We propose that these two modes are associated with two different types of octahedral tilting corresponding to Mn\(^{3.5-\delta+}\)-centered and Mn\(^{3.5+\delta+}\)-centered octahedra. The evolution of these tilting modes is sensitive to changes in charge, orbital, and spin ordering. The linewidth of octahedral tilting mode B can also only be fitted by the anharmonic four-phonon model above 215 K. The linewidth decreases to a constant value below 200 K, the reason for which is not clear. A similar observation was previously reported for La\(^{2-\delta}\)-Sr\(_2\)CuO\(_4\) where the linewidth was constant above 200 K and its saturation value was dependent on the Sr concentration [34]. However, the anomalies in the linewidth and frequency of this mode at 215 K, above which the four-phonon model is applicable, are unexpected.

In the last part of our discussion we would like to highlight the 2D character of this layered system. The CO-OO transition temperature of Pr\(_{0.5}\)Ca\(_{1.5}\)MnO\(_4\) is found to be higher than the 3D perovskite analog. In the layered system, the \(e_g\) electrons are confined in the \(ab\) plane due to a weak electronic interaction along the \(c\) axis. Therefore, the insulating CO-OO phase is found, rather than an itinerant electron phase. The CO-OO transition is marked by a sharp jump in specific heat, for which the magnitude is higher than in the perovskite Pr\(_{0.6}\)(Ca\(_{1-\delta}\)Sr\(_{\delta}\))\(_{0.4}\)MnO\(_3\) [17]. Clear evidence of 2D short-range AFM order is shown in the susceptibility curves around 200 K. Such short-range order has been previously discussed as the reason for the absence of a specific heat anomaly at \(T_N\) in the layered system [17]. Furthermore, anisotropy in the magnetic susceptibility is also observed. The susceptibility along the \(c\) axis is paramagnetic-like whereas it is typical of an AFM-ordered material along the \(a\) and \(b\) axes. This suggests a different type of magnetic interaction along the \(c\) axis, whereas in the \(ab\) plane the dominant interaction is AFM. The structure also shows more changes with temperature on cooling than the 3D perovskite, in which the lattice parameters are relatively constant below \(T_N\).

**VI. CONCLUSIONS**

In this study we have carried out a comprehensive study on the correlations between lattice dynamics and the electronic states in Pr\(_{0.5}\)Ca\(_{1.5}\)MnO\(_4\) involving charge, orbital, and spin ordering. The charge order is found to be strongly correlated with the changes in Mn-O bond lengths in the \(ab\) plane as well as with spin ordering and lattice dynamics. Our data strongly suggest the presence of orbital fluctuations in the intermediate-temperature regime, as, for instance, evidenced by the temperature evolution of the Raman intensity of the JT mode and the temperature dependence of the Mn-O bonding pattern in the \(ab\) plane. A possible stabilization of the orbital fluctuations by short-range 2D AFM ordering is suggested by the coincidence of a broad maximum in the magnetic susceptibility with an anomaly in the evolution of both the JT Raman mode frequency and the \(Q_2\) octahedral distortion around 200 K. We also report a clear change of the magnetic susceptibility at 127 K, which marks the onset of three-dimensional antiferromagnetic ordering. This transition is also observed in Raman spectroscopy and strongly influences the rotational and tilting modes. We estimate the spin-lattice coupling strength to be 2.6 and 6.8 cm\(^{-1}\) for the rotational and tilting modes, respectively. Furthermore, the O-Mn-O angles are also significantly changed in the 3D AFM ordered phase. This study provides comprehensive evidence for strong coupling of charge, orbital, and spin degrees of freedom to the lattice system as well as for the existence of orbital fluctuations in the distorted half-doped single-layer manganite Pr\(_{0.5}\)Ca\(_{1.5}\)MnO\(_4\).

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