

Soft tilt and rotational modes in the hybrid improper ferroelectric $\text{Ca}_3\text{Mn}_2\text{O}_7$ A. Glamazda,¹ D. Wulferding,² P. Lemmens,^{2,3} B. Gao,⁴ S.-W. Cheong,⁴ and K.-Y. Choi^{1,*}¹*Department of Physics, Chung-Ang University, Seoul 156-756, Republic of Korea*²*Laboratory for Emerging Nanometrology, TU Braunschweig, 38106 Braunschweig, Germany*³*Institute for Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany*⁴*Rutgers Center for Emergent Materials and Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854, USA*

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Raman spectroscopy is employed to probe directly the soft rotation and tilting modes, which are two primary order parameters predicted in the hybrid improper ferroelectric material $\text{Ca}_3\text{Mn}_2\text{O}_7$. We observe a giant softening of the 107-cm^{-1} octahedron tilting mode by 26 cm^{-1} on heating through the structural transition from a ferroelectric to paraelectric orthorhombic phase. This is contrasted by a small softening of the 150-cm^{-1} rotational mode by 6 cm^{-1} . In the intermediate phase, the competing soft modes with different symmetries coexist, bringing about many-faceted anomalies in spin excitations and lattice vibrations. Our work demonstrates that the soft rotation and tilt patterns, relying on a phase-transition path, are a key factor in determining ferroelectric, magnetic, and lattice properties of $\text{Ca}_3\text{Mn}_2\text{O}_7$.

DOI: [10.1103/PhysRevB.97.094104](https://doi.org/10.1103/PhysRevB.97.094104)**I. INTRODUCTION**

Hybrid improper ferroelectrics (HIFs) are currently of great interest because they hold promise for the electric field control of nonpolar order parameters as well as for the realization of room-temperature multiferroelectricity [1–4]. In HIFs a polarization is generated by a combination of rotation (X_2^+) and tilt (X_3^-) distortions of the oxygen octahedra (see Fig. 1). In this case, a primary order parameter is given by the amplitude of hybrid $X_2^+ \oplus X_3^-$ distortions, giving rise to rotational (designated R) and tilting (T) soft modes. Despite their technological importance, little is known about their impact on spin, lattice, and ferroelectric dynamics.

The HIF was observed in perovskite superlattices and $n = 2$ Ruddlesden-Popper materials $\text{Ca}_3(\text{Ti},\text{Mn})_2\text{O}_7$ [1–3, 5–14]. The prototypical HIF $\text{Ca}_3\text{Mn}_2\text{O}_7$ consists of an alternating arrangement of the CaO rocksalt layers and CaMnO_3 bilayers along the c axis, as shown in Fig. 1(a). The $\text{Ca}_3\text{Mn}_2\text{O}_7$ compound is known to undergo a first-order phase transition from a high- T tetragonal to a low- T orthorhombic phase through a certain intermediate phase [11, 15, 16]. An early study has shown that at room temperature the compound comprises a mixture of orthorhombic ($Cmc2_1$) and tetragonal ($I4/mmm$) phases, which evolves into a single $Cmc2_1$ phase at low temperature [15]. However, this structural model was questioned by later refined structural studies [11, 16]. With decreasing temperature the high- T tetragonal $I4/mmm$ structure undergoes a transition to an intermediate paraelectric orthorhombic ($Acaa$) and then to a polar $A2_1am$ symmetry at $T_S = 310\text{ K}$. As the temperature is further lowered, a G -type antiferromagnetic order sets in at $T_N = 115\text{ K}$ [15].

It is noteworthy that the intermediate $Acaa$ symmetry is generated by an out-of-phase rotation (X_1^-) of the MnO_6

octahedra from the undistorted $I4/mmm$ symmetry. In contrast, the ferroelectric $A2_1am$ phase below room temperature is associated with the hybridized distortions of the X_2^+ rotation in the xy plane and the X_3^- octahedral tilt in the yz plane. The transition pathway from $I4/mmm$ through $Acaa$ to $A2_1am$ symmetries results in the competition of the X_1^- out-of-phase and X_2^+ in-phase rotations, thereby bringing about peculiar physical phenomena. Unlike the isostructural $\text{Ca}_3\text{Ti}_2\text{O}_7$, on the one hand, a polarization is not switchable due to the formation of 90° ferroelastic domains stacked alternately along the c axis [16]. On the other hand, uniaxial negative thermal expansion, resulting from symmetry trapping of the soft T mode, is observed only in the $Acaa$ phase [11, 17]. Thus, tracing the tilt and rotation modes through the phase transitions is indispensable for in-depth understanding of the HIF of $\text{Ca}_3\text{Mn}_2\text{O}_7$.

In this paper, we report a successful observation of the soft octahedral tilt and rotational modes in $\text{Ca}_3\text{Mn}_2\text{O}_7$ using polarization-resolved Raman spectroscopy. The salient finding is that the antiphase octahedron tilting mode undergoes a giant softening upon heating towards T_S , while the rotational mode experiences a small softening. In the intermediate phase, we further find coexistence of the competing soft modes belonging to distinct phases, which is a main cause of ferroelectric, magnetic, and lattice anomalies.

II. EXPERIMENTAL DETAILS

Single crystals of $\text{Ca}_3\text{Mn}_2\text{O}_7$ were grown using a floating-zone method [16]. For Raman experiments, samples with dimensions of $5 \times 5 \times 2\text{ mm}^3$ were installed in an evacuated closed-cycle cryostat at $T = 5\text{--}360\text{ K}$. The incoming light was normal to the ab surface as well as parallel to the c axis for the polarized Raman scattering experiment. The scattered spectra were collected in (quasi)backscattering geometry and were dispersed by a triple spectrometer (Dilor-XY-500) and

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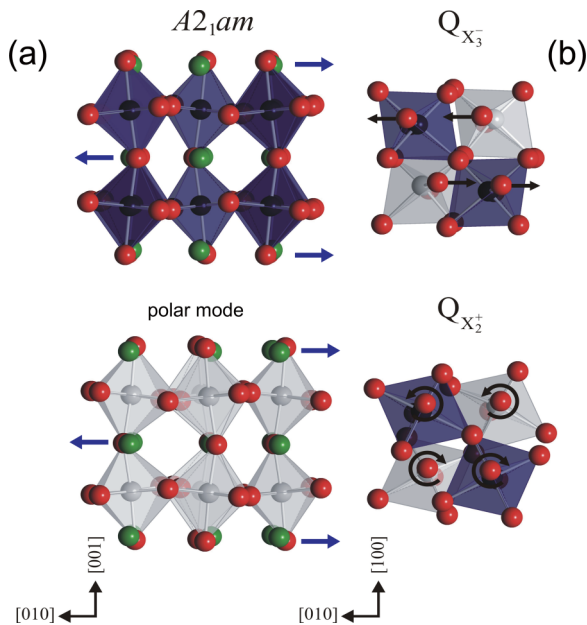


FIG. 1. (a) Low-temperature crystal structure of $\text{Ca}_3\text{Mn}_2\text{O}_7$ in its distorted ferroelectric state. Mn ions (gray) are surrounded by oxygen octahedra (red O ions) with Ca ions (green) interspersed. The arrows depict the polar displacements of Ca ions. (b) Octahedral rotation (X_2^+) and octahedral tilt (X_3^-) distortions.

a micro-Raman spectrometer (Jobin Yvon LabRam) equipped with a liquid-nitrogen-cooled CCD detector. The laser beam ($P = 8 \text{ mW}$) was used to avoid the local heating of the sample. For the resonance Raman spectra, both solid-state lasers and an Ar-Kr ion laser with excitation lines of $\lambda = 488\text{--}647 \text{ nm}$ were employed.

III. LATTICE-DYNAMICAL CALCULATIONS

For the low- T $A2_1am$ space group, the factor-group analysis yields the total irreducible representation for Raman-active modes: $\Gamma_R = 18A_1(xx,yy,zz) + 17A_2(xy) + 16B_1(xz) + 18B_2(yz)$. In this study, the intermediate phase is assumed to have $Acaa$ symmetry. The total irreducible representation of Raman-active modes for the $Acaa$ space group is given by $\Gamma_R = 6A_g(xx,yy,zz) + 11B_{1g}(xy) + 11B_{2g}(xz) + 11B_{3g}(yz)$. For the high- T $I4/mmm$ space group, the Raman-active modes are factored as $\Gamma_R = 4A_{1g}(xx,yy,zz) + B_{1g}(xx,yy) + 5E_g(xz,yz)$.

In order to assign the symmetries and eigenvectors to the observed phonon peaks, we computed the Γ -point phonon modes using shell-model lattice-dynamical calculations implemented in the General Utility Lattice Program (GULP) package. In the simple shell model, an ion Z consists of a

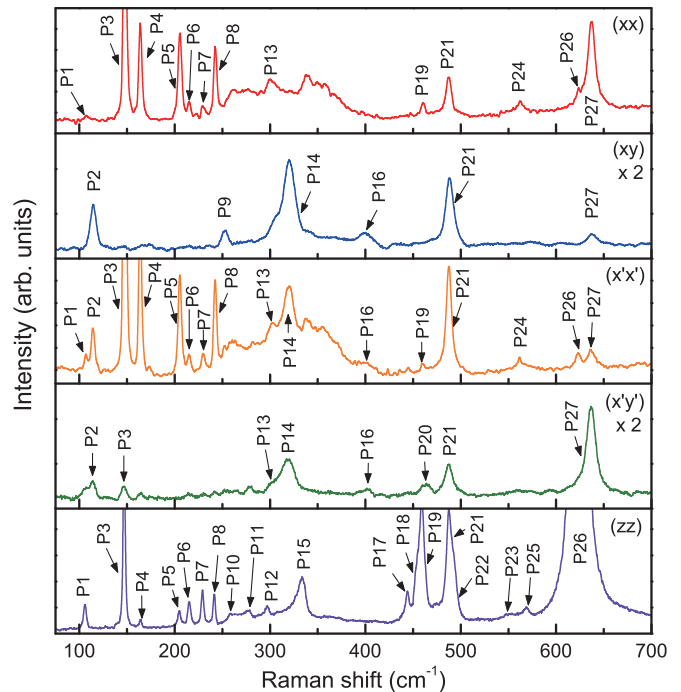


FIG. 2. Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ at an excitation wavelength of $\lambda = 532 \text{ nm}$ in (xx) , (xy) , $(x'x')$, $(x'y')$, and (zz) polarizations measured at $T = 8 \text{ K}$. The most intense peaks are marked with indexes.

point core, carrying the total mass of the ion with charge X , and a massless shell with charge Y , representing the outer valence electrons. The core and shell are coupled by a harmonic spring with a force constant K . The parameter K is related to the ionic polarizability $\alpha = Y^2/K$. The interionic interactions between Ca, Mn, and O ions are described by a combination of long-range Coulomb potentials and short-range Born-Mayer-Buckingham potentials between ions i and j :

$$V_{\text{BM}}(r) = A_{ij} \exp(-r/\rho_{ij}) - C_{ij}/r^6,$$

where A_{ij} and ρ_{ij} denote the strength and the range of the repulsive interaction, respectively, and C_{ij} describes an attractive part with the interatomic distance r . With a well-documented set of data, the shell-model parameters are optimized to reach reasonable agreement with experimental Raman data [18,19]. The resulting shell-model parameters are summarized in Table I.

IV. RESULTS AND DISCUSSION

A. First-order phonon excitations

Figure 2 presents the polarized Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ measured at $T = 8 \text{ K}$ in five different $[(xx), (xy),$

TABLE I. List of shell-model parameters for the shell-shell and core-shell interactions.

Atom	X ($ e $)	Y ($ e $)	K (eV/Å)	Atomic pair	A (eV)	ρ (Å)	C (eV Å ⁶)
Ca	2	0	0	Ca-O	1090.4	0.3437	0
Mn	4	0	0	Mn-O	1345.15	0.324	0
O	0.862	-2.862	74.92	O-O	22764.3	0.149	27.88

TABLE II. List of phonon symmetries and calculated frequencies (in cm^{-1}) at the Γ point for $\text{Ca}_3\text{Mn}_2\text{O}_7$ with $A2_1am$ symmetry.

Mode	Expt.	Calculated	Selection rule	Assignment
P1	107	113	$(xx), (x'x'), (zz)$	A_1 [MnO_6 out-of-phase tilting; Ca(2) in-phase motions in the ab plane]
P2	114	133	$(xy), (x'x'), (x'y')$	A_2 (MnO_6 bending in the ab plane)
P3	150	136	$(xx), (x'x'), (x'y'), (zz)$	A_1 (MnO_6 in-phase rotation about the c axis)
P4	164	172	$(xx), (x'x'), (zz)$	A_1 [MnO_6 in-phase bending; Ca(1)+Ca(2) out-of-phase motions along the a axis]
P5	205	192	$(xx), (x'x'), (zz)$	A_1 [MnO_6 bending; Ca(1)+Ca(2) in-phase motions along the b axis]
P6	215	227	$(xx), (x'x'), (zz)$	A_1 [MnO_6 stretching; Ca(1) motions in the ab plane]
P7	230	251	$(xx), (x'x'), (zz)$	A_1 [MnO_6 out-of-phase rotation; Ca(1)+Ca(2) stretching in the ab plane]
P8	242	264	$(xx), (x'x'), (zz)$	A_1 [MnO_6 stretching; Ca(2) out-of-phase motions along the c axis]
P9	253	274	(xy)	A_2 [MnO_6 stretching; Ca(1)+Ca(2) stretching along the c axis]
		276	(xy)	A_2 [MnO_6 bending; Ca(2) stretching along the b axis]
P10	260	282	(zz)	A_1 [MnO_6 in-phase bending; Ca(1)+Ca(2) in-phase motions in the ab plane]
P11	278	300	(zz)	B_2 [MnO_6 in-phase bending; Ca(1)+Ca(2) in-phase motions in the ab plane]
P12	297	314	(zz)	A_1 [MnO_6 in-phase bending; Ca(2) stretching motions in the ab plane]
P13	303	328	$(xx), (x'x'), (x'y')$	A_1 (MnO_6 in-phase bending in the ab plane)
P14	320	332	$(xy), (x'x'), (x'y')$	A_2 (MnO_6 in-phase bending in the ab plane)
		344	$(xy), (x'x'), (x'y')$	A_2 [MnO_6 in-phase bending in the ab plane; Ca(1) stretching in the ab plane]
P15	338	352	(zz)	A_1 [MnO_6 out-of-phase stretching; Ca(2) out-of-phase motions along the c axis]
P16	400	410	$(xy), (x'x'), (x'y')$	A_2 [MnO_6 bending; Ca(1) motions along the b axis]
P17	444	469	(zz)	B_1 [MnO_6 and Ca(2) stretching vibrations]
P18	454	470	(zz)	B_1 [MnO_6 and Ca(2) stretching motions in the ab plane]
P19	459	473	$(xx), (x'x'), (zz)$	A_1 (MnO_6 stretching in the ab plane)
P20	465		$(x'y')$	two-phonon mode
P21	488	491	$(xx), (xy), (x'x'), (x'y'), (zz)$	A_1 (MnO_6 bending)
P22	492	502	(zz)	B_2 [MnO_6 bending; Ca(1)+Ca(2) out-of-phase stretching]
P23	551	525	(zz)	B_1 (MnO_6 bending in the ab plane)
P24	562	556	$(xx), (x'x')$	B_1 (MnO_6 bending)
		571	$(xx), (x'x')$	B_1 [MnO_6 bending; Ca(2) out-of-phase motion along the a axis]
P25	568	581	(zz)	B_1 [MnO_6 bending along the b axis; Ca(2) out-of-phase motion along the b axis]
P26	623	588	$(xx), (x'x'), (zz)$	A_1 (MnO_6 out-of-phase bending in the bc plane)
P27	637	596	$(xx), (xy), (x'x'), (x'y')$	A_1 [MnO_6 bending in the ab plane; Ca(1)+Ca(2) in-phase stretching]

$(x'x')$, $(x'y')$, and (zz)] polarizations. Here, x and y correspond to the directions along the Mn-O bonds, and z corresponds to the out-of-plane direction. x' and y' are rotated in plane by 45° with respect to x and y . These scattering geometries allow probing mainly the A_1 and A_2 symmetry modes expected for the orthorhombic $A2_1am$ space group.

Below 630 cm^{-1} we were able to resolve $(15A_1 + 4A_2)$ one-phonon modes, which are smaller than the 35 Raman-active modes predicted for the $A2_1am$ structure in the selected polarizations, $\Gamma = 18A_1(xx,yy,zz) + 17A_2(xy)$. Assigning the observed phonon modes to the specific symmetry is made on the basis of the polarization-dependent Raman spectra and the lattice-dynamical calculations with the implementation of the Bilbao Crystallographic Server [20] (see Sec. III and Table II). The missing modes are ascribed to either a lack of phonon intensity or their overlap with other phonon excitations. In addition, we observe the weak symmetry-forbidden $(5B_1 + 2B_2)$ phonon modes possibly due to either a leakage of a polarizer or a slight tilting of the aligned crystal toward the c axis. The spectra were fitted using a set of Lorentz functions. The extracted frequencies of the Raman-active optical phonon modes are listed in Table II. The calculated and experimental

phonon energies agree well with each other. The representative displacement patterns for the A_1 modes are sketched in Fig. 3.

We next turn to the polarized Raman spectra of the intermediate phase recorded in (xx) and (zz) polarizations at $T = 290 \text{ K}$. As shown in Fig. 4, we observe 14 one-phonon modes. The observed phonon number is between the 18 Raman-active modes $\Gamma_R = 18A_1(xx,yy,zz)$ predicted for the $A2_1am$ symmetry and the 6 Raman-active modes $\Gamma_R = 6A_g(xx,yy,zz)$ predicted for the $Acaa$ space group. This result is consistent with the coexistence of the low- T ($A2_1am$) and the intermediate- T orthorhombic ($Acaa$) phases at room temperature [11, 15, 16]. Admittedly, it is almost impossible to assign unambiguously the observed phonon modes according to their symmetries as the phonon energies anticipated for the $A2_1am$ and $Acaa$ symmetries are nearly degenerate.

For ease of discussion, the phonon modes are tentatively described in terms of the $Acaa$ symmetry. As listed in Table III, we identify the $(5A_g + 3B_{1g} + 5B_{2g})$ modes. We sketch the displacement patterns of the representative normal modes in Fig. 5. In this assignment, the symmetry-forbidden $(3B_{1g} + 5B_{2g})$ modes can arise from local lattice distortions or a small mismatch between the laboratory and the crystal

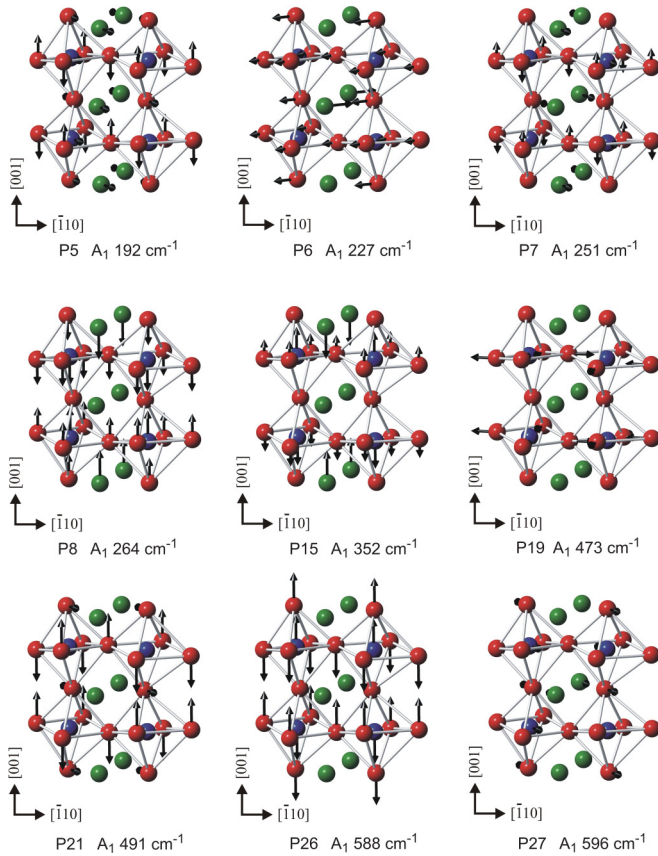


FIG. 3. Schematic representation of calculated eigenvectors for the A_{21am} symmetry. The relative amplitude of the vibrations is represented by the arrow length. The blue, red, and green balls are Mn, O, and Ca atoms, respectively. The numbers are the calculated frequencies using shell-model lattice-dynamical calculations.

coordinates. In reality, the forbidden modes may originate from the A_1 modes of the low- T A_{21am} phase, which persist to the intermediate- T phase.

B. Higher-order Raman scatterings

We now focus on the higher-order Raman spectra. Figure 6(a) shows the $T = 8$ K Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ taken in a wide frequency range of 30–2000 cm^{-1} for the (xx) , (xy) , and (zz) polarizations. In addition to the one-phonon modes, we observe the two-magnon (2M) excitation (pink shading) and a dozen higher-order scatterings, which are superimposed on top of the broad background (gray shading). It is remarkable that the higher-order mode at 1542 cm^{-1} is much more intense than the one-phonon peaks only in the (xx) polarization and the background continuum is anisotropic in its intensity and center position between the (xx) and (zz) polarizations.

Figure 6(b) exhibits the T dependence of the (xx) polarized Raman spectra. With increasing temperature, all Raman excitations are drastically suppressed. To quantify their temperature evolution, the Raman spectra are fitted to a sum of Lorentzian profiles. Shown in Fig. 6(c) are the T dependences of the frequencies ω and full widths at half maximum Γ for the representative one-phonon mode at 623 cm^{-1} and the anomalous higher-order peak at 1542 cm^{-1} . We find that both

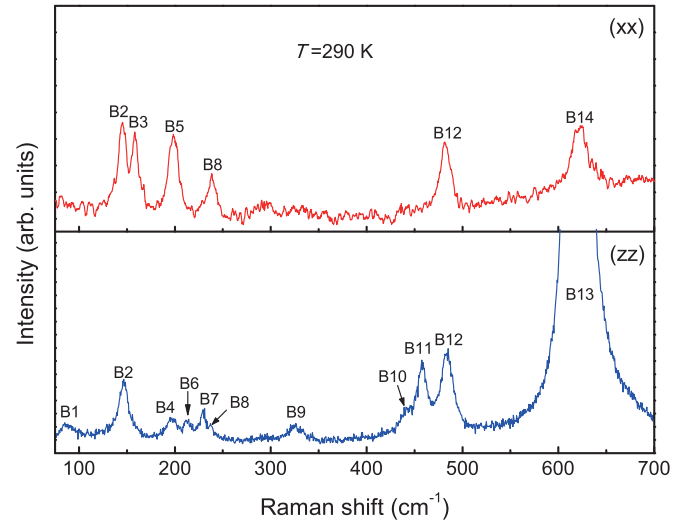


FIG. 4. Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ at an excitation wavelength of $\lambda = 532$ nm measured in the (xx) and (zz) polarizations at $T = 290$ K. The intense peaks are marked with indexes.

$\omega(T)$ and $\Gamma(T)$ of the 623 cm^{-1} mode, involving stretching vibrations of the MnO_6 octahedra, are well described by an anharmonic model [see the solid lines in Fig. 6(c)]. Unlike the one-phonon modes, $\omega(T)$ of the higher-order 1542 cm^{-1} mode shows a steeper decrease than what is expected for the lattice anharmonicity, starting at T_N . However, $\Gamma(T)$ exhibits no apparent anomaly.

In Fig. 6(d) we compare the T dependence of the normalized intensities of the one-phonon mode, the higher-order peak, and the background continuum. They commonly display an exponential-like decrease $I(T) \propto \exp(-k_B T/\Delta)$ as the temperature is raised above T_N [see the solid lines in Fig. 6(d)]. In insulating materials, the phonon intensity $I(T)$ is highly susceptible to changes in the dielectric function with respect to the displacement of the normal mode. In contrast, the variation of penetration depth and scattering volume with temperature gives minor contributions. Thus, the exponential drop of $I(T)$ above T_N suggests that the dielectric function strongly varies as soon as the magnetic order disappears. Noticeably, the X_3^- and X_2^+ modes start to soften at T_N , and the extracted empirical energy $\Delta = 95.8 \pm 1.3$ K is comparable to the frequency of the soft T mode (see Sec. IV E and Fig. 9 below).

In the bottom panel of Fig. 6(d), we present the ratio I_2/I_1 of the higher-order to first-order scattering intensity. For the (xx) polarization, I_2/I_1 undergoes a steplike increase with increasing temperature through T_N , while for the (zz) polarization, it decreases monotonically. The opposite polarization dependence of I_2/I_1 indicates that the higher-order scattering arises from a resonant optical excitation of 2.2 eV (see Sec. IV C) and that an electric state is anisotropic between the in- and out-of-plane directions. A closer look at the higher-order modes reveals that an integer multiple or combination of first-order phonon energies cannot reproduce higher-order peaks. For instance, the energy of the 1542 cm^{-1} peak corresponds to 2.47 times the one-phonon frequency at 623 cm^{-1} . This points towards a hybrid nature of the 1542 cm^{-1} peak. In HIFs, higher-order coupling of multiple degrees of freedom can lead

TABLE III. List of phonon symmetries and calculated frequencies (in cm^{-1}) at the Γ point for $\text{Ca}_3\text{Mn}_2\text{O}_7$ with $Acaa$ symmetry.

Mode	Expt.	Calculated	Selection rule	Assignment
B1	85	99	(zz)	B_{2g} [MnO_6 out-of-phase tilting; $\text{Ca}(1)+\text{Ca}(2)$ stretching vibrations in the ab plane]
B2	146	135	(xx), (zz)	A_g (MnO_6 out-of-phase rotation about the c axis)
B3	158	151	(xx)	B_{1g} [MnO_6 out-of-phase rotation about the c axis; $\text{Ca}(2)$ stretching along the b axis]
B4	198	213	(zz)	B_{2g} [MnO_6 bending in the ab plane; $\text{Ca}(2)$ stretching along the a axis]
B5	199	213	(xx)	B_{1g} [MnO_6 bending in the ab plane; $\text{Ca}(2)$ stretching along the b axis]
B6	213	215	(zz)	B_{1g} [MnO_6 bending; $\text{Ca}(1)+\text{Ca}(2)$ in-phase motion along the a axis]
B7	229	251	(zz)	B_{2g} [MnO_6 bending; $\text{Ca}(1)+\text{Ca}(2)$ out-of-phase motion along the b axis]
B8	240	258	(xx), (zz)	A_g [MnO_6 tilting; $\text{Ca}(1)+\text{Ca}(2)$ out-of-phase motion along the a axis]
B9	325	353	(zz)	A_g [MnO_6 out-of-phase stretching; $\text{Ca}(2)$ out-of-phase motion along the c axis]
B10	441		(zz)	mode of the $A2_1am$ space group
B11	458	452	(zz)	A_g (MnO_6 out-of-phase stretching motions in the ab plane)
B12	483	490	(xx), (zz)	B_{2g} (MnO_6 bending vibrations)
B13	619	589	(zz)	A_g (MnO_6 out-of-phase bending in the bc plane)
B14	621	593	(xx)	B_{2g} [MnO_6 bending in the ab plane; $\text{Ca}(1)+\text{Ca}(2)$ in-phase stretching]

to the vibronic couplings of the multiphonon scatterings to magnon and/or soft phonons. This together with strong lattice instabilities may explain the broad (two-) phonon background ranging from 100 to 2000 cm^{-1} in terms of a (two-) phonon density of states. The selective temperature, polarization, and incident laser dependences exclude fluorescence as its origin.

C. Resonance Raman scattering

We next discuss resonance behaviors of $\text{Ca}_3\text{Mn}_2\text{O}_7$. This is a particularly relevant issue because lattice instabilities can give rise to substantial modifications of electronic band structures. Figure 7(a) displays the resonant Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ measured with different wavelengths at $T = 8$ K

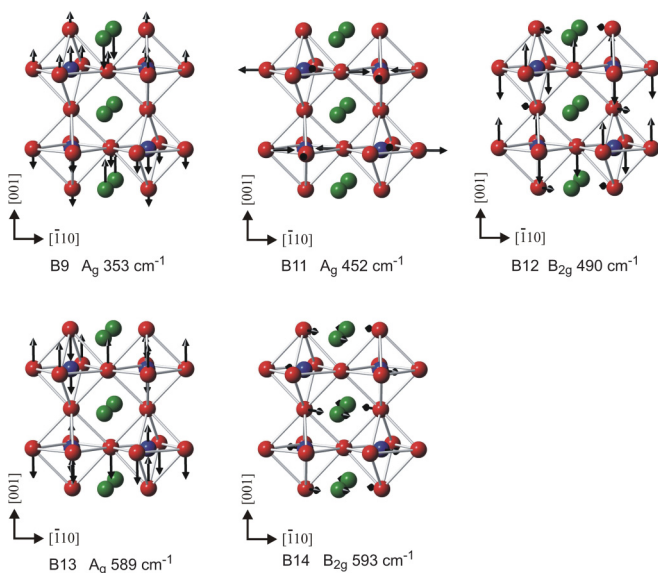


FIG. 5. Schematic representation of the calculated modes for the $Acaa$ symmetry. The numbers are the calculated frequencies. The related amplitude of the vibrations is represented by the arrow length. The blue, red, and green balls are Mn, O, and Ca atoms, respectively.

in the (xx) polarization. A large variation of the scattering intensity is observed as a function of the incident laser energies. For an analysis of the resonant behavior, all phonon and magnetic excitations were fitted using a sum of Lorentzian and Gaussian profiles. The resulting intensities versus incident laser energy are plotted in Figs. 7(b)–7(d).

As shown in Fig. 7(b), almost all the first-order phonon modes at 107, 150, 488, and 623 cm^{-1} are resonant with the excitation energy at around 2.2 eV. This is contrasted by the resonant behavior of the higher-order modes; although the 1250 cm^{-1} peaks show a resonant profile similar to that of the one-phonon peak, the 729, 1097, and 1542 cm^{-1} peaks exhibit two selective enhancements at about 2.2 and 2.54 eV [see Fig. 7(c)]. The observed resonant scatterings are ascribed to the spin-allowed electronic transition of the Mn^{4+} ion ${}^4A_{2g}({}^4F) \rightarrow {}^4T_{2g}({}^4F)$, the d - d transition ${}^4A_{2g}({}^4F) \rightarrow {}^4T_{1g}({}^4F)$, and the charge transfer transition $\text{O}^{2-}(2p) \rightarrow \text{Mn}^{4+}(3d^3)$ [21,22]. Figure 7(d) displays the resonant profiles of the magnetic and background continua, which show essentially the same behavior as the one-phonon one. Noticeably, the second moment of the background continuum increases appreciably with increasing excitation energy while undergoing a steep jump at about 2.2 eV [see Fig. 7(e)]. Overall, our resonant scattering study suggests that the higher-order scatterings are much more selectively enhanced at the 2.54 eV electronic transition than at the 2.2 eV one.

D. Two-magnon scattering

We inspect the 2M scattering arising from double-spin-flip processes of a ground state ($S = 3/2, S_z = \pm 3/2$) to a higher state [$S = 3/2, S_z = \pm 1/2$; see the sketch in Fig. 8(d)] [23]. As shown in Fig. 8(a), the 2M excitation is observed as a Gaussian-like maximum at about 301 cm^{-1} in the (xx) polarization. The magnetic excitation is strongly suppressed with increasing temperature through T_N . Figure 8(c) exhibits the T dependence of the 2M frequency, FWHM, and intensity. On approaching T_N , the magnon (2M peak) energy is renormalized by 30%, and the magnon lifetime Γ becomes two times shorter. Compared to the two-dimensional $S = 2$

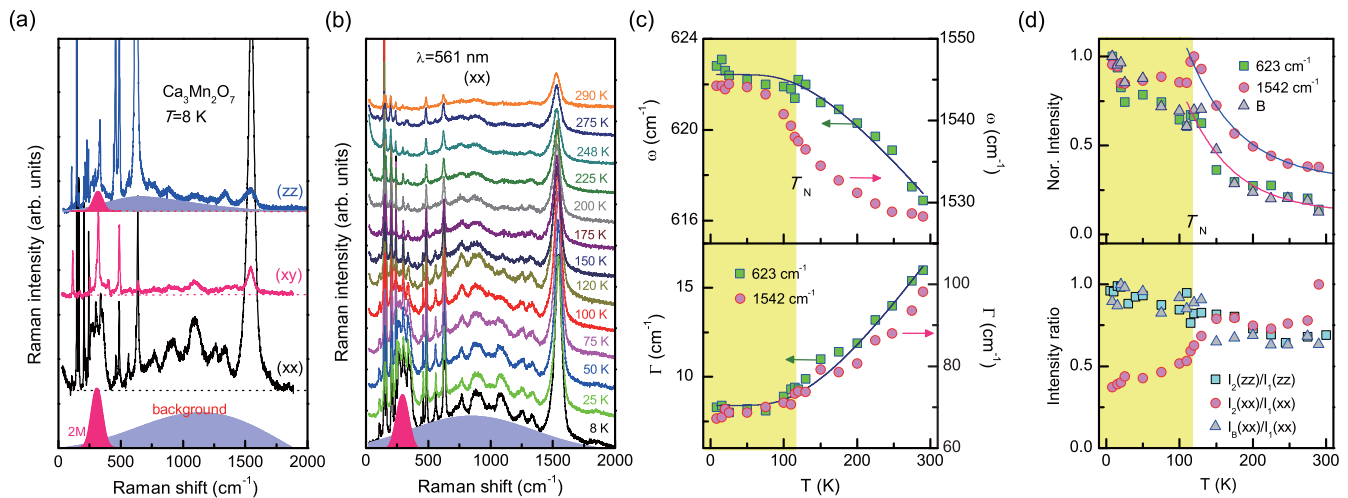


FIG. 6. (a) Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ measured at $T = 8$ K in the (xx) , (xy) , and (zz) polarizations. The spectra were recorded with an excitation wavelength of $\lambda = 532$ nm. The pink and purple shaded areas denote a two-magnon excitation and a background continuum, respectively. (b) Temperature dependence of the Raman spectra in the (xx) polarization. The spectra are vertically shifted by a constant amount. (c) Temperature dependence of the frequency and the linewidth of the one-phonon mode at 623 cm^{-1} and hybrid excitation at 1542 cm^{-1} . The solid lines are fits to the anharmonic model. (d) Normalized scattering intensity of the phonons and background continuum as well as their intensity ratios as a function of temperature and polarization. The solid lines are fits of the intensity using the exponential form $I(T) \propto \exp(-k_B T/\Delta)$.

system LaSrMnO_4 [24], $\text{Ca}_3\text{Mn}_2\text{O}_7$ experiences a stronger thermal damping and renormalization of the magnon despite its apparent smaller spin number. In addition, the 2M scattering does not evolve to a pronounced quasielastic response above T_N , unlike conventional 2M excitations, lacking well-defined paramagnons at high temperatures. These anomalies point to

the presence of another relaxation channel, possibly due to inherent coupling of the magnetic subsystem to the soft tilt mode. The peak position ω_{2M} of the 2M scattering allows the estimation of the exchange coupling constant J_{nn} of the nearest-neighbor Mn spins by the relation $\omega_{2M} = J_{nn}(2zS - 1)$, where $z = 5$ is the number of nearest-neighbor spins and

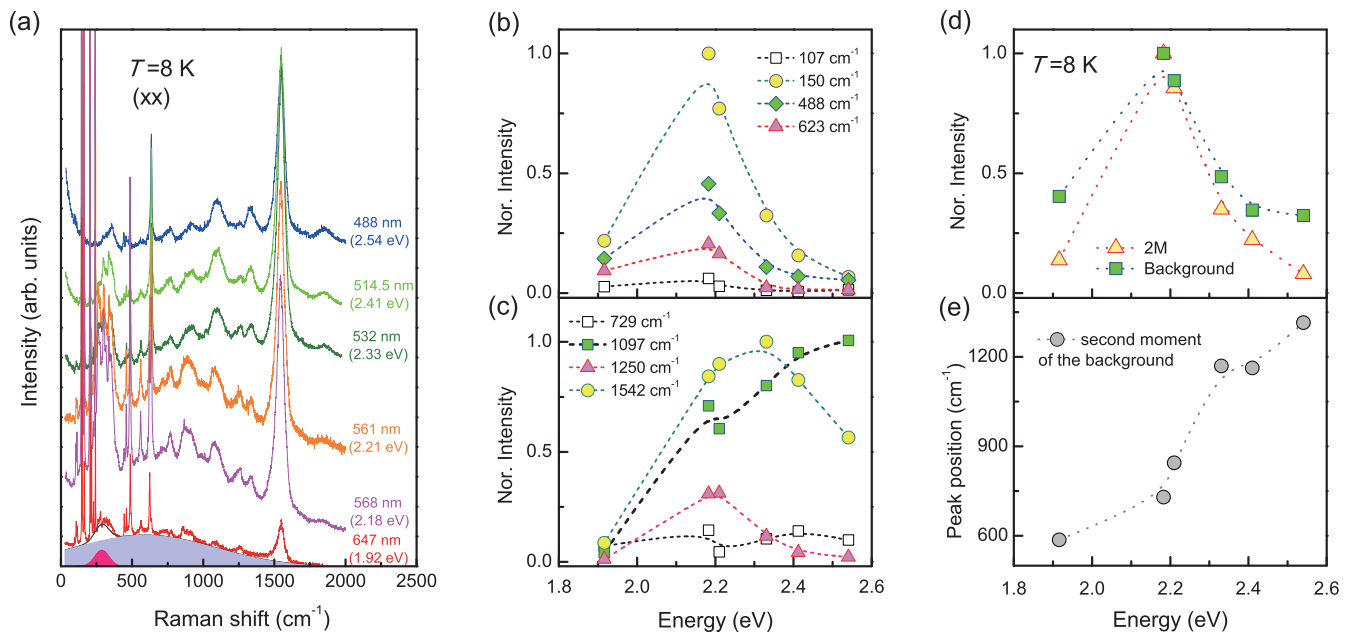


FIG. 7. (a) Resonant Raman spectra of $\text{Ca}_3\text{Mn}_2\text{O}_7$ measured at $T = 8$ K in the (xx) polarization. The excitation energy is varied from 1.92 to 2.54 eV. The spectra are vertically shifted for clarity. (b) Normalized Raman scattering intensity of the first-order phonon modes as a function of the incident phonon energy. The dashed lines represent guides to the eye. (c) Normalized Raman scattering intensity of the higher-order peaks as a function of the energy excitation. (d) Wavelength dependence of the normalized intensity of the magnetic excitation (yellow triangles) and the background continuum (green squares). (e) Second moment of the background continuum versus the laser excitation energy.

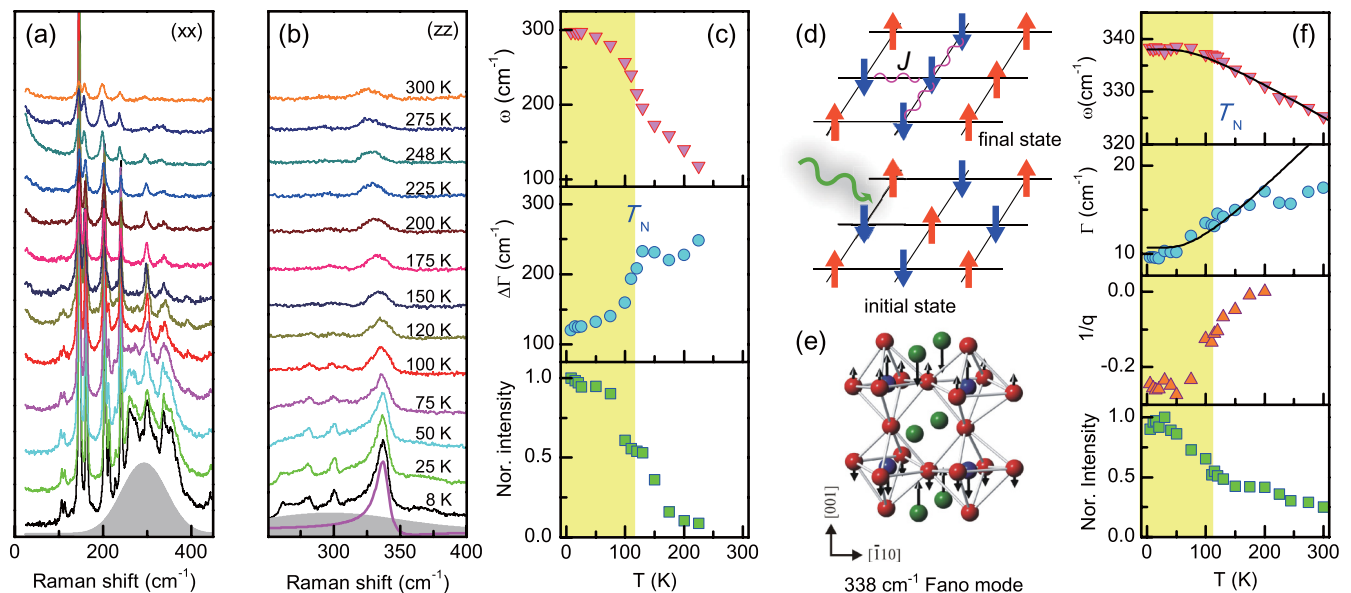


FIG. 8. (a) and (b) Evolution of two-magnon excitation (gray shading) in the (xx) and (zz) polarizations. The purple solid line is a Fano resonance. (c) Temperature dependence of the frequency, linewidth, and intensity of two-magnon scattering. The yellow shading marks T_N . (d) Cartoons of the two-magnon Raman scattering process. (e) Schematic representation of the eigenvector of the 338-cm^{-1} A_1 symmetry mode. (f) Temperature dependence of the frequency, linewidth, Fano asymmetry, and normalized intensity. The solid lines are fits using an anharmonic model.

$S = 3/2$ is the spin number. The value of $\omega_{2M} = 301\text{ cm}^{-1}$ yields $J_{nn} = 30.9\text{ K}$. This is close to the theoretical value of $J = 39\text{ K}$ [25].

Remarkably, the 2M scattering is also observed with weaker intensity in the (zz) polarization as zoomed in on in Fig. 8(b). Further evidence for a magnetic continuum is provided by a Fano resonance of the 338-cm^{-1} mode. The appearance of the 2M excitations in the out-of-plane polarization is totally unexpected for the tetragonal K_2NiF_4 -type antiferromagnets [24] and is linked to the CaMnO_3 bilayer structure, leading to significant interlayer interactions. Indeed, $\text{Ca}_3\text{Mn}_2\text{O}_7$ has the dominant G -type antiferromagnetic ordering of the Mn^{4+} magnetic moments pointing to the z axis [15]. The 338-cm^{-1} A_1 symmetry mode involves out-of-phase vibrations of the MnO_6 octahedra and the $\text{Ca}(2)$ atoms along the z axis, as sketched in Fig. 8(e). This mode is fitted using the Fano profile, $I(\omega) = I_0 \{1 + [(\omega - \omega_0)/q\Gamma]^2\} / \{1 + [(\omega - \omega_0)/\Gamma]^2\}$, where I_0 , ω_0 , Γ , and $1/|q|$ are the intensity, the bare-phonon frequency, the linewidth, and the asymmetric parameter, respectively. In Fig. 8(f), all Fano parameters are plotted as a function of temperature. The T dependence of ω_0 is well described by the conventional anharmonic model. However, $\Gamma(T)$ deviates for temperatures above 200 K. On heating above 50 K, $1/|q|$ decreases rapidly toward zero, while the intensity falls off substantially up to T_N and then decreases gradually. The Fano-parameter behaviors lend further support to a quick damping of the magnons above T_N .

E. Soft modes

Figure 9(a) zooms in on the two low-frequency phonons at 107 (T) and 150 cm^{-1} (R) measured on warming.

The data were taken in the (zz) polarization in order to separate the T and R modes from other phonon peaks. Based on our lattice-dynamical calculation, the 107 cm^{-1} (150 cm^{-1}) phonon is assigned to the octahedron tilting (rotation) mode, whose normal-mode displacements are sketched in Fig. 9(e).

With increasing temperature toward the $Acaa$ phase, the T (R) mode displays a huge (small) softening of 26 (6) cm^{-1} . For temperatures above 270 K, the T and R modes are split into additional T' and R' modes, forming the coexistence regime of the two different orthorhombic phases at least up to 360 K [see the inset of Fig. 9(c)]. This together with the drastic softening of the T mode confirms that the first-order phase transition from the $A2_1am$ ground state to the intermediate $Acaa$ phase is driven by the tilting of oxygen octahedra. Essentially the same conclusion was drawn in a recent neutron and x-ray diffraction study of $\text{Ca}_3\text{Mn}_{1.9}\text{Ti}_{0.1}\text{O}_7$ that unravels the softness of the antiphase octahedral tilt and robustness of the octahedral rotation [26]. The selective susceptibility of the antiphase tilt mode to the structural transformation is discussed in terms of the decisive role of the partially occupied d orbital of the Mn^{4+} ions in stabilizing the MnO_6 distortion. In Fig. 9(b) we show the color contour plot of the soft-mode intensity in the temperature-Raman-shift plane. Upon approaching the structural phase transition, the soft-mode intensities are strongly suppressed.

The frequencies $\omega_S(T)$ of the T and R modes are shown in Figs. 9(c) and 9(d) in the temperature range of $T = 5\text{--}360\text{ K}$. Notably, the softening modes do not shift to zero frequency, unlike the zone-center polar soft mode in a proper ferroelectric transition. $\omega_S(T)$ is described by the mean-field formula $\omega_S(T) = A(T_S - T)^{1/2} + \omega_0$. Here, the second constant term accounts for the first-order nature of the structural phase transition. We find good agreement between the experimental

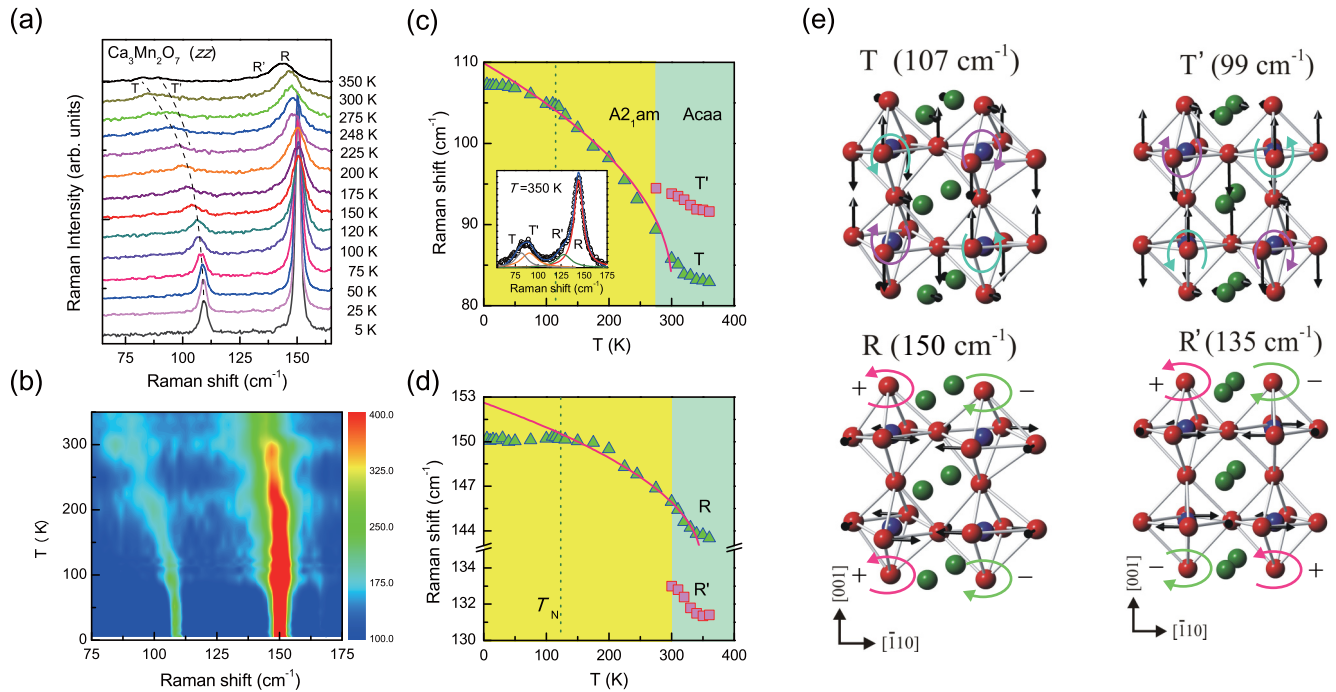


FIG. 9. (a) Temperature dependence of the low-frequency Raman spectra ranging from 60 to 160 cm^{-1} in the (zz) polarization. T and T' (R and R') denote the soft tilt (rotational) modes. (b) Color contour plot of the soft-mode intensity in the temperature-Raman-shift plane. (c) and (d) Temperature dependence of the frequencies of the soft modes. The solid lines are fittings using the mean-field model described in the text. The inset shows a representative fit of the low-energy spectrum to four Lorentzian profiles at $T = 350$ K, representing the T, T', R and R' soft modes. (e) Schematic representation of eigenvectors of the soft modes in the $Acaa$ and $A2_{1am}$ phases.

data and the mean-field theory above T_N , confirming the soft-mode-driven first-order phase transition. The apparent deviation in the antiferromagnetic ordered state is attributed to strong spin-lattice coupling λ , leading to a renormalization of the phonon energy by a scalar spin-correlation function $\Delta\omega = \lambda\langle\mathbf{S}_i \cdot \mathbf{S}_j\rangle$.

Last, we pay attention to an alteration of the rotation and tilting displacement patterns through the phase transition from the $Acaa$ to the $A2_{1am}$ symmetries. Overall, the energies of the tilting and rotational modes between the two phases differ by 12–17 cm^{-1} . This is due to a slightly different pattern of the MnO_6 tilting and the rotation distortions between them. The T and T' modes involve the respective inward and outward tilting of the MnO_6 octahedra within the perovskite bilayer, while the R and R' modes correspond to the X_2^+ in-phase and X_1^- out-of-phase rotations of the MnO_6 octahedra within the perovskite bilayer, respectively [see Fig. 9(e)]. We stress that the intermediate phase is characterized by the coexistence of the soft modes with distinct displacements, which is responsible for the observed nonswitchable polarization and uniaxial negative thermal expansion [11,16,17]. In addition, the competing structural instabilities at the intermediate phase lead to rapid destabilization of the magnetic excitation, in disfavor of strong magnetoelectric coupling. To achieve simultaneous ferroelectricity and magnetoelectricity, thus, the patterns of octahedral tilt and rotation distortions should be finely controlled through a structural transformation.

V. CONCLUSION

In conclusion, our Raman scattering study of $\text{Ca}_3\text{Mn}_2\text{O}_7$ has unveiled a set of competing soft modes, which dictate a first-order phase transition from the paraelectric to the ferroelectric orthorhombic phase. The soft rotation and tilt modes are a tuning parameter of all physical properties, leading to pronounced higher-order scatterings, anomalous magnetic excitation, and structural instability. In spite of the intertwined coupling among lattice, magnetic, and structural degrees of freedom, the soft modes with different symmetries prevent strong magnetoelectric coupling and ferroelectric switching. Our work demonstrates that competing octahedral tilting and rotational distortions created through a phase transition should be avoided to achieve room-temperature multiferroics.

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