Reinvestigating Electronic-Structural Interplays in LaMnO$_3$ from Canonical Jahn-Teller Distortion Notations

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LaMnO$_3$ is considered as a prototypical Jahn-Teller perovskite compound, exhibiting a metal to insulator transition at $T_{JT} = 750K$ related to the joint appearance of an electronic orbital ordering and a large lattice Jahn-Teller distortion. From first-principles, we revisit the behavior of LaMnO$_3$ and show that is not only prone to orbital ordering but also to charge ordering. Both charge and orbital orderings appear to be enabled by rotations of the oxygen octahedra and the subtle competition between them is monitored by a large tetragonal compressive strain, that is itself a Jahn-Teller active distortion. Equally, the competition of ferromagnetic and antiferromagnetic orders is slave of the same tetragonal strain. Our results further indicate that the metal to insulator transition can be thought as a Peierls transition. It also questions the applicability of the Kugel-Khomskii model and the cooperative Jahn-Teller Effect to LaMnO$_3$. As a basis to our discussion, we make the inventory of - and introduce canonical notations for - lattice distortions in perovskites deforming the oxygen octahedra and are connected to charge and orbital orderings.

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I. INTRODUCTION

Since the discovery of the colossal magnetoresistance effect in manganese perovskites solid solutions R$_{1+x}$A$_{1−x}$MnO$_3$ about 25 years ago, there has been a great research effort to understand the physical behavior of the end-members as well as the solution. Nonetheless, for the rare earth manganite perovskite side RMnO$_3$ no fully consistent picture has emerged yet that explains the interplay between structural, magnetic, and electronic degrees of a freedom. Hence, the prototypical member of this series LaMnO$_3$ still attracts an extensive research interest.

LaMnO$_3$ belongs to a large class of perovskite materials with a Goldschmidt tolerance factor $t < 12$. As such its lattice structure deviates from the ideal cubic perovskite phase Pm$ar{3}$m by the appearance of cooperative rotations of the MnO$_6$ oxygen octahedra. Above 1200K LaMnO$_3$ shows a rhombohedral space group $Rar{3}c$ with a $a^{-}a^{-}a^{-}$ rotation pattern (in Glazer’s notation$^{5}$). At 1200K LaMnO$_3$ undergoes a structural phase transition to the $Pbnm$ phase with a $a^{-}a^{-}e^{+}$ rotation pattern, the most common phase among the perovskites$^{6}$.

In both of these phases, oxygen octahedra rotate in a nearly rigid way. This rigid rotation preserves the cubic symmetry ($O_h$ in Schönflies notation) around the Mn atom if only the octahedron is considered. In such a regular octahedron the fivefold degenerate Mn d-states are split into three degenerate lower energy $t_{2g}$ and two degenerate higher energy $e_g$ states. In the 3+ oxidation state of Mn, four electrons formally occupy the Mn d-states. Due to strong intra site Hund’s coupling in the 3d shell, Mn adopts a high-spin configuration where three electrons occupy the $t_{2g}$ and one the $e_g$ states. As the Mn-3d states build the highest occupied states in LaMnO$_3$ it is consequently metallic in the $Rar{3}c$ and $Pbnm$ phases at high temperature.

At 750K and ambient pressure, or lower temperatures and higher pressure ($\approx 32$GPa), a second structural transition occurs, accompanied by a metal-to-insulator transition (MIT). This transition is called Jahn-Teller or Orbital Ordering transition at the temperature $T_{JT}$ or $T_{OO}$. At this transition, a sudden increase of volume is observed. The initially nearly cubic unit cell shows a strong tetragonal compression and orthorhombic deformation. The oxygen octahedra experience strong cooperative deformations lowering their symmetry from cubic to orthorhombic ($O_h$ to $D_{2h}$), incorporating a strong tetragonal compression. These are the so called Jahn-Teller distortions. However, no further symmetry reduction occurs and the structure still obeys the $Pbnm$ space group$^{11}$. Hence, the structures are called $O'(T < T_{JT})$ and $O (T > T_{JT})$$^{4,12}$. A particularity of such isosymmetrical transitions is that the order parameter - the Jahn-Teller distortions - are not restricted to zero amplitude before the transition. Consequently in the $O$ phase local Jahn-Teller distortions are reported and short-range ordered clusters with the diameter of 4 MnO$_6$ octahedra have been found$^{12,13}$.

In all of the above described phases the unpaired magnetic moments in the 3d shell of manganese are disordered and LaMnO$_3$ is paramagnetic (PM). At $T_N = 140K$ LaMnO$_3$ undergoes a magnetic transition without any structural changes to an antiferromagnetic phase with $A$-type pattern (AFM-A).

There is a long standing debate about the origin of
the MIT at $T_{IT}$ in LaMnO$_3$\textsuperscript{7,15–19}. Broadly, this discussion can be separated into two views. The approach of the cooperative Jahn-Teller Effect\textsuperscript{20–23} (C-JTE) and the spontaneous orbital ordering proposed by the Kugel-Khomskii\textsuperscript{24} (KK) model.

The C-JTE approach transfers the Jahn-Teller Effect\textsuperscript{25} from an isolated Jahn-Teller center to a solid of coupled centers. In the case of LaMnO$_3$ these are the corner shared oxygen octahedra. The origin of the transition is the local degeneracy of the $e_g$ orbitals gaining energy by inducing an local octahedral distortion removing the degeneracy. The coupled octahedra only interact harmonically through their individual deformation. The cooperative ordering of the octahedra is reached by minimizing the lattice harmonic energy and by such creates an orbital ordering.

The KK approach (based on the Mott-Hubbard Model\textsuperscript{26}) emphasizes the inter site electronic interactions and dynamical correlations between $e_g$ electrons. It deduces for a certain ratio of hopping and exchange parameters a spontaneous orbital and magnetic ordering in the undistorted cubic perovskites phases. The appearance of the cooperative deformation of the oxygen octahedra is here a secondary effect induced by the orbital ordering. It has, however, been shown that dynamical correlations alone can not account for the orbital-ordering in LaMnO$_3$\textsuperscript{27} and the lattice-electron coupling is crucial to understand the Orbital-Ordering transition. Moreover a recent first-principles study\textsuperscript{28} claims that dynamical correlations are not necessary to account for orbital ordering in perovskites. LaMnO$_3$ thereby appears to be a special case, where the principal orthorhombic Jahn-Teller distortion is only unstable in the presence of octahedral rotations.

In the present work, we probe the C-JTE and KK approaches through first-principles calculations. First we show that our calculation method properly reproduces the measured properties of LaMnO$_3$. Then, we sample the Born-Oppenheimer potential energy surfaces (PES) of the close competing AFM-A and ferromagnetic (FM) orders and characterize the inherent electronic instabilities, couplings between phonon modes, strains, insulating and metallic states. By a simple Monte-Carlo sampling we show that these PESs qualitatively reproduce the orbital-ordering transition at 750K. Finally the PESs of LaMnO$_3$ show an inherent subtle competition between charge-ordering and orbital-ordering. As a support to our analysis we reclassify all octahedra deforming cooperative distortions in perovskite systems into unified canonical notations for those kind of distortions taking into account local and global aspects and show the connection to other various notations in the present literature.

Our results challenge the applicability of both the C-JTE and the KK approach to LaMnO$_3$, while showing good agreement with experimental properties. Our results hint that the origin of the distortion might rather be a Peierls-Effect\textsuperscript{29}. The orbital-ordering transition shows order-disorder, lattice improper and electronically induced characteristics. Together with the recent explanation of the charger-ordering in $e_{g}^{1}$ alkaline earth ferrites AFeO$_3$\textsuperscript{30} and rare earth RNiO$_3$\textsuperscript{31} as a Peierls transition, it becomes apparent that the cooperative Jahn-Teller/Orbital-Ordering and Charge-Ordering transitions might have the same origin. Our results indicate that a new general and predictive model description taking into account electronic interactions and their variation with structural distortion is needed to explain the competition of different structural and electronic degrees in perovskites showing a MIT.

On a less academic level our results show the close interconnection between magnetic/electronic- and lattice degrees of freedom in LaMnO$_3$. Hence LaMnO$_3$ and similar perovskites are inherently interesting for structural engineering of magnetic and electronic properties, which has been realized in the FM phase of thin film LaMnO$_3$\textsuperscript{32–38}.

\section{ Canonical Notations for Cooperative Jahn-Teller Distortions in Perovskites}

The Jahn-Teller effect in the ideal perovskite $Pm\bar{3}m$ space group has been intensively studied over decades. Surprisingly no unified notation of cooperative Jahn-Teller distortions has been adopted yet. The reason for that seems to be the focus of many works on limited subsets of distortions for which labels are defined in the scope of the work. Here, we introduce canonical notations defining a unique label for all possible distortions. These are beyond the scope of the investigated problems in LaMnO$_3$, but will serve to simplify future discussions and comparisons between different perovskites. The new labels combine local and cooperative aspects, while being based on existing notations. As a starting point we give a brief summary on the history of the study of the Jahn-Teller effect in octahedral transition metal complexes.

In 1937 Jahn and Teller published a work stating that in a molecule ”stability and (orbital) degeneracy are not possible simultaneously unless the molecule is a linear one [...]”\textsuperscript{25}. The geometric instability of a molecule containing an orbital degenerate state is introduced by the so called vibronic-coupling terms. These couple the degenerate electronic state linearly to a vibrational mode coordinate $Q_k$. The strength of the coupling is expressed in

\begin{equation}
\alpha_{JT} = \left\langle \Psi^0_i \frac{\partial H_0}{\partial Q_k} \Psi^0_j \right\rangle,
\end{equation}

where $\Psi^0_i$, $\Psi^0_j$ are degenerate electronic states in a high symmetry structure of the molecular system and $H_0$ is the Hamiltonian of the unperturbed system.
Shortly after, researchers determined which combinations of orbitals and modes fulfill the symmetric conditions for such an effect in specific point groups. Van Vleck\(^3^9\) studied the isolated octahedral transition metal complex \(MX_6\) (Point Group \(O_h\)) within an external crystal field. From the 21 normal modes (3 times 6 atomic displacements plus 3 rigid rotations of the oxygen octahedron with respect to the external field) he identified six which are prone to a Jahn-Teller instability in conjunction with degenerate \(t_{2g}\) and/or \(e_g\) orbitals and labeled them from \(Q_1\) to \(Q_6\): \(Q_1\), the volume expansion/contraction, \(Q_2\) a planar rhombic distortion, \(Q_3\) the tetragonal distortion, where \(Q_2\) and \(Q_3\) keep the octahedral volume constant at linear order, and \(Q_4\) to \(Q_6\) the three possible shears of the octahedron (See Table I)\(^1\).

On the molecular level, \(Q_1\) does not play a role if the reference volume of \(O_h\) point group represents a stationary point with respect to volume expansion/contraction. Moreover, it does not lift the electronic degeneracy as it keeps the symmetry of the \(O_h\) group. The modes \(Q_2\) and \(Q_3\) are degenerate and possess the \(E_g\) symmetry with respect to \(O_h\). In conjunction with the \(e_g\) orbitals \((dx^2−r^2, dx^2−dy^2)\), they form the extensively studied \(E_g\otimes e_g\) Jahn-Teller system. Large static \(Q_2/Q_3\) distortions appear for unevenly occupied \(e_g\) orbitals as e.g. \(\text{Mn}^{3+}(e_g^1)\) or \(\text{Cu}^{2+}(e_g^3)\). At the harmonic level the systems forms the so called *mexican hat* potential energy surface. This surface possesses a degenerate minimum described by a circle in the \(Q_2/Q_3\) plane. Which point on the circle is stabilized depends then on the strength and sign of higher order anharmonicities\(^4^0,4^2,4^3\). The amplitudes of the distortion are quantified by

\[
Q_2 = \frac{2(l−s)}{\sqrt{2}} \\
Q_3 = \frac{2(2m−l−s)}{\sqrt{6}}
\]

where \(l\), \(m\), and \(s\), refer to long, middle, and short MX bond lengths. The angle in the \(Q_2/Q_3\) plane is

\[
\phi = \arctan \left( \frac{Q_2}{Q_3} \right)
\]

and is a direct measure for the \(dx^2−r^2/dx^2−y^2\) ratio in the stabilized state.

The modes \(Q_4\) to \(Q_6\) are relevant for degenerate \(t_{2g}\) states, since they posses the same symmetry and form a \(T_{2g}\otimes t_{2g}\) system. However, the \(t_{2g}\) orbitals can also interact with \(E_g\) modes (\(Q_2\) and \(Q_3\)), which results in many possibilities for energy lowering distortions to a degenerate \(t_{2g}\) system. For heavier center ions \(M\) it is further complicated by the spin-orbit coupling, which can introduce degeneracy splittings opposed to the distortion\(^4^4,4^5\).

The vibronic couplings are rather small since the strength of \(\pi\)-bonds formed between the \(M\) \(t_{2g}\) orbitals and neighboring \(X\) \(p\)-orbitals are weak. Consecutively compared to the \(E_g\otimes e_g\) system only small static distortions appear.

The problem of the Jahn-Teller instability in isolated \(MX_6\) was soon transferred to periodic solids with concentrated Jahn-Teller centers. In such compounds each unit cell contains a Jahn-Teller ion. Amongst them the perovskites \(ABX_3\) with their corner shared \(BX_6\) octahedral network. Degenerate electronic states possibly inducing Jahn-Teller instabilities are formed with an uneven occupation of the B-cation’s \(e_g\) orbitals such as in rare-earth manganites \(\text{RMnO}_3\) \((d^4 = e_g^1)\), \(\text{KCrF}_3\) \((d^4 = e_g^1)\), \(\text{KCoF}_3\) \((d^7 = e_g^1)\) and so on, or on an incomplete occupation of the \(t_{2g}\) orbitals such as in rare earth titanates \(\text{RTiO}_3\) \((d^1 = t_{2g})\) and rare earth vanadates \(\text{RVO}_3\) \((d^2 = t_{2g})\). The essential difference between the isolated problem studied by Van Vleck and the concentrated perovskite lies in the direct neighboring of the Jahn-Teller ions. It firstly implies that the degenerate electronic states form continuous electronic bands. The electronic band character of the degenerate states has been largely ignored by the C-JTE and KK theories. The C-JTE approach directly transfers the Jahn-Teller Hamiltonian of the isolated problem to the concentrated solid by simply exchanging the normal modes with phonon type modes and lattice strains\(^2^1–2^3,4^6\). In the KK view the band-character is quasi ignored by an assumption of very small band-widths\(^2^4\).

A second implication is that individual distortions are transferred between octahedral sites. However, the network allows for some phase freedom in the cooperative arrangement of the distorted octahedra. This additional freedom enables the system to achieve the same individual octahedral distortion by different cooperative orderings.

Regardless, it is common usage to quantify also in the concentrated perovskite case with degenerate \(e_g\) states the amplitude of \(Q_2\), \(Q_3\) distortions based on \(B−O\) distances in absolute coordinates. This notation quantifies the distortion of one individual octahedron. It does not indicate the cooperative arrangement of the distorted octahedra nor distinguish condensed phonon type distortions from homogeneous lattice strain. At the same time the quantification and notation of \(Q_4\) − \(Q_6\) - distortions seems to have been dropped in latter years\(^2\).

Carpenter and Howard gave a different notation based on the ISOTROPY software suite associating Jahn-Teller ordering schemes with labels of irreducible repre-

\(^1\) Specific linear combinations of \(Q_4, Q_5, Q_6\) lead to three trigonal distortions which reduce the octahedral to \(D_{4d}\) instead of \(D_{2h}\) (see also Table I). Those trigonal modes have sometimes been used in the analytical investigation of the problem\(^3^9\) and generally been shown to be possible coordinates of stationary points on the adiabatic potential energy surface\(^3^9–4^1\).

\(^2\) The last appearance of the \(Q_4 − Q_6\)-notation we found stems from 1997\(^4^1\).
TABLE I: Canonical labels $Q_{i\alpha}^R$ for cooperative Jahn-Teller distortions in solids with octahedral corner shared networks. The first subscript $i$ refers to the Van Vleck’s numbering of normal modes in the isolated octahedron. The second subscript $\alpha$ defines the unique axis of the local distortion pattern. Not necessary for $Q_{i\alpha}^F$ and $Q_{i\alpha}^R$. The superscript $\vec{k}$ refers to the reciprocal space vector with which the mode is translating. Shown are $\Gamma = (0, 0, 0), \mathbf{X} = (\frac{1}{2}, 0, 0), \mathbf{M} = (\frac{1}{2}, \frac{1}{2}, 0)$, and $\mathbf{R} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. $\Gamma$ is associated to lattice strains.

| Crystal Space Group (Schönflies) | Local Octahedral Symmetry | Ref. $Pm\bar{3}m$ B | Displacement Pattern | Strain Vector | Ref. $Pm\bar{3}m$ B | Displacement Pattern | Strain Vector | Crystal Space Group (Schönflies) | Local Octahedral Symmetry | Ref. $Pm\bar{3}m$ B | Displacement Pattern | Strain Vector | Crystal Space Group (Schönflies) | Local Octahedral Symmetry | Ref. $Pm\bar{3}m$ B | Displacement Pattern | Strain Vector |
|---------------------------------|---------------------------|---------------------|---------------------|---------------|---------------------|---------------------|---------------|---------------------------------|---------------------------|---------------------|---------------------|---------------|---------------------------------|---------------------------|---------------------|---------------------|---------------|
| $Pm\bar{3}m$ ($O_h^3$)          | $O_h$                      | $Pm\bar{3}m$       | $Fm\bar{3}m$       | $P4/mmm$      | $P4/mmm$           | $(a, a, 0, 0, 0)$     | $M_3^* (a, 0, 0)$ | $M_2^* (a, 0, 0)$ | $D_{2h}$                   | $D_{2h}$                   | $(0, -a, a, 0, 0)$ | $P4/mmm$       | $D_{2h}$                   | $D_{4h}$                   | $(0, 0, a, 0, 0)$ | $Cmmm$ ($D_{2h}^{19}$) | $P4/mmm$       | $I4/mmm$       |
| $Pmmm$ ($D_{2h}^4$)            | $D_{2h}$                   | $P4/mmm$           | $I4/mmm$           | $P4/mmm$      | $D_{4h}$            | $(-2a, a, 0, 0, 0)$ | $R_3^+ (a, 0)$     | $R_3^- (a, 0)$     | $D_{4h}$                   | $D_{4h}$                   | $D_{4h}$                   | $(0, 0, a, 0, 0)$ | $Cmmm$ ($D_{2h}^{19}$) | $P4/mmm$       | $I4/mmm$       |
sentations and ordering parameters thereunder. This symmetry labels are unique and distinguish between strain and phonon modes. Moreover, the symmetry adapted analysis allows to quantify the amplitudes of Jahn-Teller distortions in their own subspace, such that they can be separated from other distortions in the crystal lattice as octahedral rotations or antipolar motions. Finally, by creating invariant polynomials between the subspace of the Jahn-Teller distortions and other lattice distortions, the order, sign and strength of couplings between those different distortions can be studied. This makes the decomposition of lattice distortions into orthogonal irreducible subspace a very powerful approach. However, the application of the symmetry analysis has not found widespread application. A reason might be that the connection between the Van-Vleck-numbering and the irreducible representation labels is not obvious.

In the context of a first-principles study of rare earth nickelates RNiO₃ under epitaxial strain He and Millis defined labels \( Q^\ell_\alpha \). \( x \) took a number (different from van Vleck’s notation) and \( k \) the label associated to high symmetry \( k \)-points in the cubic brillouin zone. Through the phase factor \( e^{\imath \vec{q} z} \) the \( k \)-label emphasized the cooperative arrangement. However, they only noted the modes of interest in their study without labeling all possibilities.

Here, we introduce a canonical notation defining a unique symbol for all possible cooperative Jahn-Teller distortions in the perovskite structure. The symbols are designed in the spirit of He and Millis, which in turn could be said to be inspired by Kanamori.

The symbols have the form \( Q^\ell_\alpha \). The subscript \( i \) indicates the local distortion pattern and takes the enumeration of the octahedral normal modes from Van-Vleck. The second subscript \( \alpha \) is necessary for local patterns that break the cubic symmetry of the octahedra (All besides \( Q_1 \)). \( \alpha \) shows the alignment of the unique feature of the local distortion pattern with respect to the perovskite lattice. It takes the values \( x, y, z \), which are defined to lie along the cubic perovskite lattice axis. For a two dimensional local distortion pattern the unique feature is the axis orthogonal to the two dimensional distortion plane (applies to \( Q_2 \) and \( Q_3 \)). For a one or three dimensional local distortion pattern it shows the cartesian axes along the unique feature. The superscript \( \vec{q} \) is the label of the reciprocal space vector with which the local mode is translating in the crystal. Within this work we limit \( \vec{q} \) to zone center (\( \Gamma = (0, 0, 0) \)) and zone boundary modes at high symmetry \( \vec{q} \) points. The zone center \( \Gamma \) is thereby associated to lattice strains. However, there is no inherent limitation of the notation to the high symmetry \( \vec{q} \) - points. In the cubic Brillouin - Zone, the high symmetry \( \vec{q} \) points at the zone boundary are \( \mathbf{X} = (\frac{1}{2}, 0, 0), \mathbf{M} = (\frac{1}{2}, \frac{1}{2}, 0), \) and \( \mathbf{R} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \). The power of using such high symmetry \( \vec{q} \) points lies in their unique definition of the cooperative arrangement of the local distortion pattern and thereby also the orbital-ordering. In analogy to magnetic orderings, \( \Gamma \) leads to ferro, \( \mathbf{X} \) to a planar or \( A \)-type, \( \mathbf{M} \) to a columnar or \( C \)-type, and \( \mathbf{R} \) to a checkerboard or \( G \)-type arrangement. The freedom of the phase-factor depends on the local distortion pattern, since the corner shared atoms imply the opposite displacement for neighboring octahedra. The resulting notations for all local patterns and the high symmetry points are shown in Table I. Additionally Table I shows the crystal symmetry achieved by condensing the individual cooperative modes in the \( Pm\overline{3}m \) space-group, the local octahedral symmetry only taking into account the MX₆ complex, and the label of the irreducible subspace depending on the origin of the cubic perovskite unit cell set on the \( A \) or \( B \) cation.

The \( Q_1 \) mode is related to a homogeneous expansion/contraction of the volume of individual octahedra. It appears as a lattice strain at \( \Gamma \). As in the molecular case it can be omitted by choosing a reference stationary with respect to \( Q^1 \). Since the local distortion pattern is three dimensional, \( Q_1 \) is limited to \( \vec{q} \) between \( \Gamma \) and \( \mathbf{R} \). \( Q^\Gamma_1 \) is often called the breathing type distortion and associated to charge ordering. Two additional local volume changing modes can be thought of. First a mode that alters one bond axis (uniaxial volume change) and second two octahedral axis (planar volume change). In the molecular case these distortions do not appear as normal modes as they are not orthogonal to \( Q_1 \) and \( Q_3 \). These modes have been shown to be connected to charge ordering. Hence, we associate equally a \( Q_1 \)-label to them. In the periodic perovskite crystal the uniaxial volume change appears as a normal mode at \( \mathbf{X} (Q^X_2) \) and the planar volume change at \( \mathbf{M} (Q^\mathbf{M}_2) \) in Table I.

The \( Q_2 \) mode is planar and can hence translate with \( \Gamma, \mathbf{M}, \) and \( \mathbf{R} \) and reduce the local symmetry to \( D_{2h} \) stabilizing a mixed \( d_{z^2-r^2}/d_{x^2-y^2} \) state. \( Q_3 \) modes are tridimensional and hence appear at \( \Gamma \) and \( \mathbf{R} \). They reduce the local symmetry to \( D_{4h} \) stabilizing for a tetragonal compression a \( d_{z^2-r^2} \) and for an elongation a \( d_{z^2-r^2} \) state. At \( \Gamma \) and \( \mathbf{R} \), \( Q_2 \) and \( Q_3 \) form a twodimensional subspace equivalent to the \( Q_2/Q_3 \) space of the isolated Jahn-Teller center. An intriguing difference to the isolated center is the appearance of \( Q^\mathbf{M}_2 \) in its own subspace. This gives hence an additional degree of freedom for cooperative Jahn-Teller distortions in concentrated compounds.

For the shear modes we denote \( Q_4 \). As they are planar, they appear at \( \Gamma, \mathbf{M}, \) and \( \mathbf{R} \), where they are at each point threefold degenerate, which reflects the modes \( Q_5 \) and \( Q_6 \) in Van Vleck’s numbering. The necessity of \( Q_5 \) and \( Q_6 \) falls away using the second subscript \( \alpha \) in our notation.

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3 At the other high symmetry \( q \)-points in the cubic Brillouin zone the uniaxial \( Q_{1ua} \) and planar volume change \( Q_{1po} \) are equivalently to the molecular case not orthogonal to the other modes presented in Table I. At the \( \mathbf{M} \)-point the uniaxial volume change \( Q_{1ua} \) is represented by a sum of \( Q^\mathbf{M}_{1ua} \) and \( Q^\mathbf{X}_{2ua} \). At the \( \mathbf{R} \)-point and at \( \Gamma \) \( Q_{1ua} \) and \( Q_{1po} \) are represented by sums of \( Q^\mathbf{M}_{1R/F}, Q^\mathbf{X}_{2R/F} \) and \( Q^\mathbf{R}_{4R/F} \) (respectively the subspaces \( R^2_2/R_3^2 \) and \( \Gamma^1_1/\Gamma^3_3 \)).
$Q_4$ modes reduce the local symmetry to $D_{2h}$ albeit in a different way as $Q_2$ as the $B-O$ distances in the sheared plane stay degenerate.

All irreducible subspaces besides $X^+_t / X^-_t$ and $R^+_t / R^-_t$ given in Table I are formed exclusively by the corresponding Jahn-Teller movements of the ions at the octahedral corners. In the subspaces $X^-_t / X^+_t$ and $R^-_t / R^+_t$ additional antipolar motions of $A$-cations are found. In $X^-_t / X^+_t$ the $[100]$ A-planes move along the corresponding cubic axes. In the $R^-_t / R^+_t$ subspace it is the $[111]$ A-cation planes (see also Fig. 1). Hence, it is expected that the condensation of a $Q^+_t$ or $Q^-_t$ distortion will induce the corresponding antipolar motion and vice versa.

Finally we note that the strains $Q^+_t, Q^-_t, Q_{5o}^c, Q_{1o}^c$, and $Q^-_t$ represent a complete strain basis for the cubic perovskite system.

We hope that this canonical notation defining a unique symbol for all cooperative Jahn-Teller distortion distinguishing phonon-modes and lattice strains based on the \textit{ISOTROPY}-decomposition will facilitate the discussion of perovskite systems experiencing static Jahn-Teller distortions. As will be shown in the forthcoming of the article the rigorous orthogonality of the decomposition is most powerful in the study of the interplay of Jahn-Teller distortions with other lattice distortions and strains.

III. METHODS

Density functional theory (DFT) calculations were performed using the generalized gradient approximation (GGA) with the revised Perdew-Burke-Enzerhof parameterisation for solids (PBEsol)\textsuperscript{51} as implemented in the Vienna \textit{ab initio} simulation package (VASP)\textsuperscript{52}. A Liechtenstein $(U|J)$ correction was applied. $(U|J) = (5|1.5)$ were determined by comparing structural, electronic, and magnetic parameters to experimental results. As a point of reference we reproduced the results of Mellan et al. using $(U|J) = (8|2)$\textsuperscript{53}. Projector augmented plane waves\textsuperscript{54} were employed with a high plane-wave cutoff energy of 600 eV and a dense 14x14x14 Monkhorst-Pack k-point mesh\textsuperscript{55} with respect to the cubic perovskite unit cell. Supercells up to 40-atoms were used to include various magnetic orderings. For supercells up to 40-atoms the density of the k-point mesh was reduced accordingly to the multiplicity of the supercell. During the structural optimizations, the lattice parameters and internal coordinates of atoms were fully relaxed until the Hellmann-Feynman forces on each atom were less than $10^{-5}$eV/Å.

We used \textit{ISODISTORT}\textsuperscript{56} to analyze symmetry adapted modes and symmetry adapted strains of experimental and optimized structures. In all cases we used a hypothetical $Pmn3m$-structure of LaMnO$_3$ as reference with a lattice constant of $a_0 = 3.935\text{Å}$ that preserves the same volume per formula unit as in the experimental $Pbnm$-phase at low-temperatures.Finally we used the software \textit{INVARIANTS}\textsuperscript{57} to create invariant coupling terms including symmetry adapted modes and strains. We use the \textit{BandUP}-utility\textsuperscript{58,59} to unfold electronic band-structures of magnetically or structurally distorted structures back to the brillouin-zone of the cubic 5-atoms perovskite unit-cell. Finally we used an in-house tool to approximate PESs from DFT data with a polynomial expansion and run Monte-Carlo simulations on the determined polynomial.

IV. GROUND STATE PROPERTIES

In this section we review the structural, magnetic, and dielectric properties of the LaMnO$_3$ bulk ground-state phase. We compare the results of our DFT+$\textit{(U|J)}$ calculations to experimental values to emphasize the applicability of our chosen calculation method (See Table II).

The ground-state $Pbnm$-phase can be described as an aristotype cubic perovskite in which several phonon modes and lattice strains have been condensed. The primary unstable modes condensed with large amplitudes are one in phase rotation ($\phi^+_c$ Irrep: $M^+_t$) and two out of phase rotations ($\phi^-_x + \phi^-_y = \phi^-_{xy}$ Irrep: $R^-_5$) leading to the $a^-a^-c^+$ rotation pattern and reducing the symmetry to the $Pbnm$ space group. In this $Pbnm$-phase the rotation pattern induces two secondary antipolar motions of the La-cations\textsuperscript{67,68}. Firstly an antipolar motion of the [001] La-planes and the oxygens in those planes along the pseudocubic xy-direction ($A_X$ Irrep: $X^-_5$). Secondly an
TABLE II: Comparison of calculated quantities from DFT with PBEsol + (5/1.5) and + (8/2) with experimental values. Top: Amplitudes of the symmetry adapted Modes extracted with ISODISTORT\textsuperscript{a} of relaxed LaMnO\textsubscript{3} with imposed AFM-A magnetic order. Center: Electronic band gap and optical dielectric permittivity tensor $\epsilon_{\infty}$. Bottom: Magnetic exchange constants and Neel-Temperature $T_N$. 

| (5/1.5) | (8/2) | Expt. |
|---------|-------|-------|
| $Q^\Gamma_{4s}$ | -0.036 | -0.039 | -0.027\textsuperscript{b} |
| $\Gamma^\prime_6$ (a, 0, 0) | -0.04 | -0.04 | -0.032\textsuperscript{c} |
| $Q^\Phi$ | -0.04 | -0.04 | -0.032\textsuperscript{c} |
| $\Gamma^+_3$ (a, 0) | 0.33 | 0.34 | 0.30\textsuperscript{b} |
| $X^+_5$ (0, 0, 0, a, −a) | 0.29\textsuperscript{c} | 0.48\textsuperscript{b} | |
| $\phi^+_5$ [Å] | 0.49 | 0.51 | 0.48\textsuperscript{c} |
| $M^+_3$ (a, 0, 0) | 0.19 | 0.19 | 0.19\textsuperscript{c} |
| $Q^\Phi_{4s}$ [Å] | 0.65 | 0.67 | 0.63\textsuperscript{b} |
| $R^+_5$ (0, a, −a) | 0.06 | 0.06 | 0.06\textsuperscript{b} |

**Optical Properties**

| $\epsilon_{\infty}$ | E\textsubscript{Gap} [eV] |
|------------------|-----------------|
| $\epsilon_{\infty}$ | 7.03 | 6.02 |
| $\epsilon_{\infty}$ | 6.52 | 5.5 |
| $\epsilon_{\infty}$ | 6.77 | 5.75 | $\approx$ 7.3\textsuperscript{d,e} |
| $\epsilon_{\infty}$ | 6.15 | 5.76 | $\approx$ 6\textsuperscript{d,e} |
| $\epsilon_{\infty}$ | 1.15 | 1.77 | 1.1 - 1.9\textsuperscript{f} |

**Magnetic Properties**

| $\mu[\mu_B]$ | $J_{xx} = J_{yy}$ [meV] | $J_z$ [meV] | $T_N$ [K] |
|--------------|-----------------|------------|-----------|
| 3.68 | -0.59 | 0.34 | 142 |
| 3.75 | -0.25 | 0.18 | 64 |
| 3.8 | -0.83 | 0.58\textsuperscript{b} | Exp: $\sim$ 140 |
| Calc: 20\textsuperscript{7b,8} |

\textsuperscript{a}For this table and throughout this work we used the normalization with respect to the reference phase (Cubic $Pm\bar{3}m$).

\textsuperscript{b}Ref. [14]

\textsuperscript{c}Ref. [60]

\textsuperscript{d}Ref. [17]

\textsuperscript{e}$\epsilon_{\infty}$ and $\epsilon_{\infty}^t$ correspond to $\epsilon_{1b}$ and $\epsilon_{1c}$ in the lower frequency range below the first optical transition in 17.

\textsuperscript{f}Refs. [14,61–66]

\textsuperscript{g}Calculated in Ref.[14] with a two J mean-field approach using the measured exchange constants.

antipolar motion ($A_R$ Irrep: $R_4^-$)\textsuperscript{4} of the [111] La-planes

\textsuperscript{4}This antipolar motion appears under the same Irrep, as the Jahn-Teller Modes $Q^\Gamma_4$ defined in Table I. The respective oxygen motions - equally along the pseudocubic xy-direction. Finally, the ground state phase is completed by the Jahn-Teller mode $Q^\Gamma_4$, and sizable tetragonal and shear strains $Q^\Gamma_{4z}$ and $Q^\Gamma_{4z}$. All of those are allowed by symmetry in the $Pbnm$ phase (Compare Table I). The displacement patterns of the modes (excluding the strains and Jahn-Teller modes) are shown in Fig. 1.

In the following we list calculated physical quantities using the $(U,J)$ parameters of Melian et al.\textsuperscript{53} (8eV/2eV) and our new optimized values (5eV/1.5eV) and compare them to experimental values. In the top part of Table II the relaxed amplitudes of all the modes and strains with imposed AFM-A order are noted. Both tested $(U,J)$ combinations, deliver similar strain and mode amplitudes in good proximity to the measured values (maximum deviation for $\phi_{xy}(R_N^-) \approx 5\%$).

In the center part of Table II we compare the Kohn-Sham band gap and the optical dielectric constant $\epsilon_{\infty}$ found with the two GGA+U functionals with experimental measured values. One of the intriguing particularities of LaMnO\textsubscript{3} is the large spread of measured electronic band-gaps of nearly 1 eV\textsuperscript{14,61–66}.

This spread might give the comparison of first-principles calculations with experiments less significance. Nonetheless, an appropriate calculation method should simultaneously reproduce the lattice structure and a band-gap in the range of the measured ones. The optical dielectric tensor gives a second good measure to test the calculated electronic density. Refs [15,17] provide directionally resolved measurements of the optical dielectric tensor at low temperature along the $Pbnm$ c-axis and the pseudocubic x-direction to compare our calculations with (≈ 45° to the orthorhombic a - and b - directions)\textsuperscript{5}.

PBEsol + (8eV/2eV) and PBEsol + (5eV/1.5eV) find electronic band gaps, which lie well in the range of the experimentally measured ones, although increasing with U. Regarding the optic dielectric constant, PBEsol + (5eV/1.5eV) yields values in better agreement with experiment, which also reproduce the optical anisotropy absent with PBEsol + (8eV/2eV).

In the bottom part of Table II we compare the calculated magnetic properties with experimental values. We made a two J exchange constant mean field model, which is sufficient to justify the AFM-A order and can be found in several publications in recent literature\textsuperscript{14,53,69}. To cal-
calculate the exchange constants, we used the energy differences of the relaxed AFM-A, AFM-G and FM phases. Our experimental reference is [14], where the magnetic exchange constants were derived from magnon dispersion measurements. It is noteworthy, that $T_N$ calculated with the measured exchange constants lies 67 K above the measured $T_N$ because of the neglect of spin-fluctuations. Hence, the best benchmark is to compare measured and calculated exchange constants. PBEsol + (8eV|2eV) underestimates both exchange constants by an approximate factor of three. In contrast PBEsol + (5eV|1.5eV) underestimates less the exchange constants with respect to the experiment and finds a Neel-Temperature from mean field theory comparable to the experimental one.

In conclusion, both (5eV|1.5eV) and (8eV|2eV) produce a good description of the structural ground state of LaMnO$_3$. Considering additionally electronic, optical and magnetic properties, (5eV|1.5eV) provides the better global estimate and will be further used in this work.

V. POTENTIAL ENERGY SURFACES

In this section we discuss the shape of the Born-Oppenheimer potential energy surface (PES) around the cubic phase with respect to the central Jahn-Teller distortion in LaMnO$_3$, $Q^{M}_{2z}$ (See Table I and II). We quantify mode-mode, mode-strain couplings, and vibronic Jahn-Teller couplings by successively adding one by one the major lattice distortions found in the $Pbnm$ ground state. To do so we fit the free energy surface by potentials of the shape

$$\mathcal{F} = E_0 + \alpha_{JT} |Q^{M}_{2z}| + \alpha Q^{M}_{2z} + \beta (Q^{M}_{2z})^2 + \gamma (Q^{M}_{2z})^4,$$

where $E_0$ is the energy at $Q^{M}_{2z} = 0$, $\alpha_{JT}$ describes the vibronic-coupling terms, $\alpha$ quantifies other linear lattice terms, $\beta$ quadratic lattice terms, and $\gamma$ fourth order terms. In the fit all modes have been normalized such that 1 corresponds to their ground-state amplitude, which can be found in Table II. This approach allows to deduce how the magnetic and structural ground state is reached. The introduction of the absolute function in (5) allows to distinguish the vibronic coupling terms and linear lattice couplings in the $Q^{M}_{2z}$ coordinate. The cubic reference lattice parameter is $a_0 \approx 3.935\,\text{Å}$, which preserves the same volume per formula unit as the bulk ground-state phase. The sign and strength of the parameters will be qualitatively discussed in the following sections. A description of the fitting procedure, the whole free-energy expansion, and a Table with the values of the coefficients are given in appendix A.

### A. $Q^{M}_{2z}$ PES in the cubic Phase

In this section we analyze the relative stability of different magnetic orderings and the stability of $Q^{M}_{2z}$ distortion in the cubic phase. Inspecting the $Q^{M}_{2z}$ coordinate is a random choice at this point. Due to the cubic symmetry the following results would be exactly the same for $Q^{M}_{2x}$ and $Q^{M}_{2y}$. Following KK-approach$^{24}$, we expect an AFM-A magnetic and orbital ordered insulating ground-state with an instability of $Q^{M}_{2z}$. Following the C-JTE approach we expect an instability of $Q^{M}_{2z}$ independent of...
FIG. 3: Electronic Band Structures of LaMnO$_3$ in the range of $\pm 3$eV. a) Projection of electronic bands onto Mn-$e_g$, Mn-$t_{2g}$, and O-p orbitals in FM-cubic phase. The size of the dots indicate the character of the bands. b-d) unfolded band structure to cubic brillouin-zone. The color of the lines indicate the overlap between the supercell and primitive cell k-point. b) AFM-A ordering with cubic atomic positions. c) FM ordering with 10$\%$ $Q_{22}^M$ distortion. d) AFM-A ordering with 10$\%$ $Q_{22}^M$ distortion, where $\alpha$ is one the cubic lattice directions. In the FM cases the majority spin is shown. In the AFM-A cases one of the two equivalent spin channels are shown.

the magnetic order.
Table III shows the energy differences per formula unit for different simple magnetic orderings in the cubic phase of LaMnO$_3$. Here our calculations show that the FM ordering is by far the ground state and that huge energy jumps exists between the different magnetic orders, which appears as a contradiction to the KK approach in cubic lattices.

Fig. 2a shows the PES of the $Q_{22}^M$ mode around the cubic $Pm\bar{3}m$ phase in the dependence of the ($U|J$) parameters (5eV|1.5eV) and (8eV|2eV). The energy of the cubic AFM-A structure has been set to zero. The amplitude of the $Q_{22}^M$ distortion has been normalized to the bulk GS value. While the differences of the relaxed bulk GS with respect to the ($U|J$) parameters are subtle (shown in section IV), the differences in Fig. 2a are rather significant. On the FM surface the $Q_{22}^M$ distortions changes its character from dynamically stable to unstable for higher U and J values. Similarly on the AFM-A surface the energy gain of the $Q_{22}^M$ distortion with respect to the cubic structure is more than twice larger for the larger U and J values. At the opposite, the ferromagnetic ground state and the non-zero value of $\alpha_{JT}$ only on the AFM-A surface are independent of ($U|J$). Fig. 2a shows that the extraction of quantitative parameters from DFT calculations is a difficult task as the value can significantly change with the DFT-approach, while the relaxed GS structure might be very similar. However, qualitative our results are the same as the ones of a recent study$^{28}$ using a U-value of 3.5 eV$^{28}$.

The AFM-C and AFM-G surfaces are significantly higher in energy and not shown, but also show an vibronic coupling which is even stronger than in AFM-A. This result seems to be a contradiction to the C-JTE approach which does postulate a finite $\alpha_{JT}$ value independently of the magnetic order.

To investigate the electronic reason behind the shape of the PES, we show in Fig. 3 the electronic band-structures in the reference cubic and a distorted structure including a 10$\%$ $Q_{22}^M$ (of the ground-state amplitude) distortion in the FM and AFM-A magnetic ordering unfolded to the cubic Brillouin zone. We note that similar band-structures have been published before$^{70-73}$ but not its evolution with respect to structural distortions. Fig 3a shows the projection of the band-structures in the cubic phase with FM ordering onto Mn - $e_g$, Mn - $t_{2g}$, and O - p states. In accordance with other works$^{70-73}$ the band-structure shows that the $e_g$ states are dispersed symmetrically around the fermi-level $E_F$ in a range of about $\pm 2$eV. $E_F$ is crossed at the points X, and halfway
between $M$ and $R$, $\Gamma$ and $R$, $\Gamma$ and $M$, and $X$ and $R$. If the AFM-A magnetic ordering is imposed (Fig. 3b), the local degeneracy at $\Gamma$ of the $e_g$ bands is lifted showing the symmetry breaking produced by the magnetic order. $E_F$ crosses the $e_g$ bands at $M$, and halfway between $\Gamma$ and $X$, $\Gamma$ and $M$, $\Gamma$ and $R$, $X$ and $M$, and $X$ and $R$. The increase of many of the occupied valence states in the AFM-A cubic case with respect to the FM order (e.g. compare the section from $\Gamma$ over $M$ to $X$ of Fig. 3a and b) leads to the large increase of the total-energy from FM to AFM-A in the cubic phase (See Table III and Fig. 2). The metallicity of the AFM-A cubic phase despite the local non-degeneracy of the $e_g$ states can be explained by the degeneracy of two types of orbital orders within this phase schematically drawn in Fig. 2b. If the $Q_{2z}^M$ distortion is added, the electronic bands are split halfway between all the high symmetry points (compare Fig. 3c and d). The system will gain electronic energy if the $e_g$ bands are crossing the Fermi level at these points as virtual states are shifted to higher- and occupied ones to lower energies. Moreover, an insulating state can only be created by the application of the $Q_{2z}^M$ distortion if the $e_g$ bands cross the fermi-level at all the splitting points.

In the FM case only four splitting-points and crossings with the fermi level coincide. At $X$ and halfway between $\Gamma$ and $M$, $\Gamma$ and $R$, $X$ and $R$, and $M$ and $R$. However, halfway between $\Gamma$ and $X$, and $X$ and $M$ the $e_g$ bands are deep in the valence states at about -1.5 eV or one quarter of the $e_g$ bandwidth, where the splitting leads to an increase of the total electronic energy. The absence of the vibronic coupling can then be explained by

$$\alpha_{JT} = \int_{BZ} \sum_{n=1}^{n_{\text{e.g.}}} \frac{\partial E_n(\vec{k})}{\partial Q_{2z}^M} \bigg|_{Q_{2z}^M=0} = 0, \quad (6)$$

where $E_n(\vec{k})$ is the energy of band $n$ at $\vec{k}$ and we sum up its derivative with respect to $Q_{2z}^M$ of all occupied states, which are the number of electrons contained in the calculation $n_{\text{e.g.}}$. Eq. (6) means, that for each k-point at which the total electronic energy is decreased by a variation of $Q_{2z}^M$ there is another one at which it is increased by the same amount. Finally, in the FM case there is one direction that is unaffected by the $Q_{2z}^M$ distortion, which can be identified by one band that follows the original $e_g$ paths. Most clearly to be seen at the start of the path from $\Gamma$ over $X$ to $M$ (Compare Fig. 3a and c). This band accounts for the $z$-direction in real-space that is not affected by the $Q_{2z}^M$ distortion. In the AFM-A case the points at which the condensation of the $Q_{2z}^M$ distortion splits the $e_g$ bands and their crossing of $E_F$ in the cubic Brillouin zone coincide, such that the $Q_{2z}^M$ distortion leads to a lowering of the electronic energy and eq. (6) becomes non zero. Hence the origin of the finite vibronic coupling is a Peierls-like Effect where the destruction of the translational symmetry leads to an energy gain. The doubling of the periodicity can be seen most clearly in the oscillations from $\Gamma$ to $X$ to $M$ to $R$. Here magnetic order and $Q_{2z}^M$ distortion work together in an intriguing way to result in a finite vibronic coupling. Our result shows that future works should focus on the generalization of the spin-structural Peierls-effect in corner shared octahedra networks.

In real space the condensation $Q_{2z}^M$ with positive or negative amplitude corresponds to the stabilization of one orbital order, which will represent an non-degenerate electronic ground state in the distorted phase (See Fig. 3d) and Fig. 2b). The spin plus orbital order correspond to the doubling of the periodicity in the three space directions. In the cubic phase both orbital orders are degenerate and explain the metallicity.

Finally we want to summarize the major results of this section.

(i) Our results show contradictions to KK and CJTE approaches and question their applicability to LaMnO$_3$.

(ii) The origin of the vibronic coupling on the AFM-A surface appears to be rather a Peierls-like Effect, where AFM-A order and $Q_{2z}^M$ distortion work together to break the translational symmetry.

B. $Q_{2a}^M$ PES in Presence of other Lattice Distortions

To investigate under which structural conditions the AFM-A magnetic order is stabilized, we condensed the principal lattice distortions and strains, and sampled the $Q_{2z}^M$ surface on top of the already distorted structures. The result is shown in Fig. 4a-c. In Fig. 4a we used the cubic lattice constant $a_0 \approx 3.935\AA$ and successively condensed the octahedral rotations $\phi_x^3$ and $\phi_y^3$ ($a^+ a^- c^+$ in Glazer’s Notation) with the amplitude as they appear in the bulk ground state, and the rotations plus the $A_X$ motion with their corresponding ground state amplitudes, and sampled the $Q_{2z}^M$ surface (from left to right in (4a). In Fig. 4b we followed the same procedure for the rotations and $A_X$ distortion, but condensed on top the tetragonal strain $Q_{2z}^T$, which leads to lattice constants of $a = b = 5.66\AA$ and $c = 7.61\AA$. Finally in 4c we also condensed the shear strain $Q_{4z}^T$. Together with $Q_{2z}^T$ it leads to the ground state orthorhombic lattice constants. Energies in all graphs are referenced to the same energy (cubic AFM-A) allowing the reader to easily find the global ground state under certain conditions. Additionally we note in Fig. 4 if the relaxed electronic wave function represents a metallic (open symbols) or insulating state (filled symbols). In this section we limit ourselves to a qualitative discussion of the interplay of lattice and electronic band-structure, without an explicit demonstration of unfolded band-structures. The complete set of fitted coefficients is noted in appendix A Table IV.
The rotations alone induce on both magnetic surfaces a $Q_{2z}^M$ amplitude close to the experimental one. We emphasize that this strong coupling is related to the specific electronic constitution of LaMnO$_3$, as other Pbmn perovskites with significant octahedral rotations show only negligible $Q_{2z}^M$ amplitudes (e.g. CaMnO$_3$). Additionally there is a fourth order term incorporating the rotations and linearly the $Q_{2z}^M$ mode

$$\mathcal{F} \propto \alpha_2(\phi_x^+\phi_y^-)Q_{2z}^M.$$  \hfill (8)

This term is of no significant influence as the symmetry of the potential well is (almost completely) maintained when the rotations are condensed. Adding $A_X$, which alone is stable in the cubic phase, does further decrease the global energy together with the rotations due to a trilinear coupling term, which has been in the center of the discovery of hybrid improper ferroelectricity in cation ordered perovskite superlattices.

$$E_{0}^{\phi A_X} = \alpha(\phi_{xy}^-\phi_{z}^+)A_X,$$  \hfill (9)

where the modes take the amplitudes as in the relaxed bulk GS and $\alpha$ is coupling parameter whose value we did not quantify. In a similar way there exist a trilinear term

$$\mathcal{F} \propto \alpha_3(A_X\phi_{xy}^+\phi_{z}^-)Q_{2z}^M.$$  \hfill (10)

This term does significantly break the symmetry of the $Q_{2z}^M$ surface in contrary to term (8). The asymmetry created by the crystal field of the combination of $\phi_{xy}^-$ and $A_X$ is independent of the magnetic order as the fitted coefficient $\alpha_3$ takes close values for AFM-A and FM ordering (see Table IV). That being said, the ground state is surface is FM for all structures with cubic lattice constants. Only the AFM-A surface shows insulating behavior around its minima. The coupling terms above are
obviously equally valid in the strain distorted unit-cells and similar trends in the energy surfaces in all three examined cases can be seen.

2. $Q_{2z}^M$ PES in the tetragonally compressed lattice with octahedral rotations and antipolar motions

In this section we describe Fig. 4b adding the compressive tetragonal strain $Q_{3z}^T$ to the cubic lattice and show the PES of $Q_{2z}^M$ in terms of condensing the other lattice distortions. Adding $Q_{3z}^T$ increases energy independent of the magnetic order, but decreases their distance at $Q_{2z}^M = 0$ as $0 < E_{0}^{Q_{3z}^T}(AFM - A) < E_{0}^{Q_{3z}^T}(FM)$. On the FM surface the $Q_{2z}^M$ mode gets significantly softened. On the AFM-A surface the amplitude of the minima is shifted close to the experimental bulk value. On the FM surface the softening can be associated to linear-quadratic and a biquadratic strain-phonon coupling term

$$\mathcal{F} \propto \beta_1 Q_{3z}^T (Q_{2z}^M) + \beta_2 (Q_{3z}^M)^2 (Q_{2z}^M)^2.$$  \hspace{1cm} (11)

Here the linear-quadratic term is much more significant as $\beta_1 > \beta_2$. This implies also directly that the appearance of $Q_{2z}^M$ favors a compressive over a elongating tetragonal strain $Q_{3z}^T$ and vice versa. On the AFM-A surface it is mainly the electronic instability $\alpha_{JT}$ that is altered by $\lambda_{Q_{2z}^M} < 0$. Most interestingly, the ground state surface is no longer the FM one. If the $Q_{3z}^T$ strain and $Q_{2z}^M$ distortion are condensed together the transition is found at about 100% $Q_{3z}^T + 50\% Q_{2z}^M$. The linear-quadratic and biquadratic strain phonon coupling terms do exist between the tetragonal strain and all symmetry adapted modes condensed in the $Pbnm$ phase.

Octahedral rotations $\phi$ and $Q_{3z}^T$ shift the minima on both magnetic surfaces to values well above 1, which can be explained by the phonon-phonon couplings highlighted in eq. (7)-(10). Nonetheless, the cubic plus rotations surfaces stay lower in energy than tetragonal strained ones. Interestingly at this point the minima on the FM surface become insulating states. We can attribute this to the combined symmetry breaking of the anti-phase rotation $\phi_{xy}$ and the tetragonal compression of $Q_{2z}^M$, which together break the symmetry just like the AFM-A order. Adding $A_X$ breaks the symmetry of the energy surface. The energy-difference between the minima along the positive and negative paths of $Q_{2z}^M$ is increased, due to an intriguing quartic linear strain-phonon term,

$$\mathcal{F} \propto \alpha_1 (Q_{3z}^T \phi_{xy} A_X) Q_{2z}^M.$$  \hspace{1cm} (12)

We note that the same term exists replacing $Q_{2z}^M$ with the in phase octahedral rotation $\phi_{xy}^T$. It is due those two terms that eventually the tetragonal phase gets slightly stabilized over the cubic one.

FIG. 5: Schematic illustration of octahedral rotation and shear strain acting together as a $Q_2$ Jahn-Teller distortion of the oxygen octahedra. a) cubic phase, b) shear strain $\phi_{xy}^{+}$, c) rotation of the octahedra $\phi$, and d) shear strain $\phi_{xy}^{+}$ and rotation $\phi$ combined. In red elongated and green shortened octahedral axis.

3. $Q_{2z}^M$ PES in the tetragonally compressed and orthogonally strained lattice with octahedral rotations and antipolar motions

In this section we describe Fig. 4c adding the compressive tetragonal strain $Q_{4z}^T$ and the orthorhombic shear strain $Q_{4x}^T$, with their ground state values to the cubic lattice. The strained unit cell has then the lattice parameter of the relaxed ground state cell. Adding the shear strain $Q_{4z}^T$ on top of $Q_{3z}^T$ further increases the global energy, if no other modes are condensed. The distance between the magnetic surfaces is approximately unaltered as $E_{0}^{Q_{4z}^T Q_{3z}^T}(AFM - A) \approx E_{0}^{Q_{4z}^T Q_{3z}^T}(FM)$ (See Table IV).

Oppositional to the cubic and tetragonal case the symmetry of the PES is broken, when octahedral rotations are condensed due to a trilinear term

$$\mathcal{F} \propto \alpha_4 (Q_{4z}^T \phi_{xy}^{+}) Q_{2z}^M.$$  \hspace{1cm} (13)

In Fig. 5 we show the deformations onto the oxygen octahedra of condensing shear strain and octahedral rotations individually as well as together. Neither shear strain nor octahedral rotations induce a splitting of the bond lengths in the octahedra individually and have hence no influence on the local orbital degeneracy. However, together they serve as an effective $Q_2$ motion. If the rotation is antiphase $(\phi^-)$ the effective motion is $Q_{2z}^R$, if it is in-phase $(\phi^+)$ it becomes $Q_{2z}^M$ as it is the case in LaMnO$_3$. This effective $Q_{2z}^M$ motion explains that once $\phi_{xy}^{+}$ and $Q_{4z}^T$ are condensed the metal to insulator transition is reached for smaller $Q_{2z}^M$ amplitudes compared to the previously discussed surfaces. Finally it also explains, why the gradient discontinuity does not appear at
$Q_{3z}^M = 0$. To fit the PES in the presence of $Q_{3z}^F$ and $\phi^+_y$, we had to introduce a shift of the zero coordinate of $Q_{2z}^M$, which extracts the amplitude of the effective $Q_{2z}^M$ motion. In the presence of the GS amplitude of $Q_{3z}^F$ and $\phi^+_y$, $Q_{2z}^M$ takes $\approx 15\%$ of its GS amplitude, respectively 0.06\AA. It can be calculated in Fig. 4c at the position of the gradient discontinuity on the AFM-A surface. Despite, the trilinear term (13) tetragonally and sheared distorted unit cell stay higher in energy compared to the cubic case if only the octahedral rotations are present. It is eventually $A_X$ that induces an orthorhombic GS through a quartic term linear in $Q_{2z}^M$ similar to (12)

$$\mathcal{F} = \alpha_5(Q_{4z}^F A_X \phi^-_{xy})Q_{2z}^M. \quad (14)$$

The FM surface is also insulating around its $Q_{2z}^M$ minima and the AFM-A surface is the global ground state in all $Q_{3z}^F + Q_{3z}^F$ distorted cases.

From the discussion of the PESs we can draw the following conclusions:

(i) octahedral rotations trigger the $Q_{2z}^M$ by a negative biquadratic coupling on the FM surface and by an enhanced vibronic coupling on the AFM-A surface. This is attributed to a reduced $e_g$ bandwidth.

(ii) Tetragonal strain $Q_{3z}^F$ is responsible for the magnetic FM - AFM transition, by reducing the energy-difference between the AFM-A and FM surface. We note also that this is in accordance with a recent ab-initio studies\textsuperscript{77,78}, where $Q_{3z}^F$ as the main parameter stayed, however, unnoticed.

(iii) A band-gap can only be opened by $Q_{2z}^M$ on the FM-surface in the presence of tetragonal strain $Q_{3z}^F$ and the antiphase rotation $\phi^-_{xy}$. This is assigned to the combined strong symmetry breaking of $Q_{3z}^F$ and $\phi^-_{xy}$ along the $Pbnm$-c axis equivalent to the symmetry breaking of AFM-A order.

(iv) In none of the tested structures we found a finite value of $\alpha_{JT}$ on the FM surface. There is no vibronic coupling in the FM surface with respect to $Q_{2z}^M$.

(v) Various lattice couplings lead to almost identical GS structures for FM and AFM-A orderings. This explains the absence of a structural distortion at the magnetic transition $T_N \approx 140K$.

(vi) Shear strain $Q_{3z}^F$ and in phase octahedral rotation $\phi^+_y$ act as an effective $Q_{2z}^M$ distortion.

VI. $Q_{2z}^M$ AND OTHER LATTICE DISTORTIONS AROUND THE T$_{JT}$ TRANSITION

In this section we analyze the evolution of the amplitudes of all relevant strains and phonon modes around the orbital ordering transition at $T_{JT} \approx 750K$ as measured experimentally. We discuss the variation of the amplitudes of lattice modes and strains in connection with the coupling terms defined before. We recalculate the $Q_{2z}^M$ PES within the measured experimental structures around the transition. We show that those PESSs qualitatively reproduce the phase transition by a simple Monte-Carlo (MC) sampling of the PESs and that the mechanism at the origin of the transition should lie in an intriguing interplay of the lattice and electronic structure.

The experimental source is the recent study of Thygesen et al.\textsuperscript{13}, where the authors measured the lattice structure over $T_{JT}$ between 300 K and 1000 K. The aim of their study was to identify the differences in the local structure of the orbited ordered $O'$ and disordered $O$ phases to derive a better understanding of the $O$ phase (Sometimes also called orbital-liquid phase and the transition has been described as orbital melting\textsuperscript{8,79}).

In Fig. 6a we show the symmetry adopted strain and in Fig. 6b the symmetry adapted phonon mode analysis of the experimental data around $T_{JT}$. The low temperature amplitudes noted in Table II are shown in the dashed lines. Additionally we show the variation of the unit-cell volume through the volume strain $Q_{3z}^F$, which shows the well known volume collapse at $T_{JT}$. The tetragonal strain $Q_{3z}^F$ and shear strain $Q_{4z}^F$ show a linear decrease in amplitude for temperatures lower than $T_{JT}$. At $T_{JT}$ they suddenly disappear almost completely and have very small amplitudes in the orbital disordered $O$ phase. From the inspection of symmetry strains in Fig. 6a it is obvious that the disappearance of $Q_{3z}^F$ and $Q_{4z}^F$ are much more severe at $T_{JT}$ than the volume collapse $Q_{3z}^F$. Although this has been previously pointed out by Carpenter and...
The amplitudes of the modes at 300 K are very close to the low temperature values. The amplitude of the antiphase rotations $\phi_{xy}$ stays approximately constant and close to the low temperature value across the whole temperature range from 300 K to 1000 K. The values of the in phase rotation $\phi_{z}^{+}$ and the antipolar motion $A_{X}$ decrease linearly between 300 K and $T_{JT}$. The Jahn-Teller distortion $Q_{M}^{-2z}$ keeps an almost constant amplitude between 300 K and $T_{JT}$. At $T_{JT}$ there is a discontinuity for $\phi_{z}^{+}$, $A_{X}$, and $Q_{M}^{-2z}$ with a sudden reduction in their amplitude. However, $Q_{M}^{-2z}$ does not completely disappear directly at $T_{JT}$ as could be expected. Above $T_{JT}$, $\phi_{z}^{+}$, $A_{X}$, and $Q_{M}^{-2z}$ continue to decrease linearly ($Q_{M}^{-2z}$ until it reaches approximately zero amplitude at $\approx 900$ K).

The similar linear temperature dependence of $\phi_{z}^{+}$, $A_{X}$, $Q_{M}^{-2z}$ in the $O'$ and $O$ phases can be easily explained by (9) and (10). The amplitude evolution of $\phi_{z}^{+}$ should be associated as the driving force as $A_{X}$ is stable by itself and the amplitude of $\phi_{xy}$ is nearly constant. Then $A_{X}$ follows simply the amplitude of $\phi_{z}^{+}$ through the trilinear coupling (9). Consistently $Q_{M}^{-2z}$ follows the amplitude of $\phi_{z}^{+}$ through the trilinear coupling (10).

The small but non-zero amplitude of $Q_{M}^{-2z}$ just before the transition might suggest that the variation of $\phi_{z}^{+}$ with temperature induces the transition by the trilinear improper mechanism of eq. (10).

To get a more detailed insight we recalculated the PESs of $Q_{M}^{-2z}$ in the experimental structures extracted from Ref. [13] between 523K and 973K. We then execute a simple MC sampling on this surfaces to find the mean amplitude of $Q_{M}^{-2z}$ at a given temperature. To account for the PM state at the transition, we calculated the PESs in the four principal simple magnetic orders FM, AFMA, AFMC and AFMG (see Fig. 7a-d). Then we execute the MC-sampling on each magnetic surface individually and find the overall mean amplitude as the mean of the four surfaces. We executed the MC-sampling at a reduced temperature of 62.5% the experimental temperature. The resulting mean amplitude is shown alongside the measured one in Fig. 7e. Error bars show the standard deviation of the amplitude during the MC-sampling.

It can be seen that the qualitative features of the $Q_{M}^{-2z}$ amplitude with reducing temperatures are well reproduced. Notably a small linear increase of $Q_{M}^{-2z}$ before the transition and a sudden jump to larger amplitudes below. The error bars show a huge distribution above $T_{JT}$, which is consistent with the experimentally described liquidish behavior, and a strong reduction of the distribution below.

Through the PESs we can examine the origin of this transition. The FM surface shows that the rotation amplitudes of $\phi_{xy}$ and $\phi_{z}^{+}$ are large enough even at the highest temperature to produce a weak instability through the biquadratic coupling (7). Then through (10) a weak asymmetry of the surface is induced which increases before the transition. After the transition this asymmetry is

Howard researchers continue to emphasize the volume collapses.

FIG. 7: a)-d) $Q_{M}^{-2z}$ Born Openheimer Potential Energy Surfaces (PESs) as calculated from DFT within the lattice structures measured by Thygesen et al. at the indicated temperatures and magnetic orders. Markers show the DFT energies, continuous lines a polynomial fit. e) Experimental amplitudes of $Q_{M}^{-2z}$ and mean amplitudes resulting a Monte-Carlo (MC) sampling of the above PESs with $T_{sim}/T_{exp} = 0.625$. Error Bars show the standard deviation of the MC simulation.
greatly amplified such that the minimum on negative side of \(Q_{M}^{2}\) disappears. This change can be mainly attributed to the relaxation of the strains \(Q_{F}^{1}\) and \(Q_{A}^{1}\), and the associated couplings (11),(12),(13),(14), which are linear in \(Q_{M}^{2}\). Only taking into account the FM surface a lattice triggered picture would be convincing. However, the minima on this surface are much to shallow to explain the transition at such a high temperature.

To reproduce qualitatively the transition we had to take into account the AFM surfaces which is justified by the experimentally observed PM phase. Consistently with the results of the preceding sections the Peierls conditions for a finite vibronic coupling is always met on the AFM surfaces. The coupling strength is increased going from AFMA over AFMC to AFMG as the AFM surfaces. The coupling strength is increased going from AFMA over AFMC to AFMG as the AFM surfaces. The AFM surfaces introduce deep minima in the PESs which increase the transition temperature tremendously if taken into account.

Hence a rather complicated interlocked picture emerges to describe the origin of the transition. It is on one hand improperly induced by the lattice favoring one side of the \(Q_{M}^{2}\) surface over the other, but on the other hand incorporates also the characteristics of an order-disorder transition as deep minima for \(Q_{M}^{2}\) persist in the high temperature O phase, which is magnetically and structurally disordered.

Nonetheless our results of MC-sampling show that DFT+(\(U/J\)) calculations capture the essential physical interactions right. To get a more detailed insight into the mechanism of the transition future works should focus on building so called second-principles models\(^{81-83}\) on the basis of our DFT results taking into account the lattice dynamics and their coupling to the electronic states of interest. Those models will improve the description by including the self-correlation of PESs by the atomic displacements and by allowing for local fluctuations, while our MC sampling imposes a homogeneous material and rigid PESs.

VII. CHARGE VS. ORBITAL ORDERING IN LAMNO\(_{3}\)

Until this point we investigated the relevant statically appearing distortions in the single-crystal ground state phase of LaMnO\(_{3}\). However, at few occasions a charge disproportionation/ordering instability has been discussed as an alternative and competing mechanism to orbital-ordering\(^{84,85}\) or as the origin of the transition in the high temperature orbital liquid, which has been in that picture described as and electron-hole liquid phase\(^{86,87}\). Such a charge-ordering instability in the high temperature phase should be accompanied by the instability of the breathing type distortion \(Q_{A}^{1}\) (see Table 1). Recent works showed that the charge-ordering transition in RNI\(_{3}\) (a \(\alpha_{g}^{1}\) perovskite with doubly occupied \(t_{2g}\) states) can be understood as a Peierls transition\(^{91}\) triggered by the appearance of octahedral rotations. Moreover, that same picture applies alkali earth ferrites AFeO\(_{3}\)\(^{30}\) with the same formal occupation fo Fe \(d\)-states as Mn \(d\)-states (\(d^4 = t_{2g}^3e_g^1\)) and in those ferrites the instabilities of \(Q_{R}^{1}\) and \(Q_{M}^{2}\) compete and can be tuned by epitaxial strain. A result that has moreover equally been obtained for HoNiO\(_{3}\)\(^{88}\).

In Fig. 8 we show that the same competition exists for the RMnO\(_{3}\) series with the sample of LaMnO\(_{3}\). Here we limit ourselves to calucations within the ferromagnetic ordering. In top of fig. 8 the PESs of \(Q_{R}^{1}\) and \(Q_{M}^{2}\) within cubic LaMnO\(_{3}\) can be seen. Both show stable single wells with comparable harmonic and higher order dependencies. If the octahedral rotations are condensed the total energy of the system is significantly reduced and both distortions become dynamically unstable with slight advantage for \(Q_{M}^{2}\). This result shows that the approach of a Peierls transition in the \(Q_{R}^{1}\) coordinate triggered by octahedral rotations is equally valid in RMnO\(_{3}\). The reasoning is point by point the same as for AFeO\(_{3}\) and RNI\(_{3}\) and can be found in\(^{30,31}\). We note also that on the AFM surfaces we find the same vibronic coupling for \(Q_{R}^{1}\) as for \(Q_{M}^{2}\), which we do not show for simplicity. Finally the competition between \(Q_{R}^{1}\) as for \(Q_{M}^{2}\) is decided in favor of \(Q_{M}^{2}\) by the trilinear coupling with the antiphase rotation \(\phi_{xy}^{+}\) and the antipolar motion \(A_{X}\) (10), since there is no such coupling incorporating \(Q_{R}^{1}\). If the tetragonal and shear strain \(Q_{F}^{1}\) and \(Q_{F}^{3}\) are relaxed \(Q_{R}^{1}\) and \(Q_{M}^{2}\) get strongly separated. These results are consistent with the proposed self-trapping of the charge-disproportionated phase\(^{87}\) and the observation of the coexistence of different phases depending on heat treatments and the history of samples\(^{89}\).
VIII. CONCLUSION

In conclusion we presented first-principles calculations able to consistently reproduce the bulk properties of LMO. We systematically investigated the PESs of LMO around its aristotype cubic reference structure. To do so we used the decomposition of orthonormal symmetry adapted strains and phonon like modes. We connected those strains and modes with Van Vleck’s notation of Jahn-Teller distortion in the isolated octahedral transition metal complex. We introduced a canonical notation that shows in a simple way the local and cooperative character of such distortions.

The investigation of the $Q_{2z}^M$ PES in the cubic phase by our first principles calculations showed contradictions to the anticipated results following Kugel-Khomskii model or the cooperative Jahn-Teller effect approach and question their applicability to LaMnO$_3$. The unfolding of the electronic band structure in this cubic phase for FM and AFMA indicates that the electronic origin of the instability of the $Q_{2z}^M$ is rather a Peierls like effect. It remains to be seen, if the same result applies to other orbital-ordered materials as e.G. KCuF$_3$.

Through the analysis of the PESs under the presence of other significant lattice distortions that appear in the $Pbnm$ phase of LaMnO$_3$ we were able to explain a number of interlocking mechanisms between strain/phonon like distortions, magnetic ordering and the opening of an electronic band gap. Of these the most important are -

(i) Octahedral rotations trigger the $Q_{2z}^M$ mode on the FM surface by a negative biquadratic coupling and the AFM surfaces by an increase of the vibronic coupling. The origin of both is the reduced $e_g$ - bandwith.

(ii) The most important parameter for stabilizing FM over AFM-A magnetic ordering is the tetragonal strain $Q_{4z}^M$. Reducing this strain will favor the FM state serving as paradigm for engineering FM phases in rare-earth manganites.

(iii) The minimum of FM and AFMA surfaces have the same structural distortion. This explains the absence of any structural transformations at the AFM to PM transition at $T_N = 140K$.

Then, we went further and showed by a MC sampling that the orbital ordering transition at $T_{JT} = 750K$ can be coherently reproduced by the PESs that our DFT calculations provide. The analysis of this transition showed mixed characteristics of order-disorder, lattice improper and electronically induced transitions. This result emphasizes that all attempts to pin-point to one origin of this specific transition are doomed to fail.

Finally we showed from first-principles that a subtle competition between charge-ordering and orbital-ordering exists in LaMnO$_3$, which further enrich its behavior.

While we believe that our work will serve as a sound basis for general lattice-electronic dependencies in LaMnO$_3$ and related compounds, we are aware that not all question in this compound are resolved. Especially the electronic state in the high temperature $O$ phase and the precise mechanism of the Orbital-Ordering transition will remain highly debated and we emphasize the need for new general predictive model descriptions. Our work highlights that such model needs to self consistently include the interplay between lattice, strain and electronic degrees of freedom. This has been noted before, but never put to practice. A promising tool to achieve such a model description is the generation of so called second-principles model transferring first-principle results into local lattice and electronic effective potentials. Such second principle models would then give rise to large scale simulations at finite temperature with access to complete local information needed to study the cooperative Jahn-Teller effect in its comprehensive dynamic complexity.
Appendix A: Fitting of $Q^{M}_{2z}$ PES

In the following we discuss briefly the parametrization of the $Q^{M}_{2z}$ surface in a free energy expansion. To do so we fitted each of the PES in Fig. 4 by a polynomial of the shape

$$\mathcal{F} = E_0 + \alpha_{JT}|Q^{M}_{2z}| + \alpha_{2z}Q^{M}_{2z} + \beta (Q^{M}_{2z})^2 + \gamma (Q^{M}_{2z})^4, \quad (A1)$$

where we denote coefficients of terms that are of first-order in $Q^{M}_{2z}$ with $\alpha_{2z}$, second with $\beta$, and fourth with $\gamma$. All modes have been normalized such that 1 represents their ground-state amplitude, which can be found in Table II. Since we are not interested in the fourth-order couplings we wrote only one fourth order term and we will not list the variation of its value. Moreover, we used

$$\phi = \phi^{z}_{2z} = \phi^{-}_{xy} \quad (A3)$$

$$E_0 = E_0^{FM} + E_0^{Q_{3z}} + E_0^{Q_{3z}Q_{4z}} + E_0^{\phi} + E_0^{\phi,Q_{3z}Q_{4z}} + E_0^{\phi,Q_{3z}Q_{4z},Q_{2z}} + E_0^{\phi,A_x} + E_0^{\phi,A_x,Q_{3z}} + E_0^{\phi,A_x,Q_{3z},Q_{4z}} \quad (A4)$$

declare the stability or instability of strains and atomic displacements in the FM and AFM-A phase in the absence of the $Q^{M}_{2z}$ distortion. Finally we also investigated the variation of the strength of the electronic instability parameter $\alpha_{JT}$ as a function of the other lattice distortions

$$\alpha_{JT} = \alpha^{0}_{JT}(1 + (\lambda_{\phi} + \lambda_{\phi} + A_x)A_x)\phi + (\lambda_{Q^{m}_{2z}} + ((\lambda_{Q^{m}_{2z} + \phi} + \lambda_{Q^{m}_{2z} + \phi} + A_x)A_x)\phi \cdot (\lambda_{Q^{m}_{2z}} + \lambda_{Q^{m}_{2z}} + \phi + A_x)A_x)\phi + \lambda_{Q^{m}_{2z} + Q^{m}_{2z} + \phi + A_x}Q^{F}_{3z}Q^{F}_{4z} \quad (A5)$$

where we assume a linear dependence of the $\alpha_{JT}$ to the other lattice distortions. Further studies would need to clarify the explicit dependence of $\alpha_{JT}$ to the surrounding lattice. As mentioned in the main text $\alpha_{JT}$ is strictly zero on the FM surface, for which reason only its values for AFM-A ordering has been reported in Table IV below.

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TABLE IV: Table of fitted constants to reproduce the PES in Fig. 4. From up to down. Zero point Energies $E_0$, gathering energy gains or losses of condensing individual modes and strains without $Q_{2z}$ distortion. First and second order parameters $\alpha \& \beta$ gathering linear and quadratic lattice couplings in $Q_{2z}$. Electronic Parameter $\alpha_{JT}$ gathering the variation of the electronic instability in dependence of the condensed lattice modes.

| MO  | $E_0^{FM}$ | $E_0^{AFM}$ | $E_0^{MO}$ | $E_0^{Q_{2z}}$ | $E_0^{Q_{2z}^2}$ | $E_0^{A}$ | $E_0^{Q_{2z}^2}$ | $E_0^{Q_{2z}^2} |$ $E_0^{A}$ | $E_0^{A}$ | $E_0^{A}$ | $E_0^{A}$ | $E_0^{A}$ |
|-----|------------|-------------|------------|----------------|----------------|----------|----------------|---------------|----------|----------|----------|----------|----------|
| FM  | -0.51      | 0.21        | 0.16       | -0.56          | 0              | 0.16     | -0.40          | -0.15         | -0.27    |          |          |          |          |
| AFM-A | -          | 0.05        | 0.15       | -0.63          | 0.05           | 0.18     | -0.39          | -0.12         | -0.29    |          |          |          |          |

| MO  | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\alpha_4$ | $\beta_1$ | $\beta_2$ | $\beta_3$ | $\beta_4$ | $\beta_5$ | $\beta_6$ |
|-----|------------|------------|------------|------------|----------|----------|----------|----------|----------|----------|
| FM  | -0.02      | -0.09      | -0.03      | -0.11      | -0.01    | 0.26     | -0.53    | 0.04      | -0.22    | -0.01    | 0.003    |
| AFM-A | -0.01      | -0.10      | -0.02      | -0.11      | -0.02    | 0.29     | -0.04    | 0.02      | 0.08     | -0.01    | -0.20    |

| MO  | $\lambda_{JT}$ | $\lambda_{Q_{2z}}$ | $\lambda_{Q_{2z}^2}$ |
|-----|---------------|----------------|----------------|
| AFM-A | -0.74        | -0.20          | 0.01           |

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