Theory of nonlinear phononics for coherent light-control of solids

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We present a microscopic theory for ultrafast control of solids with high-intensity Tera-Hertz frequency optical pulses. When resonant with selected infrared-active vibrations, these pulses transiently modify the crystal structure and lead to new collective electronic properties. The theory predicts the dynamical path taken by the crystal lattice using first-principles calculations of the energy surface and classical equations of motion, as well as symmetry considerations. Two classes of dynamics are identified. In the perturbative regime, displacements along the normal mode coordinate of symmetry-preserving Raman active modes can be achieved by cubic anharmonicities. This explains the light-induced insulator-to-metal transition reported experimentally in manganites. We predict a new regime in which ultra-fast instabilities that break crystal symmetry can be induced. This non-perturbative effect involves a quartic anharmonic coupling and occurs above a critical threshold, below which the non-linear dynamics of the driven mode displays softening and dynamical stabilization.

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The use of light to control the structural and electronic properties of solids is emerging as an area of great interest for both basic research and potential applications. Much work has been dedicated to materials with strong electronic correlations, which exhibit remarkable collective properties such as superconductivity, ferroelectricity or colossal magnetoresistance, and can be switched by illumination with light [1–5].

Recently, the possibilities of materials control by light have been greatly expanded by the demonstration of phase switching through selective vibrational excitation, that is by deforming the lattice along a specific normal-mode coordinate [6–8]. Let us mention in particular the achievement of light-induced superconductivity [9–11]. Mode-selective optical control is especially attractive because it allows for the coherent excitation of only one or at most a few low-energy degrees of freedom, making control more precise. This stands in contrast to what can be achieved at near-visible wavelengths, where the excitation is highly incoherent, poorly selective and induces heating.

A qualitative explanation for mode-selective optical control has been proposed by Först et al. [12], starting from the concepts of ionic Raman scattering [13–15]. In this description, the excitation of an infra-red mode results in the displacement of the crystal structure along the coordinate of a second, anharmonically coupled Raman mode. The coherent energy transfer from the infra-red to the Raman mode was analyzed through a lowest-order perturbative expansion of the lattice potential. This mechanism was termed “nonlinear phononics” and identified as a new type of coherent coupling between light and crystal lattices, beyond the extensively studied case of impulsive stimulated Raman scattering [16–18].

In this article, we present a microscopic theory for nonlinear phononics. This theory is based on symmetry considerations, as well as first-principles calculations of the energy surface combined with classical equations of motion in order to predict the dynamical path taken by the crystal lattice. We use this approach to study the response of two materials: the parent compound of the magnetoresistive manganites PrMnO3 (PMO), in relation to the experiments of Rini et al. [6], and that of the cuprate superconductors La2CuO4 (LCO).

At low fluence of the infra-red excitation we show that, when considering non-degenerate phonon modes, it is only possible to displace the crystal lattice along a fully symmetric A1g Raman mode. This makes use of an anharmonic cubic coupling of the form Q2g R, as envisioned by Först et al. [12]. We find that this applies to PMO and, by performing electronic structure calculations based on dynamical mean-field theory (DMFT), we provide a microscopic explanation for the light-induced insulator-metal transition observed experimentally [6] in this material.

At larger fields, we predict a new class of non-perturbative dynamics that involves Raman distortions of symmetry other than A1g. This dynamics, which becomes observable in LCO, originates from a quartic coupling of the type Q2g R. In this case, a cubic coupling is forbidden by symmetry. Although at low fluence such a quartic coupling implies only a renormalization of the frequency of the Raman mode, an instability is found beyond a critical threshold, resulting in a distortion into a crystal structure of lower symmetry. Furthermore, we find that the near-threshold regime exhibits a
dynamical stabilization of the crystal lattice, analogous to the Kapitza phenomenon in driven non-linear systems \[19, 20\].

We first consider PMO, which is an insulator with orthorhombic \(P\text{m}na\) structure and four formula units per unit-cell. In order to identify the nature and strength of the coupling between various IR and Raman phonons, we performed energy-surface calculations as a function of the amplitude of these modes. The calculations were performed using density-functional theory in a plane-wave basis set (VASP code \[21\]). The 60 zone-center normal modes (see supplemental material for details \[22\]) were identified using the frozen-phonon method as implemented in the PHONOPY software package \[23\]. In the experiment of Rini et al., the IR mode corresponding to the stretching of the apical Mn-O bond was excited, but the frequency and symmetry of the excited mode was not analyzed. Hence, we used selection rules from group theory and explored several possible pairs of IR and Raman modes to infer which one might be relevant to the physics. We considered the excitation of the \(B_{1u}(54)\), \(B_{1u}(56)\), \(B_{2u}(58)\), and \(B_{3u}(60)\) IR modes, the first one corresponding to the stretching of apical Mn-O bonds and the others to in-plane ones. In the point group \(mmm\), the square of every irreducible representation is the \(A_g\) representation. Hence, any of the seven \(A_g\) modes of PMO can in principle have a non-linear cubic coupling to the \(B_u\) modes. We considered the coupling of all seven modes to the four aforementioned IR modes and found that the coupling between the apical Mn-O stretching mode \(B_{1u}(54)\) and the \(A_g(9)\) Raman mode is substantial. Furthermore, as illustrated on Fig. 1 (top panel), a positive amplitude displacement of this Raman mode reduces the rotation of the MnO$_6$ octahedra in the \(ab\)-plane. We show below that this favours the metallic state. Hence, we propose that the displacement of this mode through the non-linear coupling to the pumped \(B_{1u}(54)\) mode is responsible for the effect observed by Rini et al. \[6\].

The calculated energy surface is displayed on Fig. 1 and fits the following expression, which involves a cubic anharmonic coupling between the two modes:

\[
V(Q_R, Q_{IR}) = \frac{1}{2} \Omega_R^2 Q_R^2 + \frac{1}{2} \Omega_{IR}^2 Q_{IR}^2 + \frac{1}{3} a_3 Q_R^3 + \frac{1}{2} b_4 Q_{IR}^4 - \frac{1}{2} g Q_R Q_{IR}^2
\]

Here, \(Q_R\) and \(Q_{IR}\) are the displacements of the \(A_g(9)\) and \(B_{1u}(54)\) modes, respectively. The calculated frequencies are \(\Omega_R = 155\ \text{cm}^{-1}\) and \(\Omega_{IR} = 622\ \text{cm}^{-1}\). The values of all coefficients are given in a table in the supplemental material \[22\]. From Fig. 1 (middle panel), one sees that, for a given value of the \(B_{1u}(54)\) amplitude, the energy landscape has a unique minimum as a function of the amplitude of the \(A_g(9)\) mode. Furthermore, this mode is displaced from its equilibrium position as soon as the amplitude of the \(B_{1u}(54)\) mode is non-zero. This displacement being positive, it brings the structure closer to cubic symmetry (Fig. 1 top).

In order to substantiate that this can be responsible for the observed metallisation of PMO, we have calculated the spectrum of electronic excitations of this compound in both the orthorhombic \(P\text{m}na\) equilibrium structure and in the hypothetical cubic structure. This allows for a clear-cut comparison and for assessing the potential effect of fully undoing the orthorhombic distortion. The calculations are performed using the state-of-the-art combination of electronic structure and dynamical mean-field theory (LDA+DMFT) \[24, 25\] in order to properly account for the interplay between structural aspects and strong electronic correlations. As displayed in Fig. 1 (bottom panel),
We now turn to LCO, which forms in the orthorhombic Bmab structure with two formula units per unit cell. We looked for coupling between high-frequency IR modes and low-frequency Raman modes, as relevant to low frequency pump-probe experiments. We find that there is a substantial coupling between $B_{1g}(18)$ Raman and $B_{3u}(41)$ IR modes of LCO. This IR mode also couples to a lower frequency $A_g(11)$ Raman mode, but the coupling much smaller. An amplitude of 2.0 Å/amu for the $B_{3u}(41)$ mode shifts the minimum of the $A_g(11)$ mode to $-0.4$ Å/amu, whereas the same amplitude of the $B_{3u}(41)$ mode generates minima at $\pm 2.4$ Å/amu for the $B_{3g}(18)$ mode. Hence, we only focus on the dynamics of the $B_{1g}(18)$ and $B_{3u}(41)$ modes. The $B_{1g}(18)$ mode corresponds to the in-plane rotations of the CuO$_6$ octahedra as shown in Fig. 2 (top) and the $B_{3u}(41)$ involves in-plane stretching of the Cu-O bonds. The $B_{1g}(18)$ mode breaks the two-fold rotational symmetry along $x$ and $y$ axes as well as the reflection symmetry with the mirrors on $xz$ and $yz$ planes. Therefore, the structures generated by the positive and negative $B_{1g}(18)$ amplitudes are related by these symmetries.

The calculated energy surface for LCO is also displayed on Fig. 2 and fits the following expression (with $Q_R$ and $Q_{IR}$ the amplitudes of the $B_{1g}(18)$ and $B_{3u}(41)$ modes, respectively and the calculated frequencies $\Omega_R = 162$ and $\Omega_{IR} = 633$ cm$^{-1}$):

$$V(Q_R, Q_{IR}) = \frac{1}{2} \Omega_R^2 Q_R^2 + \frac{1}{2} \Omega_{IR}^2 Q_{IR}^2 + \frac{1}{4} a_4 Q_{IR}^4 + \frac{1}{4} b_4 Q_R^4 - \frac{1}{2} g Q_R^2 Q_{IR}^2.$$  

(2)

In contrast to PMO, we find a single-potential well around the equilibrium value for the $B_{1g}(18)$ mode at small $B_{3u}(41)$ amplitude. Remarkably, a double well is generated beyond a critical value of the $B_{3u}(41)$ amplitude. Consistent with the observation above, the energy is symmetric upon reversal of the sign of the $B_{1g}(18)$ amplitude. The non-linear coupling is here of the form $Q_R^2 Q_{IR}^2$, consistent with this symmetry. We note that only the coupling to pairs of identical, zone-center Raman modes have been considered in the analysis of the $Q_R^2 Q_{IR}^2$ coupling term. Coupling to pairs of Raman modes with opposite momenta away from zone center is in principle possible and should be considered in future work.

The disparate nature of the potential energy surface in PMO and LCO can be explained by symmetry considerations. Being associated with the trivial representation of the crystal symmetry group, an $A_g$ Raman mode does not break any symmetry. Hence, the atomic displacements associated with vibrations of this mode whose amplitude have equal magnitude but opposite sign are not related by symmetry. Their energies are in general different, resulting in terms with odd powers of $Q_{IR}$, consistent with this symmetry. We note that only the coupling to pairs of identical, zone-center Raman modes have been considered in the analysis of the $Q_R^2 Q_{IR}^2$ coupling term. Coupling to pairs of Raman modes with opposite momenta away from zone center is in principle possible and should be considered in future work.

We now turn to LCO, which forms in the orthorhombic Bmab structure with two formula units per unit cell.
tation. Indeed, $A_g \subset A_q \otimes B_{1u} \otimes B_{1u}$ for PMO, and $A_g \subset B_{1g} \otimes B_{3g} \otimes B_{3u} \otimes B_{3u}$ for LCO.

We finally discuss the dynamics of the non-linearly coupled modes when the IR mode is pumped externally. We simplify the problem by treating the Raman and IR modes as two coupled classical oscillators. These oscillators are subject to a force deriving from the calculated energy surface (Eqs. 1, 2) and to a driving term $F(t) = F \sin(\Omega t) e^{-t^2/2\sigma^2}$, where $F$, $\sigma$, and $\Omega$ are the amplitude, width and frequency of the light pulse, respectively. In the case of PMO (cubic coupling), the resulting equations of motion read:

$$\dot{Q}_{IR} + \Omega_{IR}^2 Q_{IR} = g Q_R Q_{IR} - b_4 Q_{IR}^3 + F(t)$$

$$\dot{Q}_R + \Omega_R^2 Q_R = \frac{1}{2} g Q_{IR}^2 - a_3 Q_R^2.$$  (3)

Following [22], the resulting dynamical behaviour can be easily understood in the impulsive limit $\sigma \ll 1/\Omega$ (see the analysis in supplemental material [22], which differs in details from that of [12]). On resonance, the IR mode undergoes a forced oscillation of amplitude $\propto F \Omega_{IR}^2 \sigma^3$. The effective forcing field for the Raman mode is $g Q_{IR}^2/2 \propto g F^2 Q_{IR}^2 \sigma^6 (1 - \cos 2\Omega_{IR} t)$ which has a rectified non-zero average value. Hence, the Raman mode oscillates around a displaced position as a result of the excitation of the IR mode by the light pulse, consistent with the displaced minimum of the energy surface (Fig. 1). The displacement occurs for an arbitrarily small pump amplitude, grows quadratically as $\propto g Q_{IR,max}^2/\Omega_{IR}^2 \propto g F^2 Q_{IR}^2 \sigma^6/\Omega_{IR}^2$, and the oscillation frequency $\Omega_R$ is unchanged by the light pulse. This behaviour is also confirmed by numerical integration of these equations for a finite pulse-width [22].

In the case of LCO (quartic coupling), the equations of motion read:

$$\dot{Q}_{IR} + \Omega_{IR}^2 Q_{IR} = g Q_R Q_{IR} - b_4 Q_{IR}^3 + F(t)$$

$$\dot{Q}_R + \Omega_R^2 Q_R = g Q_R Q_{IR}^2 - a_3 Q_R^3.$$  (4)

Numerical integration of these equations reveal a much richer behaviour than in the cubic case, as illustrated on Fig. 3. There is a threshold value $F_c$ of the pulse amplitude below which the Raman mode is not displaced and oscillates around its original equilibrium position. In this regime (Fig. 3A), the period of oscillation is amplified by the light pulse, as well as its amplitude. Upon increasing $F \geq F_c$, above threshold, three different regimes are successively found (Figs. 3B, C, D). In a narrow range of $F \gtrsim F_c$, a long-period oscillation reaching out to the two wells of the double-well potential is found (B). This is also the case (D) at large values of $F$ but with a much shorter period. For an intermediate range of values of $F > F_c$, a rectified regime (C) is again found, in which the Raman mode oscillates around a displaced position.

Here also, some analytical understanding can be achieved in the impulsive limit, as detailed in [22]. It is immediately apparent from the second equation in (4) that the IR mode does not act as a forcing term in this case, but rather as a time-dependent modulation of the frequency of the Raman mode $\Omega_R^2 \rightarrow \Omega_{R,max}^2 [1 - g Q_{IR}(t)/\Omega_{R}^2]$. Hence, for $F < F_c$, the dynamics is well approximated by a Mathieu equation describing a parametric oscillator. The threshold amplitude $F_c$ can be analytically calculated in the impulsive limit from known properties of this equation and is given by the condition $g Q_{IR,max}^2 / \Omega_{R}^2 = 2$, where $Q_{IR,max} \propto F^2 \Omega_{IR}^3$ is the amplitude of the excited IR mode. Remarkably, $F_c$ is $\sqrt{2}$ times larger than the value (corresponding to $g Q_{IR,max}^2 / \Omega_{R}^2 = 1$) at which the energy landscape [2] develops a double well and the original equilibrium position becomes unstable from a static viewpoint. Hence, in the range $F_c/\sqrt{2} < F < F_c$, there is a dynamical stabilisation of the unrectified oscillatory motion, analogous to the Kapitza phenomenon for a vibrating pendulum [12, 20].

The oscillation frequency in this regime is reduced by the light pulse according to $\Omega_{eff}^2 = \Omega_{R}^2 [1 - (F/F_c)^2]$, in accordance with the numerical observations.

The critical amplitude of the $B_{3u}(41)$ mode associated with the dynamical threshold for LCO is found to be $Q_{IR,max}^c \approx 1.6 \text{ Å}$. This corresponds to a typical in-plane displacement of the oxygen atoms of 0.276 Å. Previous experiments [4] have shown that atomic displacements of that magnitude can be induced by available...
light pulses, so that this effect should indeed be observable. We note furthermore that the in-plane rotations associated with the $B_{1g}(18)$ Raman mode lead to a reduction of the bandwidth of the Cu-$d_{x^2-y^2}$/O-$p_{x,y}$ antibonding band. This could be used to modify the correlation strength and superexchange coupling in this cuprate.

We have also considered the effect of damping on this dynamical behaviour, as displayed on Fig. 3 E–F. For typical values (5–10% of the linewidth) of the damping of the IR mode, the Raman mode is found to relax back to an oscillating behaviour around its original equilibrium position, as expected. However, the salient features of the above dynamical regimes are preserved. In particular, a critical value of the pump amplitude is still present, above which the pump excites a coherent oscillation of the Raman mode, with an initial large-amplitude displacement (Fig. 3 E–F).

In summary we have developed a microscopic theory of the light-control of crystal lattices by strong field THz radiation. Our theory greatly expands the understanding of this new class of phenomena, explaining many of the observations reported to date. The cubic anharmonic coupling between IR and Raman modes, already used to explain experimental results qualitatively, is shown here to apply only to totally symmetric modes (in the non-degenerate case considered here). For manganites, we combine first-principle structural studies and electronic structure calculations, and identify the microscopic pathway for the insulator to metal transition observed experimentally. More importantly, we predict a new regime for which the light can be used to initiate dynamical symmetry breaking. This latter class of phenomena is non-perturbative, involves a quartic coupling, and leads to transient mode softening and dynamic stabilization. We show that this second regime is dominant in specific crystal structures, and predict that its experimental observation is possible with current technology.

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SUPPLEMENTARY INFORMATION

PHONON CALCULATIONS FOR PMO AND LCO

Methods

The results for the phonon dispersions and the non-linear phonon coupling calculations presented in the paper were obtained using density functional theory calculations with plane-wave basis sets and projector augmented wave pseudopotentials \[1, 2\] as implemented in the VASP software package \[3\]. The interatomic force constants were calculated using the frozen-phonon method \[4\] and the PHONOPY software package was used to calculated the phonon frequencies and normal modes \[5\]. After the normal modes were identified, total energy calculations were performed as a function of the IR $Q_{\text{IR}}$ and Raman $Q_{\text{R}}$ amplitudes to obtain the energy surfaces. The atomic displacements due to an amplitude $Q_\alpha$ of normal mode $\alpha$ is given by $U_j = \frac{Q_\alpha}{\sqrt{m_j w^\alpha_j}}$, where $U_j$ is the displacement of the $j$th atom, $m_j$ is the mass of this atom, and $w^\alpha_j$ is the corresponding component of the normal-mode vector. Note that $w^\alpha$ is normalized and dimensionless.

The non-linear coupling between the IR and Raman modes were obtained by fitting the energy surfaces shown in Figs. (1) and (2) to the polynomials Eqs. (1) and (2), respectively, as given in the main text. These polynomials fit the respective energy surfaces exactly, hence there are no approximations in the calculations of the non-linear couplings, beyond that for the exchange-correlation functional.

We use the units of eV for energies, amu for masses, and Å/√amu for the normal mode amplitudes $Q_\alpha$. This means that the frequencies obtained from the fits of the energy surfaces in Figs. (1) and (2) to Eqs. (1) and (2), respectively, are in the units of $\sqrt{\text{eV/amu/Å}}$, and we use a conversion factor of 521.471 cm\(^{-1}\)/($\sqrt{\text{eV/amu/Å}}$) to get the frequencies in the familiar units of cm\(^{-1}\).

| Calc. freq. (cm\(^{-1}\)) | Symmetry |
|---------------------------|----------|
| 97.43                     | $A_g(4)$ |
| 154.80                    | $A_g(9)$ |
| 231.10                    | $A_g(21)$|
| 267.58                    | $A_g(23)$|
| 351.07                    | $A_g(36)$|
| 479.49                    | $A_g(47)$|
| 552.09                    | $A_g(51)$|
| 622.12                    | $B_{1u}(54)$|
| 633.38                    | $B_{1u}(56)$|
| 639.95                    | $B_{2u}(58)$|
| 660.54                    | $B_{3u}(60)$|
PMO

PMO exists in the orthorhombic Pbnm structure and is insulating. The distortions from the ideal perovskite structure consist of the Jahn-Teller distortion and the rotation of the O octahedra. The rotation of the O octahedra results from relatively small radii of Pr$^{3+}$ ion and the subsequent mismatch between Pr-O and Mn-O bond lengths. This distorted structure has four PMO formula units per unit cell. In our phonon calculations, we used the experimental structure for Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ with $a = 5.426$ Å, $b = 5.478$ Å, and $c = 7.679$ Å [6], but relaxed the atomic positions. The DFT+$U$ calculations were done within the generalized gradient approximation of Perdew, Burke and Ernzerhof [7]. We used a cut-off of 600 eV for plane-wave expansion. We also used an on-site Coulomb repulsion $U = 5.0$ eV and Hund's exchange $J = 0.7$ eV for the Mn atom and stabilized the antiferromagnetic ordering.

There are 20 atoms in the orthorhombic unit cell of PMO, which gives rise to 60 zone-center normal modes with the decomposition $7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g} + 8A_u + 8B_{1u} + 10B_{2u} + 10B_{3u}$. The phonon frequencies of the seven $A_g$ and the four IR modes used in our study is given in Table II. The coefficients of the polynomial for the energy surface of $A_g(9)$ and $B_{1u}$ modes are given in Table III.

TABLE III: The values of the coefficients of the polynomial for energy surfaces of Raman and IR modes obtained from fit to the calculated energy surfaces.

| Coefficient | PMO | LCO |
|-------------|-----|-----|
| $a_0$ (meV/amu/A$^2$) | 87.09 | 103.55 |
| $a_1$ (meV/amu/$\sqrt{A}$) | 1416.13 | 1462.33 |
| $a_3$ (meV/amu/$\sqrt{A}$) | 5.82 | 8.36 |
| $b_4$ (meV/amu/$\sqrt{A}$) | 80.24 | 135.18 |
| $g$ (meV/amu/$\sqrt{A}$) | 51.74 | 46.98 |

LCO

LCO exists in the orthorhombic Bmab structure. This structure is derived from the ideal body-centered tetragonal structure by alternating tilts of the O octahedra along the tetragonal [110] axes which causes a ($\sqrt{2} \times \sqrt{2} \times 1$) doubling of the unit cell. As a result, the primitive unit cell in the orthorhombic structure contains two formula units. In our calculations of the phonon frequencies, we used the experimental lattice parameters with $a = 5.3568$, $b = 5.4058$, and $c = 13.1432$ Å, but relaxed the internal coordinates. The DFT calculations were done within the local density approximation and an energy cut-off of 600 eV was used for the plane-wave basis.

There are 14 atoms in the unit cell, and this results in 42 zone-center normal modes. These phonon modes have the decomposition $5A_g + 4B_{1g} + 3B_{2g} + 6B_{3g} + 4A_u + 8B_{1u} + 7B_{2u} + 5B_{3u}$. We looked for coupling between the three highest frequency IR modes and the low frequency Raman modes. The frequencies and symmetries of these modes are given in Table III. We find that $B_{1g}(18)$ mode couples to the $B_{3u}(41)$ and $B_{1u}(42)$ modes. The $A_g(11)$ mode also couples to the $B_{2u}(42)$, $B_{3u}(41)$, and $B_{1u}(42)$, but the coupling is much weaker. Therefore, we do not consider its dynamics here. The coupling strength of the $B_{1g}(18)$ mode to the $B_{3u}(41)$ and $B_{1u}(42)$ modes is the same. Since either $B_{3u}(41)$ or $B_{1u}(42)$ mode can be exclusively excited by change in polarization of the pump, we only consider the coupled dynamics of the $B_{1g}(18)$ and $B_{3u}(41)$ modes here. The coefficients of the polynomial for the energy surface of $B_{1g}(18)$ and $B_{3u}(41)$ modes are given in Table III.

As mentioned in the main text, the $B_{1g}(18)$ mode corresponds to the in-plane rotations of CuO$_6$ octahedra. Such rotations lead to a reduction of the bandwidth of the Cu-$d_{x^2-y^2}$ antibonding band, as shown in Fig. 4.

**DYNAMICAL BEHAVIOUR**

Excitation of the IR mode

The dynamics of the IR mode under the action of the pump is described by the equation of motion:

$$\ddot{Q}_{IR} + \Omega_{IR}^2 Q_{IR} = F \Phi(t) \sin \Omega t + \cdots$$(5)

in which $F$ is a measure of the pump amplitude (with dimension of a force divided by square-root of mass) and $\Phi(t)$ is a dimensionless envelope even-function of time describing the shape of the pulse. In the following a Gaussian will often be chosen $\Phi(t) = e^{-t^2/2\sigma^2}$ with the characteristic time $\sigma$ a measure of the pulse width. Note that the the time-integral of the forcing field $F\Phi(t)\sin(\Omega t)$ integrates to zero over time as required by $\int dt E(t)dt = -\int d\sigma A(t)/\Omega t = 0$. 

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The dots (\(\cdots\)) in (5) denote non-linear terms which will be neglected in the present analysis. Under this assumption, the general solution of (5) reads:

\[
Q_{IR}(t) = \frac{F}{\Omega_{IR}} \int_{-\infty}^{t} d\tau \Phi(\tau) \sin(\Omega_{IR}(t - \tau))
\]

\[
= \frac{F}{\Omega_{IR}} \sin(\Omega_{IR}t) \int_{-\infty}^{t} d\tau \Phi(\tau) \cos(\Omega_{IR}\tau) \sin(\Omega_{IR})
\]

\[
- \frac{F}{\Omega_{IR}} \cos(\Omega_{IR}t) \int_{-\infty}^{t} d\tau \Phi(\tau) \sin(\Omega_{IR}\tau) \sin(\Omega_{IR})
\]

We focus on the resonant case \(\Omega = \Omega_{IR}\) and consider the impulsive limit \(\Omega_{IR} \ll 1\). The integrals can then be extended to \(\tau = +\infty\) and the first one vanishes by parity. In the second integral, one can approximate \(\sin(\Omega_{IR}\tau) \approx \Omega_{IR}\tau\), which yields:

\[
Q_{IR}(t) = Q_{IR,max} \cos(\Omega_{IR}t)
\]

\[
Q_{IR,max} = -F\Omega_{IR} \int_{-\infty}^{+\infty} d\tau \tau^{2}\Phi(\tau) = -\sqrt{2\pi} F\Omega_{IR}\sigma^{3}
\]

**Dynamics of the Raman mode - cubic case (PMO)**

Neglecting all non-linear terms except the cubic coupling between the IR and Raman mode, the equation of motion reads:

\[
\dot{Q}_{R} + \Omega_{R}^{2}Q_{R} = \frac{1}{2}gQ_{IR}(t)^{2} + \cdots
\]

(8)

Using (7), this reads:

\[
\dot{Q}_{R} + \Omega_{R}^{2}Q_{R} = \frac{1}{2}gQ_{IR,max}^{2}(\Omega_{IR}t)
\]

(9)

\[\text{FIG. 4: LDA band structures of the orthorhombic La}_{2}\text{CuO}_{4}\] in the equilibrium structure (solid lines) and for a structure corresponding to \(Q_{B1g(18)} = 1.5\ \text{Å}\) (dashed lines).

Rewriting \(\cos^{2}\Omega_{IR}t = (1 + \cos2\Omega_{IR}t)/2\), one sees that the Raman mode undergoes a finite displacement:

\[
\delta Q_{R} = \frac{g}{4\Omega_{R}}Q_{IR,max}^{2}
\]

\[
= \frac{g}{4} F^{2} \frac{\Omega_{IR}^{2}}{\Omega_{R}} \left[ \int_{-\infty}^{+\infty} d\tau \tau^{2}\Phi(\tau) \right]^{2} = \frac{\pi}{2} \frac{Q_{IR,max}^{4}}{\Omega_{R}^{2}} gF^{2}\sigma^{6}
\]

The Raman mode oscillates at a frequency \(\Omega_{R}\) around this displaced position. This conclusion coincides qualitatively with that of Ref. \[9\], although the details of the expressions obtained here are different.

In Fig. 5 we display the result of a numerical integration of the coupled equations for the IR and Raman mode in the case of PMO, which clearly displays the displacement of the Raman mode. The second panel of this figure also demonstrates that the displacement still holds in the presence of damping (of course, in this case, the mode eventually relaxes back to its original position).

An alternative method for analysing the dynamics of the Raman mode is to construct an effective potential for this mode by time-averaging over the fast dynamics of the IR mode. This is valid because \(\Omega_{R} \ll \Omega_{IR}\), so that the dynamics of the Raman mode is much slower. This method also allows to take into account the non-linearities in the dynamics of the Raman mode. Using the time-average:

\[
Q_{IR,max}^{2}(t) = Q_{IR,max}^{2} \cos^{2}(\Omega_{IR}t) + Q_{IR,max}^{2}/2
\]

one obtains:

\[
V_{eff}(Q_{R}) = \frac{1}{2} \Omega_{R}^{2}Q_{R}^{2} + \frac{1}{3} a_{3}Q_{R}^{3} - \frac{1}{4} gQ_{IR,max}^{2} Q_{R}
\]

(11)

The displaced position \(\delta Q_{R}\) corresponds to the minimum of this potential given by \(a_{3}Q_{R}^{3} + \Omega_{R}^{2}Q_{R}^{2}Q_{R} - gQ_{IR,max}^{2}Q_{R}/4 = 0\), and thus reads:

\[
\delta Q_{R} = \frac{\Omega_{R}^{2}}{2 a_{3}} \left[ \sqrt{1 + \frac{a_{3}gQ_{IR,max}^{2}}{\Omega_{R}^{4}}} - 1 \right]
\]

\[
\approx \frac{g}{4\Omega_{R}} Q_{IR,max}^{2} - \frac{1}{16} a_{3} \frac{gQ_{IR,max}^{2}}{\Omega_{R}} + \cdots
\]

The last expression holds for \(a_{3}gQ_{IR,max}^{2}/\Omega_{R} \ll 1\), and coincides with (11) above, plus corrections from the non-linear terms. We note that the displaced position does...
not coincide with the minimum of the static potential calculated at $Q_{IR} = Q_{IR,max}$, but rather with that of the effective time-averaged potential - the resulting estimate of the displacement is smaller by a factor of two.

The oscillation frequency at the displaced position is essentially unchanged and given by:

$$\Omega_{R, eff}^2 = \frac{\partial^2 V_{eff}}{\partial Q_R^2} |_{Q_R = \delta Q_R} = \Omega_R^2 + 2a_3 \delta Q_R$$

(13)

$$= \Omega_R^2 \left[ 1 - \frac{1}{8} \left( \frac{a_3 g Q_{IR,max}^2}{\Omega_R^2} \right)^2 + \cdots \right]$$

Dynamics of the Raman mode - quartic case (LCO)

When the coupling is quartic, the equation of motion of the Raman mode reads:

$$\ddot{Q}_R + \Omega_R^2 Q_R = g Q_{IR}^2(t) Q_R - a_4 Q_R^4$$

(14)

which can be rewritten using (7):

$$\ddot{Q}_R + \Omega_R^2 Q_R \left[ 1 - \frac{g Q_{IR,max}^2}{2 \Omega_R^2} \cos^2(\Omega_{IR} t) \right] Q_R = -a_4 Q_R^4$$

Neglecting the non-linear term in the r.h.s, this equation describes a parametric oscillator with a frequency which is modulated over the fast time-scale corresponding to the period of the IR mode. In the limit where $\Omega_{IR} \gg \Omega_R$, the condition for the stability of the oscillatory motion around the undisplaced position $Q_R = 0$ can be derived from a simple physical consideration. Indeed, averaging over the fast motion of the IR mode, the effective potential for the Raman mode reads in this case:

$$V_{eff}(Q_R) = \frac{1}{2} \Omega_R^2 Q_R^2 \left[ 1 - \frac{g Q_{IR,max}^2}{2 \Omega_R^2} \right] + \frac{1}{4} a_4 Q_R^4$$

(16)

The motion becomes unstable when this effective potential acquires a negative curvature, so that to first approximation (ie neglecting corrections of order $\Omega_R/\Omega_{IR} \ll 1$, see below) the instability threshold is given by:

$$\frac{g Q_{IR,max}^2}{2 \Omega_R^2} = 1 \Rightarrow$$

$$\Rightarrow F_c = \sqrt{\frac{(\Omega_R/\Omega_{IR})}{g}} \left[ \int_{-\infty}^{+\infty} d\tau \tau^2 \Phi(\tau) \right]^{-1} = \frac{\Omega_R}{\Omega_{IR}} \frac{1}{\sqrt{\pi}} g \sigma^3$$

Restoring the non-linear term $a_4 Q_R^4/4$, the effective (time-averaged) potential develops a double well for $F > F_c$. Note that for $F \in [F_c/\sqrt{2}, F_c]$ ($g Q_{IR,max}^2/\Omega_R^2 \in [1, 2]$), the instantaneous potential seen by the parametric oscillator has negative curvature around $Q_R = 0$ (and hence a double-well shape) for part of the period. Nonetheless, the undisplaced motion is stable in this regime: this is analogous to the Kapitza-Stephenson[10, 11] stabilization of a nominally unstable motion by a fast driving force. Rewriting the equation of motion as (neglecting the non-linear term):

$$\ddot{Q}_R + \Omega_R^2 \left[ 1 - \frac{g Q_{IR,max}^2}{2 \Omega_R^2} \right] Q_R - g Q_{IR,max}^2 \cos(2\Omega_{IR} t) Q_R = 0$$

(18)

we see that the frequency of the Raman mode is renormalized for $F < F_c$ according to:

$$\Omega_{R, eff}^2 = \Omega_R \left[ 1 - \frac{g Q_{IR,max}^2}{2 \Omega_R^2} \right]^{1/2} = \Omega_R \sqrt{1 - \frac{F^2}{F_c^2}}$$

(19)

Close to threshold, the effective frequency vanishes and the actual behaviour of the amplitude depends of course on the non-linearity $a_4$ neglected above (if $a_4$ is neglected, the amplitude formally diverges at $F_c$).

A more precise determination of the critical threshold can be obtained by noting that (13) is actually a Mathieu equation, of the form:

$$\frac{d^2 y}{dv^2} + [a - 2q \cos(2v)] y = 0$$

in which we have used the standard notations of Abramowitz and Stegun[12] with:

$$y \equiv Q_R, v \equiv \Omega_{IR} t, \quad a \equiv \left( \frac{\Omega_R}{\Omega_{IR}} \right)^2 \left[ 1 - \frac{g Q_{IR,max}^2}{2 \Omega_R^2} \right], \quad q \equiv \frac{g Q_{IR,max}^2}{4 \Omega_R^2}$$

As the dimensionless control parameter $\lambda \equiv \frac{g Q_{IR,max}^2}{2 \Omega_R^2}$ is increased, $q$ also increases. The threshold is not exactly located at $\lambda = 1$ but in fact corresponds to the crossing of the separatrix associated with the first characteristic value of the Mathieu equations, given as a power-series in $q \ll 1$ by the equation:

$$a = -\frac{1}{2} q^2 + \frac{7}{128} q^4 + \cdots$$

(22)

Using the above expressions of the coefficients $a$ and $q$, this leads to the improved estimate of the threshold, including corrections of order $\Omega_R^2/\Omega_{IR}^2$:

$$\frac{g Q_{IR,max}^2}{2 \Omega_R^2} |_{c} = 1 + \frac{1}{8} \frac{\Omega_R^2}{\Omega_{IR}^2} + \cdots$$

(23)

where the dots stand for higher corrections in $\Omega_R^2/\Omega_{IR}^2 \ll 1$.

DETAILS ON ELECTRONIC STRUCTURE AND DMFT CALCULATIONS - PMO

The DFT+DMFT calculations on PMO were performed using a combination of an all-electron full-potential electronic structure method as implemented in
WIEN2k package [13, 14] and DMFT treatment for the Pr 4f and Mn 3d states as implemented in TRIQS package [15]. The DFT calculations were done within the local density approximation. We performed calculations on the experimental orthorhombic structure [16] as well as a hypothetical cubic structure with the same per formula unit volume. The band structure calculations show that both the Pr 4f and Mn 3d states lie around the Fermi level. Hence, it was necessary to treat both the Pr 4f and Mn 3d states using DMFT. We used the Hubbard-I approximation for the Pr 4f states and the numerically exact hybridization-expansion continuous time quantum Monte-Carlo [15, 17] for the Mn 3d states. The Wannier orbitals were constructed using the projection scheme of Ref. 26. We used the energy windows of [-2.0, 4] eV for the cubic structure and [-2.0, 3.4] eV for the orthorhombic structure. All seven Pr 4f and five Mn 3d orbitals lie within this window. We used $U = 6.0$ and $J = 0.7$ eV for Pr 4f orbitals and $U = 5.0$ and $J = 0.75$ eV for Mn 3d orbitals. The calculations were done at an inverse temperature of $\beta = 80$ eV$^{-1}$ ($kT \simeq 150$ K).

The LDA band structures for the orthorhombic and cubic PMO is shown in Fig. 6. It can be seen that the orthorhombic distortions reduce the band width of the whole Mn 3d manifold (by $\sim 0.7$ eV) as well as of the $e_g$ subset of bands (by $\sim 1.0$ eV) relative to that of the cubic structure. As a result of the reduced band width, the on-site Coulomb repulsion and Hund’s coupling are effective in making the distorted structure insulating. This can be seen from the opening of a gap in the orthorhombic structure in the spectral functions of the Mn 3d orbitals as obtained from our LDA+DMFT calculations that are presented in Fig. 4 of the main text. We also present in Fig. 7 the imaginary part of the Green’s functions as a function of the Matsubara frequencies for Mn 3d orbitals that were analytically continued using maximum entropy method to obtain the spectral functions on the real axis.

For the cubic PMO, the imaginary part of the Green’s function for $e_g$ orbital extrapolates to a non-zero value at $\omega_n = 0$, indicating a finite density of states at the
Fermi level. On the other hand, the imaginary part of the Green's function for all orbitals extrapolate to zero for the orthorhombic PMO, indicating an insulating state. It can also be seen that there is minimal noise in the imaginary part of the Green's functions. The spikes in the spectral function on the real axis apparent on Fig. 4 of the main text are not due to numerical noise, but to sharp excitations involving multiplets of the Pr-4f shell (treated here in the Hubbard-I approximation).

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