From Charge to Orbital Ordered Metal-Insulator Transition in Alkaline-Earth Ferrites

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While CaFeO₃ exhibits upon cooling a metal-insulator transition linked to charge ordering, SrFeO₃ and BaFeO₃ keep metallic behaviors down to very low temperatures. Moreover, alkaline-earth ferrites do not seem prone to orbital ordering in spite of the d⁴ formal occupancy of Fe⁴⁺. Here, from first-principles simulations, we show that the metal-insulator transition of CaFeO₃ is structurally triggered by oxygen rotation motions as in rare-earth nickelates. This not only further clarifies why SrFeO₃ and BaFeO₃ remain metallic but allows us to predict that an insulating charge-ordered phase can be induced in SrFeO₃ from appropriate engineering of oxygen rotation motions. Going further, we unveil the possibility to switch from the usual charge-ordered to an orbital-ordered insulating ground state under moderate tensile strain in CaFeO₃ thin films. We rationalize the competition between charge and orbital orderings, highlighting alternative possible strategies to produce such a change of ground state, also relevant to manganite and nickelate compounds.

ABO₃ perovskite oxides, with a transition metal at the B-site, form a vast class of functional materials, fascinating by the diversity of their unusual properties [1–3]. Amongst them, different families of compounds with a formal occupation of the d orbitals at the B-site, like rare-earth manganites (d⁴ = t⁴g⁴ in R₃⁺Mn³⁺O₃, with R a rare-earth element), rare-earth nickelates (d⁴ = t⁴g⁴ in R₃⁺Ni³⁺O₃), or alkaline earth ferrites (d⁴ = t⁴g⁴ in A₂⁺Fe⁴⁺O₃, with A = Ca, Sr or Ba) are similarly prone to show metal-insulator transitions (MIT). However, the mechanism behind such a transition can be intriguingly different from one family to the other.

RNiO₃ (except R=La) and RMnO₃ compounds crystallize in the same metallic Pbnm GdFeO₃-type phase at sufficiently high-temperature. This phase is compatible with their small tolerance factor and labeled (a−a−c⁺) in Glazers notation[4]. It differs from the aristotype cubic perovskite structure, only expected at very high temperature and not experimentally observed, by the coexistence of two types of atomic distortions: (i) in-phase rotation of the oxygen octahedra along z direction (Mz) and (ii) anti-phase tilts of the same oxygen octahedra with identical amplitude around x and y directions (Rx,y).

On the one hand, RNiO₃ compounds show on cooling a MIT (TMIT = 0 – 600K) concomitant with a structural transition from Pbnm to P2₁/n [5]. This lowering of symmetry arises from the appearance of a breathing distortion of the oxygen octahedra (Boc), recently assigned to a structurally triggered mechanism [6] and producing a kind of charge ordering (CO)[7–10]. On the other hand, RMnO₃ compounds also exhibit on cooling a MIT (TMIT ≈ 750K) but associated to orbital ordering (OO) and linked to the appearance of Jahn-Teller distortions (M_IT) compatible with the Pbnm symmetry [11, 12].

In comparison, AFeO₃ compounds do not behave so systemically and adopt seemingly different behaviors. While SrFeO₃ and BaFeO₃ keep the ideal cubic perovskite structure and show metallic behavior at all temperatures [13, 14], CaFeO₃, which crystallizes above room temperature in a Pbnm GdFeO₃-type phase, exhibits a behavior similar to nickelates. At 290K, a MIT takes place at the same time as its symmetry is lowered to P2₁/n due to the appearance of a breathing distortion [15, 16]. A variety of explanations have been previously proposed to elucidate the MIT in CaFeO₃, including orbital hybridization [17], electron-lattice interactions [18, 19], and ferromagnetic coupling [20]. However, no net picture has emerged yet to rationalize its behavior and that of other ferrites.

Here, we show from first-principles calculations that the CO-type MIT in bulk CaFeO₃ arises from the same microscopic mechanism as in the nickelates and must be assigned to a progressive triggering of Boc atomic distortions by Mz and Rx,y atomic motions. We demonstrate that this triggered mechanism is universal amongst the ferrite family and that an insulating phase can be induced in metallic SrFeO₃ from appropriate tuning of oxygen rotations and tilts. Going further, we reveal that CO and OO compete in AFeO₃ compounds and we unveil the possibility to switch from CO-type to OO-type MIT in CaFeO₃ thin films under appropriate strain conditions. This offers a convincing explanation for the enormous resistivity at room-temperature recently found in CaFeO₃ films grown on SrTiO₃ [21].

Methods - Our first-principles calculations relied on density functional theory (DFT) as implemented in VASP [22, 23]. We worked with the PBEsol [24] exchange-correlation functional including U and J corrections as proposed by Liechtenstein [25]. We used (U,J) = (7.2,2.0) eV, a plane-wave energy cutoff of 600 eV and Monkhorst-Pack[26] k-point samplings equivalent to 12 × 12 × 12 for a 5-atoms cubic perovskite cell. The lattice parameters and internal atomic coordinates were relaxed until atomic forces are less than 10⁻⁵ eV/Å.
phonon dispersion curves were calculated with $2 \times 2 \times 2$ supercells using finite displacement method. A special care was devoted to the determination of appropriate U and J parameters, which is discussed in detail in the Supplementary Material (SM) [35]. We found that $U$ and $J$ parameters, which is discussed in detail in [35], and the origin of its appearance in the cubic phase. Calculations are reported in Fig. 1a), reporting the evolution of the energy with respect to the breathing distortion amplitude ($Q_B$) at fixed rotation ($Q_M$) and tilts ($Q_R$) amplitudes in CaFeO$_3$ (d), SrFeO$_3$ (e), and BaFeO$_3$ (f). Opened (resp. filled) symbols denote insulating (resp. metallic) states. (g) Electronic band structure of CaFeO$_3$ along selected lines of the $Pbnm$ or $P2_1/n$ Brillouin zone (coordinates in pseudo-cubic notations) for different amplitude of distortions. All results were calculated with FM spin order and using a fixed cubic cell with the same volume as the ground state. Distortion amplitudes are normalized to those calculated by ISODISTORT [27] in the CaFeO$_3$ AFM ground state.

Bulk CaFeO$_3$ – In order to clarify the mechanism behind the $P2_1/n$ insulating ground state of CaFeO$_3$, we first focus on the phonon dispersion curves of its parent cubic phase (Fig. 1a). Calculations are reported in a ferromagnetic configuration, which is representative to unravel the essential physics. On the one hand, Fig. 1a) shows expected unstable phonon modes at M point ($M^z_2$, $\omega_M = 1811cm^{-1}$) and R point ($R^z_2, \omega_R = 1971cm^{-1}$) of the Brillouin zone, related respectively to the $M_z$ and $R_{xy}$ distortions yielding the $Pbnm$ phase. On the other hand, it attests that the $R^z_2$ mode related to the $B_{oc}$ distortion is significantly stable ($\omega^z_2 = 343cm^{-1}$), so questioning the origin of its appearance in the $P2_1/n$ phase.

The answer is provided in Fig. 1b), reporting the evolution of the energy with the amplitude of $B_{oc}$ ($Q_B$) at fixed amplitudes of $M_z$ ($Q_M$) and $R_{xy}$ ($Q_R$). It demonstrates that, although initially stable (single well – SW – with a positive curvature at the origin $\alpha_B \propto \omega^2_B > 0$) in the cubic phase, $B_{oc}$ will be progressively destabilized (double well – DW – with a renormalized negative curvature at the origin $\tilde{\alpha}_B < 0$) as $M_z$ and $R_{xy}$ develop in the $Pbnm$ phase. The curvature $\tilde{\alpha}_B$ changes linearly with $Q^2_M$ and $Q^2_R$ ($\tilde{\alpha}_B = \alpha_B + \lambda_{BM} Q^2_M + \lambda_{BR} Q^2_R$) so that its evolution must be assigned to a cooperative biquadratic coupling ($\lambda_{BM}, \lambda_{BR} < 0$) of $B_{oc}$ with $M_z$ and $R_{xy}$ as highlighted by the following terms in the Landau-type energy expansion around the cubic phase:

$$E \propto \alpha_B Q^2_B + \lambda_{BM} Q^2_M Q^2_B + \lambda_{BR} Q^2_R Q^2_B$$

For large enough amplitudes of $M_z$ and $R_{xy}$, $B_{oc}$ becomes unstable and will spontaneously appear in the structure. In Fig. 1b) we further notice that the amplitude of $B_{oc}$ required for making the system insulating decreases for increasing $M_z$ and $R_{xy}$, yielding therefore an insulating $P2_1/n$ ground state.

This behavior is point by point similar to that reported recently in rare-earth nickelates by Mercy et al. [6] who subsequently assigned the MIT to a structurally triggered phase transition, in the sense originally defined by Hulcovský [28]. In Ref. [6], the unusual cooperative coupling of $B_{oc}$ with $M_z$ and $R_{xy}$ at the origin of this triggered mechanism was moreover traced back in the electronic properties of nickelates and further related to a type of structurally triggered Peierls instability.

Fig 1g) shows that this explanation still holds for ferrites. In the cubic phase of CaFeO$_3$ (Fe$^{4+}$ with formal occupation $d^4 \equiv t^2_d e^2$), the Fermi energy, $E_F$, crosses anti-bonding Fe 3$d$ – O 2$p$ states with a dominant $e_g$ character. Activation of $B_{oc}$ can open a gap in these partly occupied $e_g$ bands at $q_B = (1/4, 1/4, 1/4)$, but around an

FIG. 1: (a-c) Phonon dispersion curves of cubic CaFeO$_3$ (a), SrFeO$_3$ (b), and BaFeO$_3$ (c) on which most relevant modes are pointed. (d-f) Evolution of the energy with respect to the breathing distortion amplitude ($Q_B$) at fixed rotation ($Q_M$) and tilts ($Q_R$) amplitudes in CaFeO$_3$ (d), SrFeO$_3$ (e), and BaFeO$_3$ (f). Opened (resp. filled) symbols denote insulating (resp. metallic) states. (g) Electronic band structure of CaFeO$_3$ along selected lines of the $Pbnm$ or $P2_1/n$ Brillouin zone (coordinates in pseudo-cubic notations) for different amplitude of distortions. All results were calculated with FM spin order and using a fixed cubic cell with the same volume as the ground state. Distortion amplitudes are normalized to those calculated by ISODISTORT [27] in the CaFeO$_3$ AFM ground state.
energy $E_B$ initially above $E_F$. The role of $R_{xy}$ and $M_z$ is to tune Fe $3d - O 2p$ hybridizations in such a way that $E_B$ is progressively lowered towards $E_F$. As they enter into the structure, activating $B_{oc}$ affects more and more substantially energy states around $E_F$ and yields an increasing gain of electronic energy explaining the progressive softening of $\omega_B$. The $e_g$ bandwidth in CaFeO$_3$ being smaller than in the nickelates, $E_B$ is initially closer to $E_F$ consistently with a softer $\omega_B$ and the smaller amplitude of $R_{xy}$ and $M_z$ required to destabilize $B_{oc}$.

**Bulk SrFeO$_3$ and BaFeO$_3$** – The triggered mechanism highlighted above further straightforwardly explains the absence of MIT in other alkaline-earth ferrites. Because of their larger tolerance factors and as confirmed from the absence of unstable mode in their phonon dispersion curves (Fig. 1b and c)) SrFeO$_3$ and BaFeO$_3$ preserve their cubic structure down to zero Kelvin[13, 14] and so do not spontaneously develop the oxygen rotation and tilts mandatory to trigger the MIT. The cooperative coupling of $B_{oc}$ with $M_z$ and $R_{xy}$ remains however a generic feature of all ferrite compounds.

As illustrated in Fig. 1c) and 1f), $B_{oc}$ is progressively destabilized when increasing artificially the amplitudes of $M_z$ and $R_{xy}$ distortions in SrFeO$_3$ and BaFeO$_3$. Since, in the cubic phase of these compounds, $\omega_B$ is originally at frequencies slightly larger than in CaFeO$_3$ ($\omega_B = 362cm^{-1}$ in SrFeO$_3$ and $\omega_B = 415cm^{-1}$ in BaFeO$_3$), larger distortions are required to induce the MIT. In SrFeO$_3$, amplitudes of $M_z$ and $R_{xy}$ corresponding to 75% of their ground-state values in CaFeO$_3$ are nevertheless enough to force an insulating ground state. In BaFeO$_3$, the cooperative coupling is less efficient and much larger amplitudes would be required.

This highlights the possibility of inducing a MIT in SrFeO$_3$ thin films or heterostructures under appropriate engineering of $R_{xy}$ and $M_z$. Moreover, it provides a vivid explanation to the decrease of $T_{MIT}$ experimentally observed in Ca$_{1-x}$Sr$_x$FeO$_3$ solid solutions as $x$ increases [29]. For increasing Sr concentrations, the average tolerance factor increases and the mean amplitudes of $M_z$ and $R_{xy}$ decrease. This analysis is supported by DFT calculation at 50/50 Ca/Sr composition using an ordered supercell (see SM [35]).

**Charge versus orbital ordering** – It remains intriguing why CaFeO$_3$ ($t_{2g}^3 e_{g}^1$) prefers to exhibit a breathing distortion ($B_{oc}$) and CO as RNiO$_3$ compounds ($t_{2g}^6 e_{g}^1$) rather than a Jahn-Teller distortion ($M_{JT}$) and OO as RMnO$_3$ compounds ($t_{2g}^5 e_{g}^1$). In Ref. [30] Whangbo et al. argue that $B_{oc}$ is favored in CaFeO$_3$ by the relatively strong covalent character of the Fe-O bond while the $M_{JT}$ distortion is preferred in LaMnO$_3$ by the weak covalent character of the Mn-O bond. So, we anticipate that weakening the covalency by increasing the Fe-O distance might favor $M_{JT}$ and OO in CaFeO$_3$. To realize practically this idea, we investigated the role of tensile epitaxial strain on the ground state of CaFeO$_3$ thin films.

**CaFeO$_3$ thin films** – The phase diagram of CaFeO$_3$ films epitaxially grown on a cubic perovskite (001)-substrate is reported Fig. 2a). The evolution of the energy with the lattice constant of the substrate is shown for FM and A-type AFM orders with either charge or orbital ordering. Although S- and T-type spiral magnetic orders (not shown here) possess a slightly lower energy at the bulk level, the FM order becomes quickly the GS under small tensile strain; C-type and G-type AFM order are much higher in energy and not shown. Both possible orientations of the orthorhombic ($a^+a^-c^+$) oxygen rotation pattern, with the long c-axis either in-plane or out-of-plane were also considered: while c-axis in-plane is favored at zero strain, c-axis out-of-plane becomes more stable under tensile strains.

Fig. 2a) demonstrates the possibility of switching from a CO to an OO ground state in CaFeO$_3$ using strain engineering: under increasing tensile strain, the ground state of the film changes from an insulating FM-CO P2$_1$/n configuration at small strain to an insulating A-type AFM-OO P$ar{4}$mm configuration above 3% tensile strain (a=3.88Å). Fig. 2b) highlights the strain evolution of $B_{oc}$ and $M_{JT}$ distortions together with the change of band gap. Under increasing tensile strain, $B_{oc}$ slightly decreases and is abruptly suppressed at the phase transition; at the same time, the band gap – already reduced in this FM phase – decreases, although much faster than $B_{oc}$ and the transition appears precisely when the bandgap converges to zero. Conversely, $M_{JT}$ is nearly zero below 3% tensile strain while it suddenly appears at the transition and then continuously increases. Amazingly, the amplitude of $M_{JT}$ (0.37 Å) in a CaFeO$_3$ film grown on a SrTiO$_3$ substrate (a = 3.905 Å) is comparable to that of bulk LaMnO$_3$ (0.36 Å). Such similar amplitude suggests that the $T_{MIT}$ associated to the OO state in strained
CaFeO$_3$ films might be much larger than the $T_{\text{MIT}}$ associated to the CO state in bulk and comparable to the one of LaMnO$_3$ ($T_{\text{MIT}} = 750$K).

Our findings provide a convincing explanation for the insulating character of CaFeO$_3$ films on SrTiO$_3$ at room temperature and for the absence of CO MIT in the 100-300K temperature range as recently pointed out in Ref.[21]. They suggest to probe the presence of OO MIT at higher temperature. A key feature, highlighted in the insert in Fig. 2a), is the jump of $c/a$ ratio at the transition boundary, which provides another concrete hint for experimentalists to probe the CO-OO transition.

**Competition between charge and orbital orders -** To rationalize the emergence of an OO ground state in CaFeO$_3$ films, we quantify the lowest-order couplings of M$_{JT}$ with other distortions in a Landau-type free energy expansion and investigate their sensitivity to magnetic order and epitaxial strain:

\[
E \propto \alpha_{JT}Q_{JT}^2 + \lambda_{MJ}Q_M^2Q_{JT}^2 + \lambda_{RJ}Q_R^2Q_{JT}^2 + \gamma Q_RQ_X Q_{JT}
\]

The first term quantifies the proper harmonic energy contribution $\Delta E_{JT}^{(1)}$ associated to the appearance of M$_{JT}$. The second and third terms in Eq. (2) account for a change of energy $\Delta E_{JT}^{(2)}$ in presence of M$_z$ and R$_{xy}$, linked to their lowest bi-quadratic coupling with M$_{JT}$. Finally, sizable anti-polar motions of the Ca cations and apical oxygens ($X_{AP}$ mode of amplitude Q$_X$, see Table I), which are driven by M$_z$ and R$_{xy}$[31], couple in a trilinear term with R$_{xy}$ and M$_{JT}$ (last term in Eq.(2)). This coupling produces an energy lowering $\Delta E_{JT}^{(3)} < 0$, through a so-called hybrid improper mechanism yielding an asymmetry in the M$_{JT}$ energy well [36]. Compendiously, appearance of a M$_{JT}$ distortion requires $\Delta E_{JT} = \Delta E_{JT}^{(1)} + \Delta E_{JT}^{(2)} + \Delta E_{JT}^{(3)} < 0$.

In bulk CaFeO$_3$, $\alpha_{JT}$ is large ($\omega_{JT}(FM) = 390$ cm$^{-1}$) in the FM cubic phase, which prohibits $\Delta E_{JT}$ to become negative for sizable amplitudes of M$_{JT}$. Switching to the A-type AFM spin order tremendously lowers $\alpha_{JT}$ ($\omega_{JT}(AFM - A) = 144$ cm$^{-1}$) but simultaneously increases the total energy by $\Delta E_{AFM - A}$. The stabilization of an OO phase with M$_{JT}$ against the CO phase with B$_{oo}$ so depends eventually on the counterbalance between $\Delta E_{AFM - A}$ and $\Delta E_{JT}$.

This is quantified for epitaxial thin films in Fig. 3 and Table I. Under negligible tensile strain (a= 3.76 Å, Fig. 3a), with A-type AFM order, $\omega_{JT}$ is even softer than in bulk CaFeO$_3$, yielding $\Delta E_{JT}^{(1)} \approx 0$. Then, similarly to what was discussed for B$_{oo}$ in bulk compounds, R$_{xy}$ and M$_z$ trigger M$_{JT}$ ($\lambda_{Mz}$, $\lambda_{Rxy} < 0$), yielding $\Delta E_{JT}^{(2)} < 0$. Finally, the hybrid improper coupling with X$_{AP}$ and R$_{xy}$ provides a further $\Delta E_{JT}^{(3)} < 0$. However, although globally negative, $\Delta E_{JT}$ cannot overcome $\Delta E_{AFM - A}$(Fig. 3c). Under large tensile strain (a= 3.91 Å, Fig. 3b) $\alpha_{JT}$ is significantly reduced by coupling with the epitaxial tetragonal strain $e_{1z}$ ($\alpha_{JT} \propto \gamma e_{1z}^2 + M_{JT}e_{1z}^2$ [32]), yielding a huge negative $\Delta E_{JT}^{(1)}$. Then, although $\lambda_{Mz}$ and $\lambda_{Rxy}$ are reduced and $\gamma$ remains unaffected (see SM
in CaFeO
a CO-type MIT in alkaline-earth ferrites, showing that, an important complementary role and tuning
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work.
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instability usually associated to OO phases[33]. Such a
strain. We have shown that the appearance of the OO-
type insulating ground state can be engineered in thin films under moderate tensile
Conclusions - We have rationalized the appearance of a CO-type MIT in alkaline-earth ferrites, showing that, in CaFeO, such a MIT arises from the triggering of \( B_{oc} \) by \( M_z \) and \( R_{xy} \) and that this mechanism can induce a CO insulating ground state in SrFeO
under appropriate tuning of \( M_z \) and \( R_{xy} \). Going further, we found that OO is also incipient to CaFeO and that an OO-type MIT can be engineered in thin films under moderate tensile
We have shown that the appearance of the OO-type insulating ground state arises from a delicate balance between different energy terms, suggesting different strategies to stabilize it. Interestingly, the emergence of the OO phase in ferrites is the result of a purely structural
energy (corner point), fingerprint of the electronic
strategies to stabilize it. Interestingly, the emergence of the OO phase in ferrites is the result of a purely structural instability and we did not find any gradient discontinuity in the energy (corner point), fingerprint of the electronic instability usually associated to OO phases[33]. Such a structural stabilization of the OO phase might offer a reasonable explanation to the emergence of an OO phase in other materials like RNiO
compounds [34][37].

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