

Local distortions and *B*-site-resolved environments in $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ solid solutions

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A series of Ruddlesden-Popper perovskite solid solutions, $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ ($0.25 \leq x \leq 0.65$), is examined by combining density functional theory (DFT) calculations with local-scale experimental studies conducted at ISOLDE-CERN over a broad temperature range (10–1220 K). Perturbed angular correlation (PAC) spectroscopy probes the $I4/mmm$ to $I4_1/acd$ structural phase transitions for all compositions between 900 and 1200 K. For $x = 0.65$, measurements below 160 K show that a second structural phase condenses, coexisting with the $I4_1/acd$ phase down to 10 K. DFT structural models reproduce a key experimental observation: in the $I4_1/acd$ phase, the c lattice parameter shows only a minor increase upon Ti substitution, whereas the ab plane expands significantly, reducing the c/a ratio linearly. This anisotropic response can be attributed to a corkscrewlike mechanism, where the enhancement of in-plane BO_6 octahedral rotations induces a contraction of the rocksalt layers, thereby mitigating the expansion of the c axis. PAC data, supported by DFT calculations, demonstrate that Ca sites apically connected to MnO_6 octahedra exhibit experimentally distinguishable Electric Field Gradients from those connected to TiO_6 octahedra.

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I. INTRODUCTION

The Ruddlesden-Popper (RP) perovskite structural phases, denoted $\text{AO}(\text{ABO}_3)_n$ or $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$, organize into a periodic stacking of n layers of the ABO_3 perovskite intercalated by an AO rocksalt layer. The breaking of the connectivity (corner sharing) of BO_6 octahedral units along the stacking axis gives rise to new types of structural phases. Distortions can then be explored for new functionalities, which could be otherwise inaccessible to the ABO_3 parent perovskite phase. Over the years, the layered nature of RPs has proven to be ubiquitous to important phenomena such as magnetoelectric coupling [1,2], superconductivity [3], and anisotropic negative thermal expansion (NTE) [4–7].

In RP perovskites, such as Ca_2MnO_4 ($I4_1/acd$) [5] and $\text{Ca}_3\text{Mn}_2\text{O}_7$ (*Acaa*) [4,8], uniaxial NTE is characterized by a contraction of the (long) c -lattice parameter with increasing temperature over wide temperature ranges. Here, where Ca and Mn are respectively occupying the A and B sites, two mechanisms have been shown to be behind the uniaxial-NTE: (i) a competition between the frozen antiphase ($a^0a^0c^-$) and

the in-phase ($a^0a^0c^+$) in-plane octahedral rotations, leading to the trapping of a soft but nonfrozen out-of-plane tilting phonon mode [4,9]; (ii) an atomic corkscrew mechanism, whereby an expansion of the ab plane induces a contraction of the c axis. The latter is mediated by the coupling between the amplitude of the octahedral rotation mode P_4 ($a^0a^0c^-$) and the thickness of the rocksalt layers, ensuring that the lengths of the four stiffest A-O and B-O bonds remain nearly constant [10,11].

Using x-ray (XRD) and neutron powder diffraction (NPD), it was possible to show in the $n = 1$ compound that, concomitant with a phase transition to the undistorted $I4/mmm$ phase above 1050 K in which the magnitude of the P_4 distortion mode is fully suppressed, a change in the thermal expansion coefficient along c from negative to positive is observed [5,12]. Combining this observation with perturbed angular correlation (PAC) spectroscopy and density functional theory (DFT) calculations, Rocha-Rodrigues *et al.* [12] confirmed the atomic corkscrew mechanism in Ca_2MnO_4 . They observed that as temperature increases toward the $I4_1/acd$ to $I4/mmm$ phase transition, the c axis exhibits its most negative coefficient of linear thermal expansion (CLTE). This was accompanied by a sharp decrease in the local asymmetry parameter, η , measured by PAC, evidencing the suppression of the P_4 antiphase rotations, which could not be measured through XRD or NPD.

Recently, Oka and Hayakawa [13] proposed a new local structure for Ca_2MnO_4 based on Mn x-ray absorption

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near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) measurements. They argue that, locally, the B cations are displaced along the apical axis in a zigzag configuration, a distortion which they proposed to be enhanced by the Ti addition to the system, i.e., in $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ ($0 \leq x \leq 0.25$) compounds. However, other structural studies [5] have consistently shown that for $x < 0.65$, the tetragonal $I4_1/acd$ phase seems to be the only stable structure at room temperature.

Ablitt *et al.* [5] have also shown that the magnitude of the uniaxial-NTE increases with x , as the low-temperature instability of the $I4_1/acd$ phase grows near the compositional stability window of the $Pbca$ phase. Particularly, the CLTE can be controlled by tuning the Goldschmidt tolerance factor [14], $\tau = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, as the system is drawn toward or out of tilting-mode instabilities, where r_α is the ionic radius of the α species [5,8]. As the Ti concentration increases, the B-site average radius also increases and, conversely, τ decreases, making the CLTE more negative, since the tilting mode becomes softer and less stable. Nevertheless, for $x \geq 0.65$ and temperatures below 165 K, the CLTE switches from negative to positive, i.e., the system shows a transition from negative to positive thermal expansion. XRD measurements [5] at 100 K revealed that $x = 0.65$ and $x = 0.7$ compositions exhibit super structure peaks, compatible with the condensation of a X_3^+ ($a^-a^-c^0$) tilting distortion combined with a X_2^+ ($a^0a^0c^+$) in-phase rotation along the c axis. The exact low-temperature phase remains undetermined; however, the orthorhombic $Pbca$ phase was suggested [5].

In this work we address the following: (i) we investigate how chemical pressure, induced by Ti substitution at the Mn site of the Ca_2MnO_4 lattice, affects the crystal structure; (ii) adopting structural models from DFT simulations, we combine electric-field-gradient (EFG) calculations with perturbed angular correlation (PAC) experiments to probe structural phase transitions at a local scale, complementing previous diffraction-based studies; and (iii) we examine how the EFG at specific nuclear sites evolves with varying Mn/Ti concentrations, showing that the EFG can distinguish among several configurations of the Mn/Ti neighbors.

II. METHODOLOGY

A. Synthesis, structure, and composition

Polycrystalline samples of $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ ($0.25 \leq x \leq 0.65$) were synthesized using the sol-gel reaction method as reported in Ref. [5] and described in the Supplemental Material (SM) [15]. The crystal structure was verified through Rietveld refinement of x-ray powder diffraction data, collected using a Rigaku SmartLab diffractometer (45 kV, 200 mA) operating with $\text{Cu K}\alpha$ in Bragg-Brentano geometry and analyzed with the GSAS-II open-source software [16] (see Fig. S1 in the SM [15]). The obtained lattice parameters are in good agreement with those reported in Ref. [5]. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) measurements were carried out to evaluate the composition of each sample (see Figs. S1–S2 and Table S1 in the SM [15]).

B. Local-scale measurements

When studying structural distortions in layered perovskite systems, conventional diffraction techniques frequently lack the sensitivity required to resolve subtle structural modulations. As a result, they can yield inconsistent or even contradictory structural interpretations [4,17–19]. Local scale techniques, which are sensitive to a small region in space around probe atoms/nuclei (local environment), can provide indirect, but compelling, evidence regarding structural nuances and electronic phenomena. This is the case of hyperfine techniques such as NMR, Mössbauer effect, and PAC spectroscopy [20,21]. These techniques aim to probe local environments through the coupling of a nuclear moment to the EFG or the magnetic hyperfine fields [20–23].

The EFG is the second derivative of the Coulomb potential at a given nuclear site and gives information on the local charge distribution. This is a second-order traceless symmetric tensor, V_{ij} , that can be diagonalized with the eigenvalues convention $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Accordingly, it is usually described by two parameters, the principal component V_{zz} and the axial asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, such that $0 \leq \eta \leq 1$. When $V_{zz} = 0$, the probes are sitting on a local environment with cubic or spherical symmetry. When $V_{zz} \neq 0$ and $\eta = 0$, the local environments present axial symmetry.

The fundamental quadrupolar frequency of the electric hyperfine interaction, from which we obtain the magnitude of the EFG main component, $|V_{zz}|$, is defined as

$$\omega_0 = \frac{\kappa e Q}{4I(2I - 1)\hbar} |V_{zz}|, \quad (1)$$

where Q is the nuclear electric quadrupole moment of the probing nuclear state, I its total angular momentum, e the electron charge, and $\kappa = 6$ ($\kappa = 3$) for half-integer (integer) I . It is worth highlighting that experiments can measure ω_0 while DFT calculations can determine V_{zz} . Therefore, the correspondence between theory and experimental results will be dependent on the Q reported in the literature. In this work we used $Q = 0.83(13)$ b [24], as used in similar works [17,18,25].

PAC measurements were carried out at ISOLDE/CERN [26]. Bulk polycrystalline pellet pieces of roughly 4 mm^3 were implanted with a 30-keV ion beam of $^{111\text{m}}\text{Cd}$, reaching a concentration in the sample of approximately 10 ppm of Cd. The samples were then annealed in air at approximately 800°C for 20 min to restore the crystal structure from the resulting lattice defects. Following cooling, the samples were mounted either in a furnace (air) or a He closed-cycle refrigerator (vacuum) at the desired temperature, surrounded by six crystal scintillator detectors coupled to photomultiplier tubes to detect the photons emitted from the $^{111\text{m}}\text{Cd} / ^{111}\text{Cd}$ decay. Each measurement required approximately 3 h of data acquisition. We used both analog and digital data acquisition setups identical to the ones presented in Refs. [27–29].

The $^{111\text{m}}\text{Cd}$ probes decay to stable ^{111}Cd through a $\gamma_1(141 \text{ keV}) - \gamma_2(245 \text{ keV})$ cascade with half-lives of 48.5 min and $\tau_n = 85 \text{ ns}$, respectively [30]. The intermediate state (before the emission of γ_2) is characterized by a nuclear quadrupole moment Q and total angular momentum $I = 5/2^+$. If the nucleus is unperturbed, the angle θ between the emission of γ_1 and γ_2 follows a well-known static and

anisotropic distribution (A_{kk}) [20] modulated by a Legendre polynomial expansion ($P_k(\cos \theta)$). However, when the ^{111}mCd nuclei are introduced into a crystal lattice, the nuclear quadrupole moment Q couples to the EFG tensor (electric quadrupole hyperfine interaction) and the angular correlation becomes perturbed (time dependent). For PAC experiments on polycrystalline samples, the angular correlation is given by [20]

$$W(\theta, t) = e^{-t/\tau_N} \sum_k A_{kk} P_k(\cos \theta) G_{kk}(t), \quad (2)$$

where $G_{kk}(t)$ is the perturbation factor, containing all time-dependent information of the angular correlation and is therefore related to the sample details. For static electric quadrupole interactions in polycrystalline samples [31],

$$G_{kk}(t) = s_{k0} + \sum_{n=1}^3 s_{kn} \cos(\omega_n t) e^{-\delta \omega_n t}, \quad (3)$$

with t being the time spent by the nucleus in the ^{111}mCd intermediate state. The damping term, δ , will be observed as a broadening in Fourier space and is used to approximate the presence of randomly distributed vacancies, defects, lattice strains, etc. [23]. The ω_n are related to the transition frequencies between the nuclear states when the intermediate one is split by the hyperfine interaction such that $\omega_3 = \omega_1 + \omega_2$. Consequently, each local environment being probed, L_α , will contribute with a triplet to the overall spectrum, $R(t)$, given by

$$R(t) = 2 \frac{W(180^\circ, t) - W(90^\circ, t)}{W(180^\circ, t) + 2W(90^\circ, t)} \approx A_{22}^{\text{eff}} \sum_{L_\alpha} f_{L_\alpha} G_{22}^{L_\alpha}(t), \quad (4)$$

where each distinct EFG contribution is weighed by a population factor, f_{L_α} , and A_{22}^{eff} is a correction to the solid angle anisotropy coefficient. The measurements were analyzed with exact numerical methods that construct the expected observable by solving the exact characteristic equation of the hyperfine interaction Hamiltonian [31] using the GFIT19 software [32–34].

The ω_n transition frequencies and s_{kn} amplitudes are related with the fundamental quadrupolar frequency ω_0 [31,35]. If $\eta = 0$, ω_0 matches the lower observable, i.e., $\omega_1 = \omega_0$, $\omega_2 = 2\omega_0$, and $\omega_3 = 3\omega_0$; on the other extreme, if $\eta = 1$, $\omega_1 = \omega_2 \approx 1.76\omega_0$ and $\omega_3 = 2\omega_1$.

C. Computational details

The first-principles calculations were performed using the QUANTUM ESPRESSO (QE) package [37,38] within the framework of DFT [39,40]. The exchange-correlation potential was treated using the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) [41]. The localized Mn-3d states were properly described by employing the DFT + U approach in the simplified rotationally invariant formulation of Dudarev *et al.* [42]. A value of $U_{\text{eff}} = 4.5$ eV was adopted, consistent with prior studies on Ca_2MnO_4 and related Mn^{4+} oxides [12]. This value of U_{eff} is known to improve the description of magnetic ordering, Mn-O bond lengths, and the local electric-field gradient. The electronic wave functions were described using the projector augmented-wave

(PAW) method [43]. Scalar-relativistic PAW pseudopotentials from the standard PSLIBRARY [44] distributed with QE were employed, with a 80-Ry kinetic-energy cutoff for the plane-wave basis and 320 Ry for the charge density. These values were verified to provide converged total energies, forces, and electric-field gradients. Integrations in the Brillouin zone for electronic states were sampled using a Γ -centered Monkhorst-Pack $4 \times 4 \times 1$ k -grid for the conventional 56-atom cell. Spin-polarized calculations were used in all simulations. Self-consistency was achieved when the total energy differences between cycles were less than 10^{-4} Ry. Structural relaxations were performed, to obtain the ground-state properties, using the damped variable-cell shape molecular dynamics method of Wentzcovitch *et al.* [45,46], allowing full optimization of both lattice vectors and internal atomic positions without imposing symmetry constraints. All ions were relaxed until the maximum residual force was lower than 0.05 eV/Å.

The computational simulations of Ca_2MnO_4 were performed using a 56-atom cell in the $I4_1/acd$ structural phase and G-type antiferromagnetic (AFM) alignment, as it has already been shown that this phase is the most favorable energetically [12], consistent with experimental findings [47]. To investigate the effect of Ti substitution in this cell, several chemical substitutions of Mn by Ti were performed to generate structural models to study the impact of Ti concentration in the $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ alloy properties, generating the compositions $x = \{0, 0.25, 0.50, 0.75\}$. This layered substitution approach provides a controlled way to introduce local chemical pressure from Ti without resorting to extremely large and disordered supercells, required to model random Mn/Ti substitutions. The layers were constructed maintaining the AFM-G ordering of the Mn atoms [47]. This procedure resulted in five distinct structural models, illustrated in Fig. 1, including two nonequivalent configurations for $x = 0.50$ to account for different relative arrangements of Mn- and Ti-rich planes. All structures were fully relaxed with variable-cell optimization. A similar procedure was adopted to a fifth model, named 75D, and explained further in the text in order to understand what would vary if the Ti substitution did not respect the layering.

In addition to 56-atom cells, supercell calculations were performed to simulate the Ca to Cd substitution for $x = 0$ concentration, since the PAC technique uses Cd probes at extremely dilute concentrations. Therefore, a $2 \times 2 \times 1$ supercell (224 atoms) was constructed from the pristine system (model-0 defined in Fig. 1), and a $2 \times 2 \times 1$ k -point mesh was used for the calculations. This procedure ensured a minimum distance of 10 Å between periodic Cd images, being enough to avoid spurious interactions between the probes. After replacing a Ca atom with Cd, two calculations were performed: (i) the atomic positions were kept fixed in those of the pristine system; (ii) a partial relaxation, without any symmetry constraints, involving the Cd atom and its neighbors within a radius of 3.7 Å. The latter approach allowed for the accommodation of the local distortion induced by the impurity. The supercells were used to evaluate the local structural response around Cd and to obtain converged EFG tensors at the impurity site. Two additional simulations were performed in the 56-atom cell of model 50-1, where the Cd atom replaced one of the Ca atoms located in the positions highlighted by

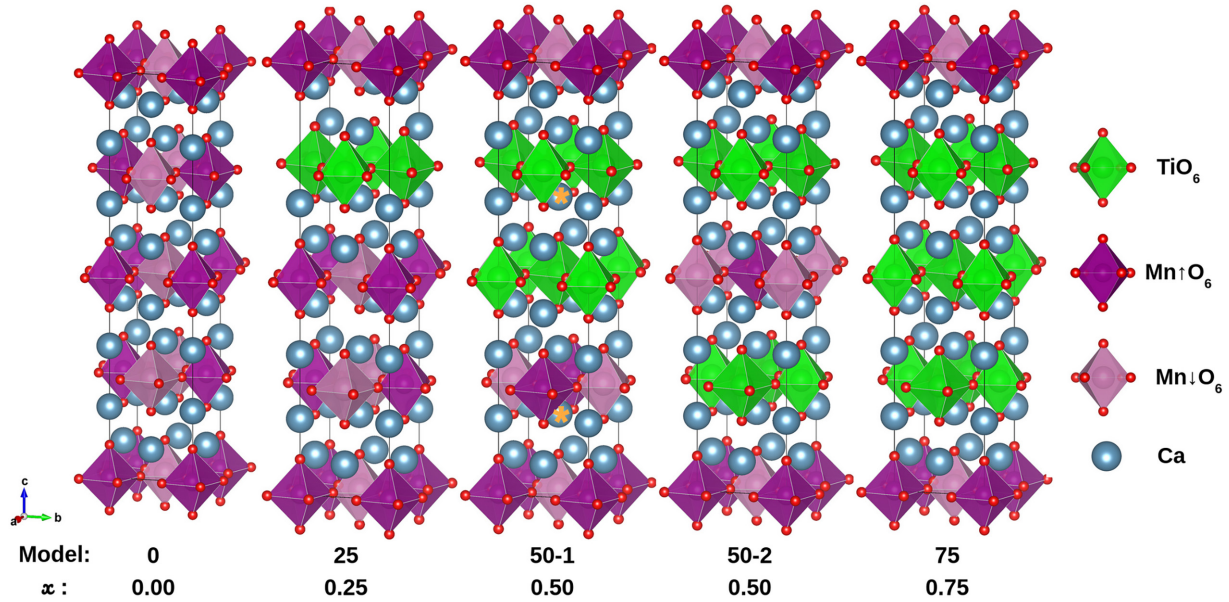


FIG. 1. Models of layered structures constructed to study the effect of Ti on the crystal structure and local environments of $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$, with $x = 0.0, 0.25, 0.50$, and 0.75 . For the $x = 0.50$, two distinct configurations are shown. Oxygen atoms are represented by red circles, and the remaining atoms and their coordination environments are shown to the right. Octahedra containing spin-up Mn ions are shaded dark purple and those with spin-down are shaded light purple, while those containing Ti ions are shaded green. The Ca atoms in model 50-1 highlighted with orange asterisks indicate the two different Ca sites where the Cd substitutional impurity was simulated in the DFT calculations. The figures were drawn using VESTA software [36].

asterisks in Fig. 1 to obtain the EFG values in both Mn-rich and Ti-rich environments.

III. RESULTS AND DISCUSSION

A. DFT calculations

1. Structural results

Within the tetragonal $I4_1/acd$ phase, when Ti is stoichiometrically added to the Ca_2MnO_4 Mn site, the lattice is expected to expand since Ti^{4+} cations have a larger ionic radius than Mn^{4+} , $0.61 \text{ \AA}$ and $0.53 \text{ \AA}$ in sixfold coordination environments, respectively [48]. Figure 2 shows the evolution of the lattice parameters and the c/a ratio with Ti concentration x obtained from DFT calculations, compared to XRD measurements at 100 and 300 K from Ref. [5]. It is worth noting that due to the use of the PBE-GGA approach for the exchange-correlation energy, the DFT lattice parameters are expected to be overestimated compared to the experimental ones. Similarly to what has been observed experimentally by other groups [5,49], the a lattice parameter linearly increases with Ti content (x) and the c lattice parameter also increases, but at a slower rate, reducing the c/a ratio linearly. While this has been previously observed and commented on in Refs. [5] and [49], its origin has not been addressed as we do in this section. A summary of the trends of the lattice parameters is presented in Table S2 of the SM [15]. Considering a simple rigid unit modes framework, the observed literature deviation from linearity for $x \geq 0.65$ at 100 K (Fig. 2) may be attributed to the condensation of the BO_6 octahedral tilts ($a^-a^-c^0$), which will reduce the c -axis length [5]. In contrast, since the relaxations in our DFT simulations preserved the distortion modes characteristic of the local symmetry of the $I4_1/acd$

space-group phase, this behavior was not observed, as the octahedral tilt pattern remained absent.

The good agreement between the experimental and theoretical trends up to $x \leq 0.65$ lead us to study the influence of chemical pressure through the addition of Ti and the natural epitaxial strain between Mn-rich and Ti-rich layers at a local scale. We examined several structural changes as a function of the Ti concentration in the DFT models from Fig. 1, such as bond lengths and rotation angles, as described in Fig. 3, and correlated them with the macroscopic picture.

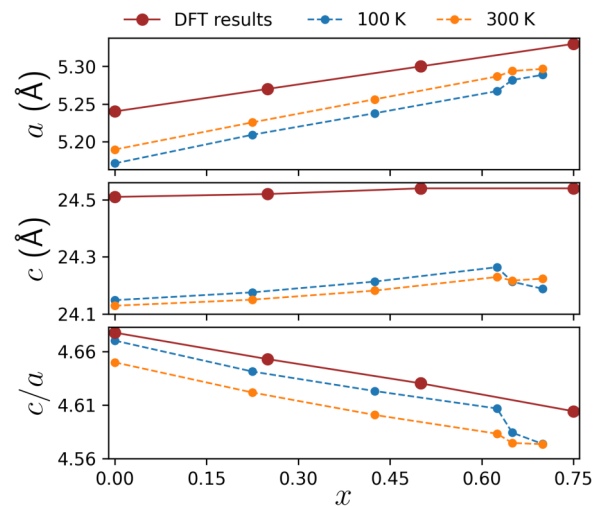


FIG. 2. Variation of the lattice parameters as a function of the Ti concentration (x): red circles are from DFT relaxed structures depicted in Fig. 1; blue and orange circles are experimental XRD values from Ref. [5], measured at 100 and 300 K, respectively.

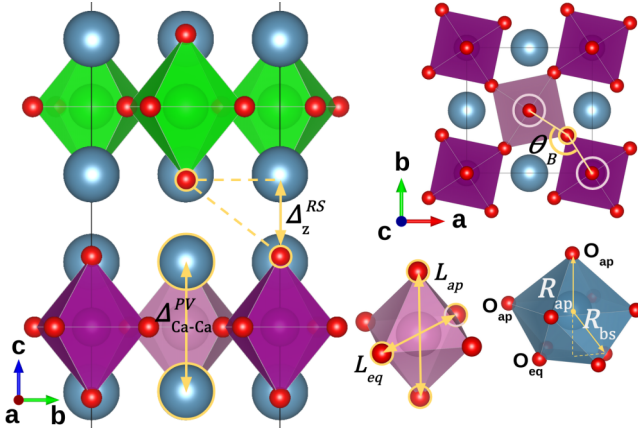


FIG. 3. DFT-obtained distances and angles on the $I4_1/acd$ phase: Δ_z^{RS} is the thickness of the rocksalt (RS) layers; Δ_{Ca-Ca}^{PV} is the distance between Ca atoms adjacent to a given BO_6 layer, $B = \text{Mn}$ (purple), Ti (green); θ_B is the angle of the B -O- B in-plane rotations of the BO_6 octahedra; L_{ap}^B and L_{eq}^B are, respectively, the apical and equatorial lengths of the octahedra. The blue polyhedron is the CaO_9 coordination environment, where R_{bs} connects the Ca atoms to the BO_6 equatorial plane, and R_{ap} connects the Ca to the apical oxygen atom belonging to the neighboring BO_6 layer.

The TiO_6 octahedra are larger than MnO_6 across both the apical ($L_{ap}^{\text{Ti}} > L_{ap}^{\text{Mn}}$) and equatorial ($L_{eq}^{\text{Ti}} > L_{eq}^{\text{Mn}}$) directions. As a consequence, so is the thickness of the TiO_6 layers with respect to the MnO_6 layers, which increases the overall c parameter. However, as x increases, both L_{ap}^{Ti} and L_{ap}^{Mn} decrease while L_{eq}^{Ti} and L_{eq}^{Mn} increase (see Table S3 and Fig. S4a in the SM [15]). A decrease in the mean rocksalt layer thickness is also observed with increasing x (Fig. S2d in the SM [15]).

In the series of studies dedicated to understand the origin of uniaxial-NTE in RP perovskites, the atomic corkscrew mechanism was proposed [5,8,9,11], where the B -O- B rotation angle (θ_B in Fig. 3, $B = \text{Mn, Ti}$) has proved to be a key parameter [12]. According to that model, as temperature increases, an expansion of the ab plane is followed by an increase of θ_B . As a consequence, the Ca atoms are pulled toward the BO_6 equatorial plane through a stiff Ca-O_{eq} bond (R_{bs} in Fig. 3), leading to a contraction of the c axis, as the Ca atom also pulls the neighboring layer through the stiff apical Ca-O_{ap} bond (R_{ap} in Fig. 3) [9,11].

In our DFT structural models, the θ_B rotation angles increase with increasing x , maintaining the $\theta_{\text{Mn}} > \theta_{\text{Ti}}$ relation (Fig. S4b [15]). Given that the CaTiO_3 perovskite is associated with a lower Goldschmidt tolerance factor than CaMnO_3 , a higher distortion (smaller θ_B) is expected for the Ti layers. The effect of θ_B variation on the Ca atomic positions (and ultimately on the c parameter) can be understood by first focusing on model-25 (Fig. 1): when the Ti-layer is introduced, Ca atoms adjacent to the MnO_6 layers become closer (decrease of Δ_{Ca-Ca}^{PV}) following an increase of θ_{Mn} . Meanwhile, the Ca atoms adjacent to the TiO_6 layer are more apart along the c direction, as the TiO_6 units occupy a larger volume and have smaller θ_{Ti} . On the other models (Fig. 1), and as the Ti concentration x increases, so do the θ_{Mn} and θ_{Ti} angles, and the individual Δ_{Ca-Ca}^{PV} distances become smaller (Fig. S4c

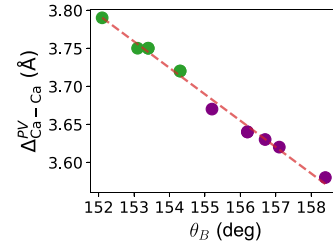


FIG. 4. Δ_{Ca-Ca}^{PV} distances (defined in Fig. 3) with respect to the rotation angle of MnO_6 (purple) and TiO_6 (green) layers. The dashed line is a guide to the eye.

in the SM [15]). This suggests a linear relation between the Ca-Ca distances and the respective rotation angles, as can be observed in Fig. 4.

Remarkably, our calculations suggest that as the Mn^{4+} cations are replaced with the larger Ti^{4+} , the operation of the corkscrew mechanism couples the expansion of the ab plane to a contraction effect in the perpendicular direction via the octahedral rotation, thereby competing with the expected expansion of the c parameter, leading to the decrease of the c/a ratio. Thus these results indicate that effects related to the corkscrew mechanism [11] can be induced not only by increasing temperature but also through chemical pressure caused by chemical substitution.

Although the models and calculations reported in this section are not expected to accurately represent real solid solutions, they nonetheless provide insight into the mechanisms underlying experimental observations, such as the pronounced decrease in the c/a ratio upon substitution of a smaller cation by a larger one, which may be extended to related materials. Ablitt *et al.* [5] show that as the larger Sr^{2+} cation replaces the smaller Ca^{2+} in $\text{Ca}_{2-z}\text{Sr}_z\text{MnO}_4$, the c/a ratio also decreases linearly with increasing z , while the $I4_1/acd$ phase is maintained at 300 K and for $z \leq 0.8$. However, when $z = 1$ the system adopts an undistorted $I4/mmm$ structural phase and the c/a is observed to increase. This suggests, based on the analyses reported here, that since the MnO_6 units are no longer allowed to rotate further due to symmetry constraints, the corkscrew mechanism is no longer active and the $\Delta_{A-A'}^{PV}$ distance ($A, A' = \text{Ca, Sr}$) is not driven to decrease.

2. Local environments

For a combined theoretical and experimental study on the local environments present in the $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ solid solutions, we have carried out Electric Field Gradient (EFG) calculations on several models to aid the experimental discussion in the next section. Our focus will lie on the EFG at the Ca sites, as $^{111\text{m}}\text{Cd}$ PAC probes usually substitute Ca sites. Upon substitution of Mn by Ti, the $I4_1/acd$ space-group symmetry is broken and four nonequivalent Ca atomic positions are created within our models. As displayed in Fig. 5(a), Ca-I sits between two MnO_6 layers and Ca-IV between two TiO_6 layers, while Ca-II and Ca-III sit between a MnO_6 and a TiO_6 layer, with Ca-II (-III) being closer to the Mn (Ti) one. Calculations and measurements of the EFG can indicate similarities between these Ca positions and show how the local environments evolve as Ti ions replace the Mn ones in

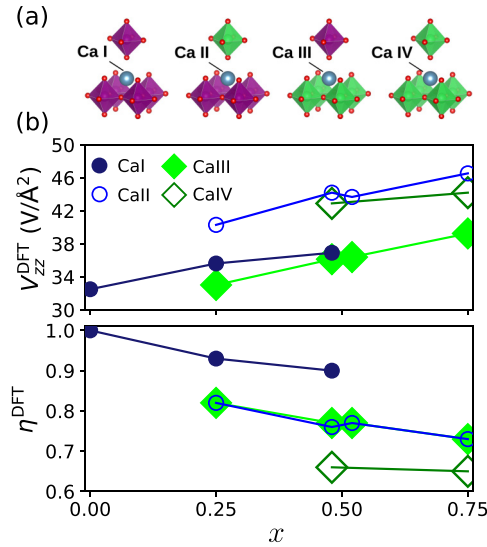


FIG. 5. (a) Distinct Ca sites with respect to the relative positions of neighboring BO_6 layers ($B=\text{Mn,Ti}$); Mn ions shaded purple and Ti ions shaded green. (b) DFT calculated hyperfine parameters $|V_{zz}|$ (top) and η (bottom) at Ca sites for the structures displayed in Fig. 1. For easy visualization, we set $x = 0.48$ and $x = 0.52$ for models 50-1 and 50-2, respectively.

the lattice. By calculating the hyperfine V_{zz} and η parameters across our models at the Ca sites [Fig. 5(b)], we can easily distinguish four distinct local environments (V_{zz} , η pairs).

The η parameter serves as a remarkably sensitive indicator of the Ca local environment. Here, it can distinguish whether a Ca atom is situated within two MnO_6 layers ($\eta \approx 0.9$), two TiO_6 layers ($\eta \approx 0.6$), or within a MnO_6 and a TiO_6 layer ($\eta \approx 0.75$). Furthermore, $|V_{zz}|$ is consistently lower when the Ca atom is apically connected to a MnO_6 octahedron than to a TiO_6 . This ability to discriminate between several Mn/Ti environments is particularly valuable, as some experiments may reveal local chemical ordering and local distortions that remain hidden in diffraction averaged models.

From the results shown in Fig. 5(b), an EFG experimental measurement in perfect conditions probing the Ca site would be expected to yield four distinct local environments. However, for the case of a PAC experiment, the line broadening (δ) defined in Eq. (3) can limit the distinction between local environments. With the benefit of hindsight, we can consider Ca-I and Ca-III to be similar to each other, characterized by a lower $|V_{zz}|$ and medium-to-high η : we name this local environment Ca-A. The Ca-II and Ca-IV sites can also be grouped and characterized by a higher $|V_{zz}|$ and medium-to-low η , which we name Ca-B. The origin for this grouping and the seemingly counterintuitive observation that, from an EFG perspective, Ca-I resembles Ca-III (Ca-II resembles Ca-IV) comes from the fact that Ca-I and Ca-III (Ca-II and Ca-IV) are connected to a Ca- O_{ap} -Mn (Ca- O_{ap} -Ti) chain along the c axis, which is collinear to the V_{zz} principal direction, and where structural variations may exert the largest changes. The percentage of Ca atoms (f) in each group (A or B) depends on the concentration of Ti, x , such that $f_{\text{Ca-A}} = 1 - x$ and $f_{\text{Ca-B}} = x$.

3. Approximation to a disordered system

To simulate a disordered system, a new model was created named 75D where, from model-75, the position of one Mn atom was swapped with one Ti atom (see Fig. S5 of the SM [15]). Afterward, a variable-cell structural relaxation was carried out, followed by EFG calculations. The total energy of the system decreased by 310 meV (5.5 meV/atom) compared to model-75. The structural and hyperfine parameters are respectively presented in Tables S3b and S4. The newly calculated V_{zz} and η parameters are close to those from model-75, with some variation possibly introduced by distinct lattice dimensions. In summary, model-75D verifies that there is a tendency for the Ca atoms apically connected to a TiO_6 octahedra to exhibit a larger $|V_{zz}|$ and smaller η than those connected to a MnO_6 , hence supporting the Ca-A/Ca-B grouping.

We notice that although the lattice parameter a and the rotation angles θ_B are both larger than in model-75, the parameter c decreases. This is because we now have two Mn-containing layers instead of just one, which reduces the rocksalt thickness while maintaining the average thickness of the octahedra (see Table S3b of the SM). The observation that the c parameter is smaller in model-75D than in model-0 highlights the complexity behind the simulation of solid solutions and the challenges to computationally compare several dopant concentrations. Despite this, model-75D is fully consistent with the systematic trends observed and analyzed in previous models, shown in Fig. 1, where the substitution of Mn by Ti in the BO_6 octahedra induces competing mechanisms that can either expand or contract the lattice parameter along the stacking direction.

Finally, we computed the density of states (DOS) and the projected DOS (PDOS) for models- 0, 50-1, and 75D, shown in Figs. S6–S8 of the SM [15]. We highlight that the DOS results are in good agreement with the ones reported in Ref. [49], where three Mn/Ti arrangements were studied for $x = 0.25$, including one similar to our model-25.

B. PAC spectroscopy results

Figure 6 shows experimental $R(t)$ perturbation functions and corresponding Fourier transforms (FTs) from 22 to 1195 K on $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$. For each PAC measurement, Fig. 7 shows the fitted fundamental quadrupole frequency [ω_0 , Eq. (1)] and the asymmetry parameter (η). More information, including population factors and δ values, can be found for all compounds in Figs. S9–S11 of the SM [15].

1. Probed site assignment

Based on previous works [12,17,18], the ^{111}mCd probes are expected to migrate to substitutional Ca sites after annealing, as Ca^{2+} and Cd^{2+} should hold similar valence charges and ionic radii in the crystal lattice [48]. Due to the symmetry-related effects that we want to probe, the first step is to assign where the ^{111}mCd probes are sitting in the crystal lattices.

The presence of two local environments is immediate from the 1195 K measurement in Fig. 6, implied by the presence of more than three FT peaks, as each local environment contributes with three frequencies [Eq. (3)]. This means that ^{111}mCd probes are being observed at two distinct sites within

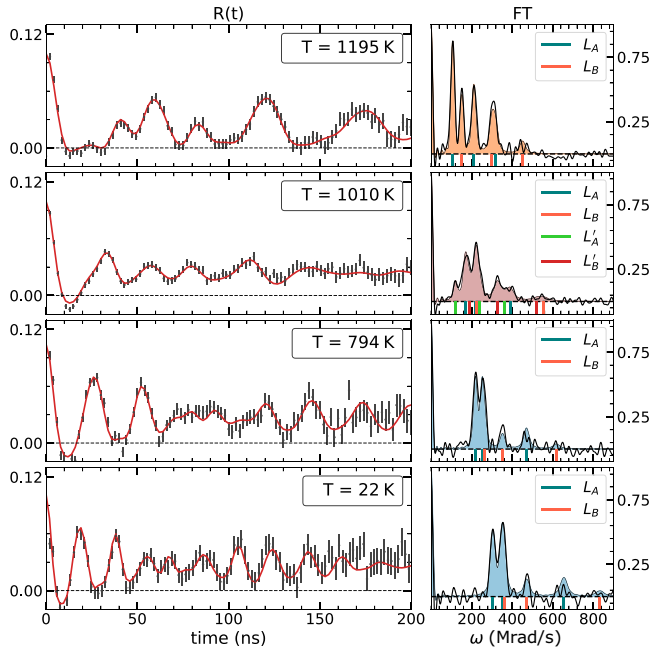


FIG. 6. Left: Experimental (black) and fitted (red) ^{111}mCd PAC spectra, $R(t)$, on $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$. Right: Corresponding Fourier transforms (FTs) of experimental (black line) and fitted (colored shading) $R(t)$. FT shadings correspond to the probing of distinct structural phases (see text). The observable frequencies due to each probed local environment (L_α) are colored accordingly at the bottom of each FT.

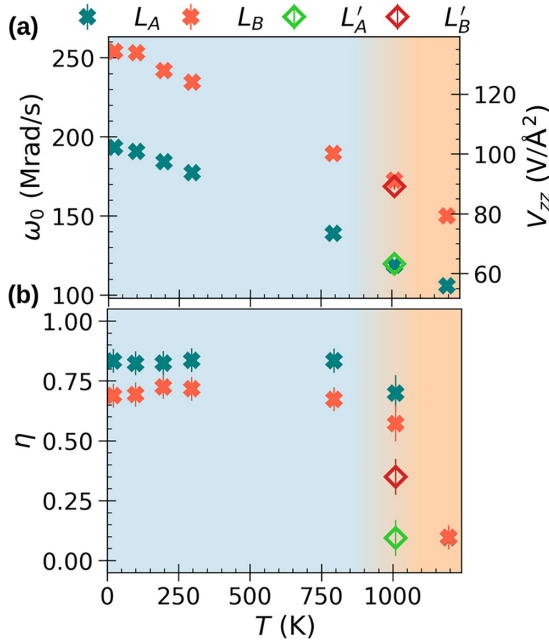


FIG. 7. Fitted (a) EFG magnitude (ω_0 and $|V_{zz}|$) and (b) asymmetry (η) parameters from Eq. (3) to PAC $R(t)$ experimental results on $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$. The blue and orange shaded regions correspond to the $I4_1/acd$ and $I4/mmm$ phases, respectively. L_A and L_B are the probed local environments, which at 1010 K coexist with L'_A and L'_B (discussed in the text).

the crystal lattice, either substitutional or interstitial. We will name L_A the local environment with the smallest observable frequencies and L_B the one with the highest. Figure 7 shows that the two local environments have very similar temperature dependencies on $\omega_0(T)$ and $\eta(T)$. The L_A and L_B populations are close to 75% and 25%, respectively, which correspond to the nominal concentrations of the Mn and Ti atoms in the $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$ solid solution. At 22 K, the set of measured hyperfine parameters, (ω_0 , η), is (190 Mrad/s, 0.84) and (255 Mrad/s, 0.70) for L_A and L_B , respectively.

The PAC measurements reported by Rocha-Rodriguez *et al.* [12] on Ca_2MnO_4 , performed under the same conditions and probe, reported a single local environment from 10 to 1129 K, where Cd occupied a substitutional Ca site (with a single Wyckoff position) corresponding to a set of hyperfine parameters (181 Mrad/s, 0.85) at 10 K. The decreasing trends of $\omega_0(T)$ and the plateau of $\eta(T)$ up to high temperatures observed in Fig. 7 are also present in the Ca_2MnO_4 system [12]. From this comparison we can deduce that L_A in $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$ is related to the single local environment observed in Ca_2MnO_4 [12]. Here we observe a slight increase of about 5% in the EFG strength ($|V_{zz}|$ or ω_0) and, remarkably, a new local environment, L_B , with very similar thermal evolutions in ω_0 and η , albeit with a distinctively higher EFG magnitude and slightly lower η . This is what we predicted by DFT in Fig. 5. PAC measurements on the remaining Ti concentrations reveal that both $|V_{zz}^{L_A}|$ and $|V_{zz}^{L_B}|$ increase with increasing x , while there is a slight overall decrease of the measured η values, as displayed in Fig. 8. Meanwhile, the population of L_B is roughly equal (within approximately 15%) to the nominal Ti concentration in the solid solution, meaning that the local environment populations can be given by $f^{L_A} \approx 1 - x$ and $f^{L_B} \approx x$. It is remarkable that L_A and L_B exhibit very similar x dependencies of $|V_{zz}|$, η , and f as those computationally determined for Ca-A and Ca-B in Sec. III A 2.

Here we have shown that our DFT models, albeit simple, are able to adequately reproduce the experimental measurements and, notably, assign a physical origin to the experimental verification of two distinct local environments: L_A probes a substitutional Cd impurity in a Ca site where a MnO_6 octahedron is apically connected to it, while L_B probes the substitution of Ca by Cd where a TiO_6 octahedron is apically connected to the probe.

2. Local probing of structural phase transitions

In Ca_2MnO_4 a second-order structural phase transition, from $I4_1/acd$ to $I4/mmm$, has been reported at approximately 1050 K [12] through a suppression of the ($a^0a^0c^-$) antiphase MnO_6 octahedral rotation amplitudes as temperature is increased [5, 12]. In $\text{Ca}_2\text{Mn}_{0.40}\text{Ti}_{0.60}\text{O}_4$, this phase transition has been observed at 1205 K with XRD [5].

From 22 to 794 K, in $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$ we observe plateaus of η^{L_A} and η^{L_B} above which the L_A and L_B go from asymmetric environments ($\eta^{L_A} \approx 0.8$ and $\eta^{L_B} \approx 0.7$) to almost fully axially symmetric ones ($\eta^{L_A} \approx \eta^{L_B} \approx 0.1$), marked in Fig. 7 by blue and orange shaded regions, respectively. This is expected, as the point symmetry for the Ca site is expected to go from 2 (at the $I4_1/acd$ phase) to $4mm$ (at the $I4/mmm$ phase). The intermediate 1010 K measurement

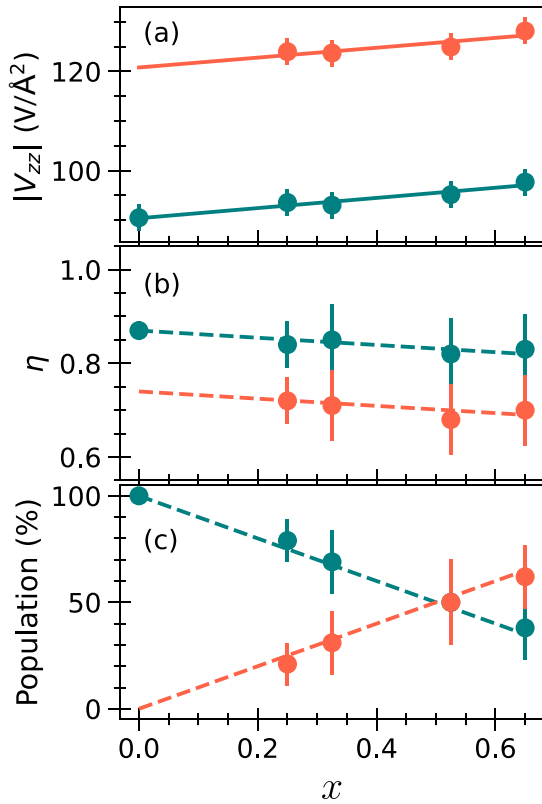


FIG. 8. $R(t)$ fit parameters on $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ with respect to x at room temperature. Green and orange colors refer to the L_A and L_B local environments, respectively. (a) EFG magnitude $|V_{zz}|$; (b) asymmetry parameter η ; (c) local environment populations, f^{L_A} and f^{L_B} . Dashed lines are guides to the eye and solid lines are linear fits (defined in Table S5 of the SM [15]).

shows a decrease of the η parameters and an increased broadening of the frequencies in Fourier space. The latter is due to a coexistence of local environments with similar ω_0 and distinct η : in Fig. 7, at 1010 K, crosses represent L_A (blue) and L_B (orange) with high η values, while diamonds represent L'_A (green) and L'_B (red) with smaller η values. This is linked to the existence of different amplitudes of BO_6 $a^0a^0c^-$ rotations in the polycrystal, as it is possible for the order parameter to change with negligible energetic costs through the transition temperature window. The same observations have been reported in Ref. [12]. Therefore we conclude that the structural phase transition $I4_1/acd$ to $I4/mmm$ is of the second order in $\text{Ca}_2\text{Mn}_{0.75}\text{Ti}_{0.25}\text{O}_4$ and occurs near 1010 K. Similar results are also observed for the remaining compositions (see Fig. S11 in the SM). This implies that $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ ($0 \leq x \leq 0.65$) polycrystalline systems undergo second-order structural phase transitions from $I4_1/acd$ to $I4/mmm$ at high temperatures.

A PAC measurement at 988 K for the $x = 0$ composition clearly evidences that the system presents the $I4_1/acd$ phase [12]. However, here, a measurement in $x = 0.325$ at 899 K already presents the coexistence of different local environments with distinct η 's, as mentioned earlier. On the other hand, a measurement in $x = 0.65$ at 1064 K shows that the system is still undergoing the transition, while for the $x = 0$ composition, at the same temperature, the system had already

reached the aristotype $I4/mmm$ phase. Similarly to what has been found in other $n = 1$ RPs, such as $\text{Ln}_{2-x}\text{A}_x\text{CuO}_4$ (with a mix of Ln^{3+} and A^{2+} cations) [50,51], the tolerance factor of the solid solution may not be the only factor controlling the phase transition temperature. In $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ the variance [50] of the B sites could also be playing a key role due to its quadratic dependence on x , explaining the initial decrease and subsequent increase of the $I4_1/acd$ to $I4/mmm$ transition temperature relative to $x = 0$.

In addition to the high-temperature phase transition, the composition with $x = 0.65$ was previously reported to undergo a low-temperature transition to a coexistence of the $I4_1/acd$ phase with an undetermined phase, although the $Pbca$ was proposed [5]. This coexistence is supported by our observations through an anomalous attenuation of the $R(t)$ spectrum and a large FT broadening below 175 K (discussed in detail in Appendix). Remarkably, our data suggest that the $I4_1/acd$ and $Pbca$ phases show a coexistence to as low as 10 K, where the $Pbca$ never becomes the dominant phase. This reinforces the hypothesis [5] that the disappearance of the uniaxial NTE below 160 K is not due to the vanishing of the $I4_1/acd$ phase (since we can still measure it at 10 K) but rather to the subtle balance between these two coexisting structures.

3. On the zigzag local configuration

In Ref. [13] a new local structure was proposed for $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ ($0 \leq x \leq 0.25$) based on the analysis of XANES Mn-K pre-edge peaks. Local apical displacements of Mn and Ti cations in a zigzag configuration were suggested, and the distortions were argued to be enhanced with increasing Ti content. Our results and those from Ref. [12], however, do not agree with this interpretation. Local-scale measurements on Ca_2MnO_4 have very small broadening and should be very sensitive to the zigzag displacements. Since they are expected to originate two distinct Ca crystallographic positions, they should show a coexistence of two local environments, even for the $x = 0$ composition. The PAC spectra have shown no signatures of symmetry-lowering distortions, even though PAC is extremely sensitive to them. In addition, neither of our DFT calculations showed a significant off-centering of the B sites from the octahedral plane, although we lifted any symmetry constraints in the simulations. Moreover, these were not observed neither in XRD nor NPD studies [5,12].

C. Combined PAC + DFT

PAC experiments are performed with Cd nuclei as probes in very dilute concentrations (around ppm) which sit at the native Ca sites. The magnitude of the EFG is enhanced at the Cd nucleus compared to a Ca nucleus due to the different core electron shells [21], as seen from the distinct magnitudes of $|V_{zz}|$ in Figs. 5 and 7.

We have carried out several Ca/Cd substitutions in the DFT simulations in order to calculate the EFG at the Cd probe. As detailed in Sec. II C, these were performed in $2 \times 2 \times 1$ supercells with 224 atoms built from model-0 in Fig. 1. We first substituted a single Ca atom by Cd and obtained the EFG values (calculation (i) in Table I). This yielded $|V_{zz}| = 70 \text{ V}/\text{\AA}^2$ and $\eta = 0.79$ at the single Cd site. As this substitution is

TABLE I. EFG parameters at a Cd probe substituting a Ca site in 224-atom supercells of Ca_2MnO_4 , without (i) and with (ii) local relaxations. Enhancement factors, $|V_{zz}^{\text{Cd}}/V_{zz}^{\text{Ca}}|$, are given relative to the EFG calculated in a Ca nucleus.

Calculation	Relaxation	$ V_{zz} $ ($\text{V}/\text{\AA}^2$)	η	$ V_{zz}^{\text{Cd}}/V_{zz}^{\text{Ca}} $
(i) Ca $\rightarrow$ Cd	No	70	0.79	2.2
(ii) Ca $\rightarrow$ Cd	Yes	88	0.98	2.8
Expt. [12]		96	0.85	

expected to disturb the Cd nearest neighbors to some extent, the atomic positions within a 3.7- $\text{\AA}$ radius were allowed to relax with no constraints and the EFG was recalculated (calculation (ii) in Table I), yielding $|V_{zz}| = 88 \text{ V}/\text{\AA}^2$ and $\eta = 0.98$. The V_{zz} and η parameters at all sites were confirmed to converge to values similar to those in the pristine cell as the distance to the Cd-site impurity increased, with $r \gtrsim 8 \text{ \AA}$ being enough to restore the original EFG environment (see Fig. S12 in the SM [15]). We verified a displacement of the Cd impurity toward the neighboring apical oxygen atom in the adjacent Mn layer of $\approx 0.07 \text{ \AA}$, while the rotation angle increased by $\approx 1.5^\circ$ in the closest neighbors. Calculation (ii) is a closer approximation to the experimental $|V_{zz}| = 96 \text{ V}/\text{\AA}^2$ and $\eta = 0.85$ measured, at 10 K, in the Ca_2MnO_4 system [12]. Relative to the EFG at Ca nuclei, these calculations in Cd nuclei reveal increases in the V_{zz} magnitude by factors of 2.2 and 2.8 for calculations (i) and (ii), respectively, as shown in Table I. These ratios are close to those already observed in similar Ruddlesden-Popper perovskites [17,18].

To investigate the local sensitivity of the EFG magnitude to Mn/Ti stacking, a Ca atom was replaced by a Cd atom in model 50-1, in the positions indicated by asterisks in Fig. 1: one simulation with a Cd between two layers of TiO_6 , and the other simulation with a Cd between two layers of MnO_6 . The former resulted in $|V_{zz}| = 83 \text{ V}/\text{\AA}^2$ and $\eta = 0.80$, while the latter in $|V_{zz}| = 75 \text{ V}/\text{\AA}^2$ and $\eta = 0.89$. These calculations aimed to simulate the behavior of the EFG at the Cd nucleus in Mn- and Ti-rich environments rather than reproducing the diluted PAC impurity conditions. In this case the shortest distance between a Cd probe and its periodic images was approximately 5.3 $\text{\AA}$.

Finally, by combining our DFT results with experimental local-scale observations, we find that the asymmetric (pyramidlike) configuration of B sites (see Fig. 9) causes the

species at the top corner of the pyramid to dominate the magnitude of the electric field gradient (EFG) interaction ($|V_{zz}|$). Meanwhile, the rotation angle of the octahedral units at the base dominate the asymmetry parameter (η) [12]. This shows that the physical contributions to the EFG can be differentiated depending on whether the top site of the pyramid is occupied by Mn or Ti. This effect may not be limited to our current case study and may be observable in other materials and solid solutions through hyperfine techniques (as PAC, NMR/NQR, and Mössbauer effect) where the local probes are surrounded by a mix of near-neighbor species in an asymmetric arrangement.

IV. CONCLUSION

This work provided a new DFT-based perspective on the structural behavior of $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ Ruddlesden-Popper (RP) perovskites as chemical pressure is exerted into the system through Ti substitution at the octahedral B sites. The DFT structural models were able to attribute a physical origin to the anisotropic expansion of the lattice upon Mn by Ti substitution. We link these findings with the atomic corkscrew mechanism that drives a uniaxial Negative Thermal Expansion behavior in Ca_2MnO_4 and related RP perovskites. Our studies suggest that chemical substitution can also activate the corkscrew mechanism, as the Ti incorporation modulates the in-plane BO_6 octahedral rotations and the associated anisotropic lattice expansion.

Supported by DFT calculations, local-scale measurements of $^{111\text{m}}\text{Cd}$ probes at Ca sites of $\text{Ca}_2\text{Mn}_{1-x}\text{Ti}_x\text{O}_4$ reveal a discretization of the EFG magnitude instead of a continuous distribution between the projected $x = 0$ and $x = 1$ end members. This results from the local nature of the Perturbed Angular Correlation (PAC) technique where the probe is sensitive only to a limited number of B-site nearest neighbors. This poses an interesting case study that may motivate further works aiming to understand how nanoscopic properties change with distinct B/B' arrangements in alloys or solid solutions.

The local PAC measurements also provide clear evidence of the second-order structural phase transitions from $I4_1/acd$ to $I4/mmm$ for all measured samples. Below 160 K, the broadening of the EFG distribution for the $x = 0.65$ composition is consistent with the coexistence of $I4_1/acd$ and $Pbca$ structural phases proposed in the literature. Remarkably, we show that this coexistence persists down to at least 10 K. This reinforces the hypothesis that the disappearance of uniaxial NTE below 160 K is not caused by the full stabilization of the $Pbca$ phase but rather by the subtle balance between these two coexisting phases.

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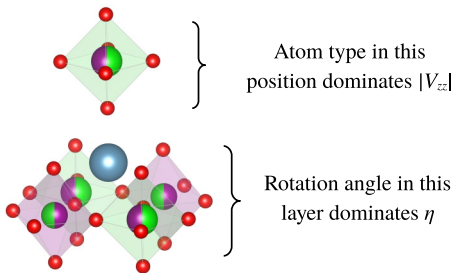


FIG. 9. Illustration of five nearest BO_6 neighbors to a Ca atom (blue sphere) at a Ruddlesden-Popper rocksalt layer. The Mn (purple) and Ti (green) mixing is represented by half-filled spheres.

2024.00223.CERN (funded by the PRR, RE-C06-i06.m02, through EMRP and FCT) [52], No. LA/P/0095/2020 [53], No. 2023.01884.BD [54], No. PRT/BD/154996/2023 [55], No. 2023.07340.CEECIND/CP2833/CT0006 [56], and No. 2022.04845.CEECIND/CP1719/CT0008 [57]. The authors also acknowledge the Federal Ministry of Research, Technology and Space (BMFTR) through Grants No. 05K22PGA and No. 05K22PGB, and by the European Union's Horizon Europe Framework Programme for Research and Innovation under Grant Agreement No. 101057511 (EURO-LABS), supporting work conducted under Proposals No. LOI 276 and No. IS738. L.V.C.A. and H.M.P. acknowledge funding from CNPq (Grants No. 314884/2021-1 and No. 308438/2022-1) and FAPESP (Project No. 2022/10095-8). M.S.S. acknowledges the Royal Society for a fellowship (UF160265 and URFR231012). The authors acknowledge the Centro Nacional de Processamento de Alto Desempenho em São Paulo (CENAPAD-SP, Brazil, proj696) for computer resources.

DATA AVAILABILITY

The data that support the findings of this article are openly available [58], embargo periods may apply.

APPENDIX: ON THE $I4_1/acd$ - $Pbca$ COEXISTENCE

Ablitt *et al.* [5] proposed that $\text{Ca}_2\text{Mn}_{0.35}\text{Ti}_{0.65}\text{O}_4$ would undergo a structural phase transition at 160 K through the condensation of a BO_6 tilting mode $a^-a^-c^0$, resembling the X_3^+ irreducible representation with respect to the arsitotype $I4/mmm$. Although they could not experimentally confirm, the $Pbca$ phase was proposed, which combines the X_3^+ ($a^-a^-c^0$) and X_2^+ ($a^0a^0c^+$) distortions. This was suggested as the uniaxial positive thermal expansion disappears for $T < 160$ K, from which PTE is observed, and by the appearance of XRD peaks indicative of the condensation of a $a^-a^-c^0$ distortion.

Figure 10 shows that as we decrease the temperature below ≈ 175 K in $\text{Ca}_2\text{Mn}_{0.35}\text{Ti}_{0.65}\text{O}_4$ there is a clear increase in frequency broadening (δ) and an anomalous increase in the population of EFGs with lower frequencies. We argue that these observations are related to the coexistence of $I4_1/acd$ and $Pbca$ phases and that they coexist down to 10 K.

To address whether a $I4_1/acd$ + $Pbca$ phase is compatible with our measurements, the expected EFG from the $Pbca$ space group was estimated based on a DFT calculation for AFM-G Ca_2MnO_4 , after a variable-cell structural relaxation. This calculation is expected to simulate only how the Mn-rich local environment (L_A) would change from the $I4_1/acd$ phase to the $Pbca$. The calculated $|V_{zz}|$ at the Ca sites went from 32 ($I4_1/acd$) to 27 V/Å² ($Pbca$), while η went from 0.99 to 0.76.

The EFG values calculated for pure Ca_2MnO_4 in $I4_1/acd$ and $Pbca$ space groups were introduced into Eqs. (3) and (4) to simulate theoretical $R(t)$ spectra to understand whether our PAC experiments have sufficient resolution to distinguish the mixing of the L_A signals of the two phases. To ensure that the theoretical and experimental spectra are comparable, we rescaled all DFT V_{zz} values by a multiplicative factor such that $V_{zz}^{\text{DFT}}(x=0)$ matches the experimental value of $V_{zz}^{\text{PAC}}(x=0)$

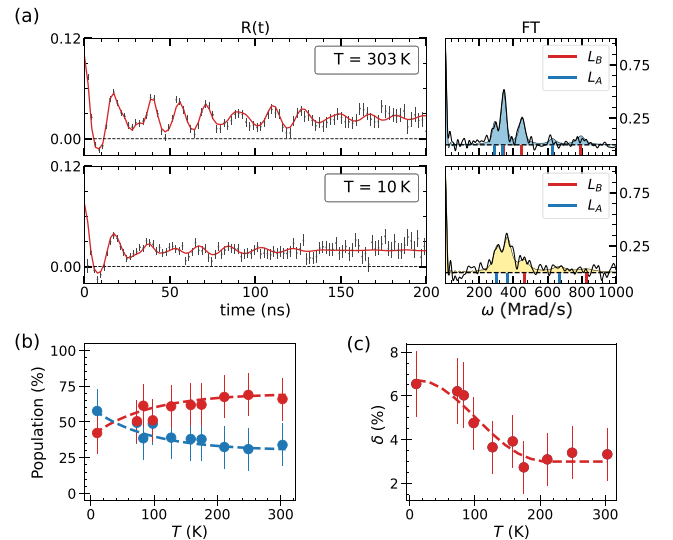


FIG. 10. (a) $R(t)$ spectra and corresponding fits measured in $\text{Ca}_2\text{Mn}_{0.35}\text{Ti}_{0.65}\text{O}_4$ at 303 and 10 K. The increased broadening is evident in the FT of the 10 K measurement. (b) Population factors, and (c) broadening coefficients, δ , for local environments L_A (blue) and L_B (red) with respect to temperature. Dashed lines are guides to the eye. We forced $\delta^{L_A} = \delta^{L_B}$ to reduce overfitting since they are correlated with the population factors.

for the $I4_1/acd$ phase measured in Ref. [12]. A line broadening of $\delta = 5\%$ was assigned to each local environment to roughly simulate the chemical disorder and lattice defects in our solid solutions. Figure 11 displays the $R(t)$ estimates and the respective FTs for several mixings of the $I4_1/acd$ and $Pbca$ phases. An inspection of the spectra reveals that small concentrations of the $Pbca$ phase (of at least 25%) would not significantly alter the experimental $R(t)$ or its respective FTs, presenting as a left shoulder to the main peak of the FT and a larger attenuation in the $R(t)$, as seen in Fig. 11. Thus, a coexistence of, e.g., 75% $I4_1/acd$ and 25% $Pbca$ may be perceived in the $R(t)$ and FT as a broader EFG contribution to the L_A signal of the $I4_1/acd$ phase, as we

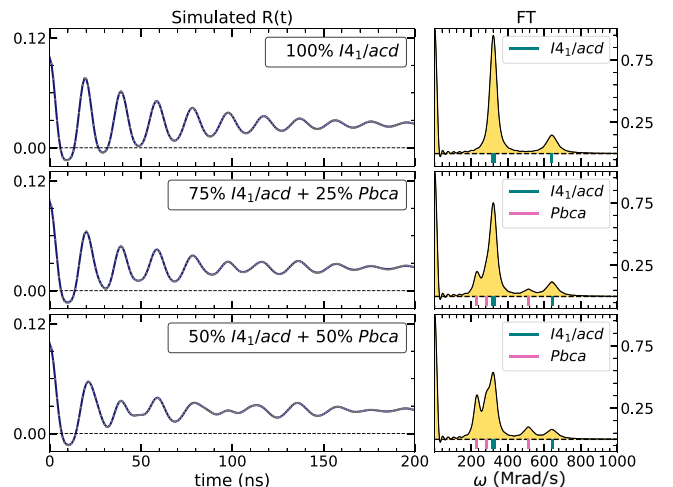


FIG. 11. Simulated $R(t)$ spectra and respective FTs for several mixings of $I4_1/acd$ and $Pbca$ phases based on the EFGs calculated by DFT on Ca_2MnO_4 respective phases.

observed experimentally, highlighting how such coexistence is unresolved but detectable in our current samples/experimental conditions.

Notice that we have not added Gaussian error deviations to the simulated $R(t)$ in order to test the physical limits of PAC in our current samples. Although the *Pbca* (or a similar) phase is only expected to condense for high Ti concentrations, these

simple calculations reveal that a phase coexistence may be difficult to distinguish in a PAC experiment in solid solutions, as the $(\omega_1, \omega_2, \omega_3)$ triplet [defined in Eq. (3)] from L_A of the $I4_1/acd$ phase may overlap substantially with that of the *Pbca* phase. This limitation is intensified when working with solid solutions, as it will result in larger $R(t)$ attenuations (and FT broadenings).

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