Manuscript Title: Geometric frustration of Jahn-Teller order in the infinite-layer lattice

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

Authors claimed in their manuscript the creation of a novel low-dimensional phase via topochemical reaction, observation of site-specific 2D Jahn-Teller effect (JTE) and JTE-driven cation displacement, and associated molecular structures in the complex oxides, represented as ordered dipole arrangement (two-in/two-out arrangement). The work is a challenging task, since it is typically difficult to fully characterize such complex structure. However, they successfully tackled this issue with right analytical tools: STEM/EELS, synchrotron XRD and refinement, and computation. (Still, quantitative analysis of oxygen position is puzzling.) However, the following points are certainly addressed and/or proved for further consideration: experimental evidence of Jahn-Teller mode (i.e. any properties due to Jahn-Teller effect and/or geometric frustration) and O K-edge spectra and analysis as to see TM-O hybridization.

Referee #2 (Remarks to the Author):

1 Summary of the key results
The authors present a new infinite-layer structured material, $CaCoO_2$, and show a complex displacement pattern that they attribute to Jahn-Teller (JT) distortions and local degeneracy of the Co 3d orbitals. The structure is characterized using a combination of aberration corrected scanning transmission electron microscopy (STEM) and X-ray diffraction (XRD). Density-functional-theory (DFT) is then used to provide understanding of the complex microstructure with relation to the complex electronic structure. The authors results suggest that the oxide results in cooperative JT distortions, local degeneracy of orbitals ordering at Co atoms, and increased hybridization in CoO_2 planes giving rise to two-dimensional JT lattice.

2 Originality and significance
The manuscripts experiments are impressive and is a relevant scientific topic in functional materials. Materials with square-planar coordination and Jahn-Teller distortions are rare, but they do exist, and this is not the first time.[1] The square-planar geometry is therefore not what makes this manuscript unique. Orbital ordering in layered materials with 2D Jahn-Teller or pseudo-Jahn-Teller distortions is not uncommon.[2-6] That being said, and as mentioned by the authors, the transition metals are typically coordinated with more than four anions. The orbital ordering, 2D Jahn-Teller effect, and complex displacement structure are not in themselves unique or a new significant finding. As to my knowledge, the combined Jahn-Teller and Ca cation frustration mechanism is unique. If this the Ca

cation frustration is what makes the article unique then the authors should emphasize this impact more and dig deeper into the bonding of Ca atoms. That being said, I think this is a high-quality manuscript with information and ideas that are worthy for publication. The findings of planar JT distortions and Ca layer frustration in a functional oxide have the potential to lead to many works by other researchers. Clarification should be made, and portions of the manuscript refocused to what is the new impact. Additional experiments could also dramatically strengthen the manuscript.

Additionally, the manuscript would be stronger if clearly made applicable to a broader audience. It is predominantly of interest to the Material science community, but it could also be broadly of interest to physics and chemistry.

1. Wurzenberger, Xaver, Holger Piotrowski, and Peter Klüfers. "A Stable Molecular Entity Derived from Rare Iron(II) Minerals: The Square-Planar High-Spin-D6 FeIIO4 Chromophore." Angewandte Chemie International Edition 50, no. 21 (May 16, 2011): 4974–78. https://doi.org/10.1002/anie.201006898.
2. Halcrow, Malcolm A. "Jahn–Teller Distortions in Transition Metal Compounds, and Their Importance in Functional Molecular and Inorganic Materials." Chem. Soc. Rev. 42, no. 4 (2013): 1784–95. https://doi.org/10.1039/C2CS35253B.
3. Aguado, F, F Rodríguez, R Valiente, A Señas, and I Goncharenko. "Three-Dimensional Magnetic Ordering in the Rb2CuCl4 Layer Perovskite—Structural Correlations." Journal of Physics: Condensed Matter 16, no. 12 (March 31, 2004): 1927–38. https://doi.org/10.1088/0953-8984/16/12/003.
4. Kokoszka, G. F., J. Baranowski, C. Goldstein, J. Orsini, A. D. Mighell, V. L. Himes, and A. R. Siedle. "Two-Dimensional Dynamical Jahn-Teller Effects in a Mixed-Valence Benzotriazolato Copper Cluster, Cu5(BTA)6(RNC)4." Journal of the American Chemical Society 105, no. 17 (August 1983): 5627–33. https://doi.org/10.1021/ja00355a017.
5. Hidaka, M., K. Inoue, I. Yamada, and P.J. Walker. "X-Ray Diffraction Study of the Crystal Structures of K2CuF4 and K2CuxZn1-xF4." Physica B+C 121, no. 3 (August 1983): 343–50. https://doi.org/10.1016/0378-4363(83)90067-0.
6. Cammarata, Antonio, and James M. Rondinelli. "Ferroelectricity from Coupled Cooperative Jahn-Teller Distortions and Octahedral Rotations in Ordered Ruddlesden-Popper Manganates." Physical Review B 92, no. 1 (July 2, 2015): 014102. https://doi.org/10.1103/PhysRevB.92.014102.

3 Data & methodology: validity of approach, quality of data, quality of presentation
The figures and figure panels are well organized and visually appealing.

The HAADF imaging are good quality images, especially for a beam sensitive material. The relation between STEM, XRD, and theory is well constructed. I very much like the style of using local, global, and theoretical experiments to understand the physics occurring in the material.

I only have one major concern regarding the HAADF-STEM comparison in Figure 2(f) with the structural model Figure 2(h). The issue could merely be the way the schematic is drawn. Specifically, the projection from the 001 to 100 zone axis. I am looking at Figure 2(h) and agree that there are displacements. However, it does not appear that the projections in (h) are self-consistent. h-001 shows the splitting of single Co columns to two Co projected positions along [100]. The 001 projection shows that every atom on the top half should mirror to the atoms on the bottom half. h-

100 shows a splitting from one to three positions. This is further emphasized by the four-fold rotational symmetry of the space group. Should there not be two columns instead of three? I have created a structure file from the data presented in Extended Data Table 4. What I have mentioned above, Co split to two columns, is indeed the correct projection and the analysis is therefore not self-consistent.

Panel (f) does not have sufficient resolution or signal-to-noise to definitively resolve individual atoms in the cation column splitting, so two overlapping columns would look similar to three. Panel g looks believable.

Figure 2(d) is only used to explain the sample before reduction and does not provide any content to the story. It would be better suited as an extended figure or supporting information. In its place I would recommend adding a plane view HAADF image here so that you have a comparison for all three projections. You can then use Figure 3 to concentrate on GIXRD and refinement of the oxygen positions. Figure 3(d) is also a near repeat of figure 2(h).

The contrast of the images and signal-to-noise is not adequate to identify the oxygen columns in Figure 3. In Figure 3h, there are not dark columns where some of the annotated oxygen atoms are and some of the places where there are dark oxygen columns the annotations do not agree. For instance, the two oxygen columns in the top left corner of Figure 3h. The left one does not match with the dark position underneath the annotation. The top one does not have a dark column of atoms under the annotation. Figure 3g and h are not sufficient quality to make the claim that the ABF-STEM images agree with the XRD refinement. Better quality ABF imaging, integrated differential phase contrast, or related technique should be performed.

Although the use of DFT to explain the orbital degeneracy and displacement structure works, I feel that the authors have methods available to them to experimentally understand the orbital ordering. Extended Data Fig. 3 presents electron energy-loss near edge fine structure (ELNES) analysis to confirm the valance state of Co. This data could equally be used to map the crystal field spitting with atomic to near atomic resolution. Such experiments should be feasible with the microscopes available to the authors and would provide a more direct comparison between experiments, theory, and the overall conclusions.

In Figure 2(h), the atom legend does not match the image, specifically the Co.

4 Appropriate use of statistics and treatment of uncertainties
The use of statistics and uncertainties is used where appropriate.

5 Conclusions: robustness, validity, reliability
The data and conclusions drawn from the data are reliable. Except for the structure inconsistencies mentioned in Figure 2, which is a vital component of the paper and could use clarification. It would also be more reliable to measure hybridization or electronic structure using experiments rather than simply stating hybridization must be included in the electronic structure calculations for structural agreement between theory and experiments.

6 Suggested improvements: experiments, data for possible revision

As suggest above, better light element STEM imaging in recommended and necessary for the quality expected of a <i>Nature</i> publication.

1. Eric R. Hoglund, De-Liang Bao, Andrew O'Hara, Sara Makarem, Zachary T. Piontkowski, Joseph R. Matson, Ajay K. Yadav, et al. "Emergent Interface Vibrational Structure of Oxide Superlattices." Nature 601, no. 7894 (January 27, 2022): 556–61. https://doi.org/10.1038/s41586-021-04238-z.

2. Yücelen, Emrah, Ivan Lazić, and Eric G. T. Bosch. "Phase Contrast Scanning Transmission Electron Microscopy Imaging of Light and Heavy Atoms at the Limit of Contrast and Resolution." Scientific Reports 8, no. 1 (December 2018): 2676. https://doi.org/10.1038/s41598-018-20377-2.

3. Lazić, Ivan, Eric G.T. Bosch, and Sorin Lazar. "Phase Contrast STEM for Thin Samples: Integrated Differential Phase Contrast." Ultramicroscopy 160 (January 2016): 265–80. https://doi.org/10.1016/j.ultramic.2015.10.011.

4. Ohtsuka, Masahiro, Takashi Yamazaki, Yasutoshi Kotaka, Iwao Hashimoto, and Kazuto Watanabe. "Imaging of Light and Heavy Atomic Columns by Spherical Aberration Corrected Middle-Angle Bright-Field STEM." Ultramicroscopy 120 (September 2012): 48–55. https://doi.org/10.1016/j.ultramic.2012.06.006.

5. Findlay, S.D., Y. Kohno, L.A. Cardamone, Y. Ikuhara, and N. Shibata. "Enhanced Light Element Imaging in Atomic Resolution Scanning Transmission Electron Microscopy." Ultramicroscopy 136 (January 2014): 31–41. https://doi.org/10.1016/j.ultramic.2013.07.019.

6. Huang, Rong, and Yuichi Ikuhara. "STEM Characterization for Lithium-Ion Battery Cathode Materials." Current Opinion in Solid State and Materials Science 16, no. 1 (February 2012): 31–38. https://doi.org/10.1016/j.cossms.2011.08.002.

I would suggest considering more ELNES analysis. The authors have suggested that spatially varying crystal field splitting, correlations effects, and Ca bonding are responsible for the highly distorted structure. They have the capabilities to understand the spatial changes in electronic structure using microscopes at their disposal. These suggested experiments would also help alleviate the differences between the STEM-HAADF – DFT structure and XRD electron density – DFT electron density differences. Rather than saying increased hybridization brings DFT predictions closer to the experimental predictions, the authors can through experiments show that hybridization is key and corroborate with DFT.

Likewise, it would be nice to see O-K edge data in either the main text or extend figures. The O-K edge is often equally or more telling as the metal L23 edges and are worth investigating to inform more about local bonding in the material.

Two key references are listed below, but there are many others out there.

1. Stoyanov, E., F. Langenhorst, and G. Steinle-Neumann. "The Effect of Valence State and Site Geometry on Ti L3,2 and O K Electron Energy-Loss Spectra of TixOy Phases." American Mineralogist 92, no. 4 (April 1, 2007): 577–86. https://doi.org/10.2138/am.2007.2344.

2. Varela, M., M. P. Oxley, W. Luo, J. Tao, M. Watanabe, A. R. Lupini, S. T. Pantelides, and S. J. Pennycook. "Atomic-Resolution Imaging of Oxidation States in Manganites." Physical Review B 79, no. 8 (February 23, 2009): 085117. https://doi.org/10.1103/PhysRevB.79.085117.

7 References: appropriate credit to previous work?
The manuscript appropriately references prior works in most places.
The authors reference a review that well summarizes oxide systems with octahedral and tetrahedral coordination, ref 5-6. It would be worth including references of other systems with orbital ordering

of square planar JTE, then explain what makes this system unique or how this manuscript adds additional and significant understanding of the prior works.

8 Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

The paper as a whole is well written. The statement "As we will demonstrate, the collective response is considerably richer." in the introduction might be meant to bait the audience to read more, however it would be a better use of space to emphasize what makes this system "richer" and unique.

On page 4 in the second paragraph, "square plane" should be "square planar"

9 Final remarks

Just to emphasize, I do very much like this work and feel it should publish with changes. They have logical progression of the story and the story itself is exciting from a very fundamental and moderately broad perspective. The story just needs a few "guess and check" or "black box connections" fixed and the manuscript should be made self-consistent. The manuscript could easily go from a good manuscript to exceptional manuscript with a few more experiments. The story is predominantly of interest to the Material science community, but it could also be broadly of interest to physics and chemistry. This work is worthy of publication in a high impact journal, but I will leave the <i>Nature</i> worthiness decision to the Editor.

Referee #3 (Remarks to the Author):

Following their observation of superconductivity in infinite-layer rare-earth nickelate, authors use a similar strategy in order to stabilize an infinite-layer CaCoO2 . Within this new phase, authors expect to achieve an unprecedented Jahn-Teller effect and subsequent orbital orders in infinite-layer transition metal oxides. This would be a breakthrough as JTE and JTD are at the core of several properties and applications.

The manuscript is well written, well presented and largely accessible for non-specialist. Nevertheless, the main motivation (getting a JTE) is finally not really reached at the end of the study, and the material prefers to adopt a different distorted structure following ice rules. Furthermore, even though authors explain that there is a competition between ice rules and JTE, there is no evidence of the existence of a JTE and JTD (see below). Thus, at the moment, I am not convinced that the manuscript warrants publication in Nature as its impact, beyond stabilizing the CaCoO2 phase, appears more limited.

I explain below the different points:
1) Having a Jahn-Teller active ion in terms of electronic configuration is not a guarantee of having a JTE. It is a prerequisite but one also needs compact bands with limited hybridization between transition metal d and O p states. If the electronic structure is too hybridized, the Jahn-Teller force

can be too weak and annihilate the JTE (Phys. Rev. B 21, 5662 (1980), Phys. Rev. Res. 1, 033131 (2019)). In the present case, authors identify a hybridized Co d – O p state with the creation of a ligand hole. I suspect that it could prevent a JTE and promote the observed structural distortions.

2) Looking at Co-O bond lengths is not necessarily a good indicator of a JTE as the coupling of several distortion can produce a virtual "JTE" (see Phys. Rev. B 101 214304 (2020), Nat. Comm. 10, 1658 (2019)). An appropriate manner to extract this propensity is to perform a symmetry mode analysis that identifies which eigen displacement of the high symmetry undistorted cell contributes to the global lattice distortion (each eigen displacement of the undistorted cell defines a precise lattice distortion, see amplimodes software for instance, https://www.cryst.ehu.es/cryst/amplimodes.html).

Assuming a ($\sqrt{2}$,$\sqrt{2}$,1) primitive P4/mmm supercell with only the oxygen motion of the Q2 mode as sketched in Figure 1.e, one would get a P4/mbm cell with a M3+ lattice distortion corresponding to expectation for a Q2 JTE in CaCoO2. Repeating the analysis but with the atomic coordinates reported in extended Table 4, we end up with a structure in which the M3+ amplitude is exactly zero from a symmetry mode analysis point of view. It means that there is no Q2 JTD (and so no JTE) in the material. Thus, what is stabilized in the compound is not associated with a Jahn-Teller effect.

3) Aiming at identifying the propensity of the material to show the JTE and subsequent JTD, I suggest to try to extract from first-principles DFT simulations the ability of the compound to stabilize the Q2 distortion alone. If it is more stable than the initial undistorted P4/mmm cell, it suggests that Co2+ cations are willing to undergo a JTE. Then of course, competition between "ice rules" and JTD can stabilize some distortions over the others.

4) I am also puzzled by the relaxed DFT structure that is quite far from the experimental one with less distortion. Have the authors pushed a bit the solver toward different solutions ? If authors started from the high symmetry cell with no distortion as it seems to be, there is 99% chance that the solver has been trapped in false local minimum. At least, different starting points have to be tested in order to be sure to converge to the structure minimizing the total energy.

5) In terms of JTE and JTD, orbital and spin orders are strongly entangled, a fact explained by the Kugel-Khomskii rules (Zh. Eksp. Teor. Fiz. 64, 1429 (1973). Sov. Phys. Usp. 25, 231 (1982)). What is the magnetic order used in the simulations ? Can it affect the global explanation ?

6) Do the authors have an explanation for the large difference of band gaps between DFT and experiments ? Usually, DFT gaps are underestimated with respect to experiment, which is not the case here. Are lower U values giving a similar trend ?

7) I have also another minor comment: the data provided in extended table 3 yields a non-stoichiometric cell with 8 Ca, 12 Co and 16 O ions. There might be a typo on some atomic coordinates.

Author Rebuttals to Initial Comments:

We greatly appreciate the referees for their careful readings, positive appraisal of the work, and very constructive comments. We address these comments below and made appropriate changes in our revised manuscripts. In the following, we attach each referee's comments (in blue color) and our responses (in black color), and we also indicate the associated changes in the revised manuscript in red color.

Referee #1 (Remarks to the Author):

Authors claimed in their manuscript the creation of a novel low-dimensional phase via topochemical reaction, observation of site-specific 2D Jahn-Teller effect (JTE) and JTE-driven cation displacement, and associated molecular structures in the complex oxides, represented as ordered dipole arrangement (two-in/two-out arrangement). The work is a challenging task, since it is typically difficult to fully characterize such complex structure. However, they successfully tackled this issue with right analytical tools: STEM/EELS, synchrotron XRD and refinement, and computation. (Still, quantitative analysis of oxygen position is puzzling.) However, the following points are certainly addressed and/or proved for further consideration: experimental evidence of Jahn-Teller mode (i.e. any properties due to Jahn-Teller effect and/or geometric frustration) and O K-edge spectra and analysis as to see TM-O hybridization.

We thank the referee for their strong appraisal of our work and providing suggestions to improve our paper. Following the referee's suggestion, we performed spatially averaged O K-edge EELS measurement to better understand the orbital hybridized states in $CaCoO_2$. [Please see also response to Referee #2 regarding technical aspects of EELS measurements for this system.] As shown in Fig. R1, we observed three characteristic peaks within 15 eV above the edge onset at 525 eV. The first peak with the lowest energy loss is assigned to O $2p$ character in the transition metal $3d$ band. The other two peaks above are assigned to O $2p$ character in the metal $4s$ and $4p$ bands, respectively [F. M. F. de Groot *et al*. *Phys. Rev. B* **40**, 5715 (1989)]. Note that the EELS spectra were taken across the cross-section of $CaCoO_2$ and therefore we can exclude the contribution of O-K edge spectra from the $SrTiO_3$ substrate. From the O K-edge EELS spectra we observed an O K-edge pre-peak at ~ 530 eV (the peak *a* in Fig. R1), which is in good agreement with the hybridization pre-peak observed for $SrCoO_{3-\delta}$ which has a negative charge transferred state [ref.[49] in the revised manuscript]. The reduced intensity compared with this previous work is reasonable: considering that large hybridization is occurring on the $Co_{(1)}O_4$ plaquettes (strongly-JT-distorted sites), the low pre-peak intensity reflects the partial (25%) fraction of $Co_{(1)}O_4$ among the total CoO_4 plaquettes in the distorted $CaCoO_2$ unit cell. We added this discussion on page 10 (lines 13-15) in the revised manuscript. We also added Fig. R1 as Extended Data Fig. 5 in the revised manuscript.
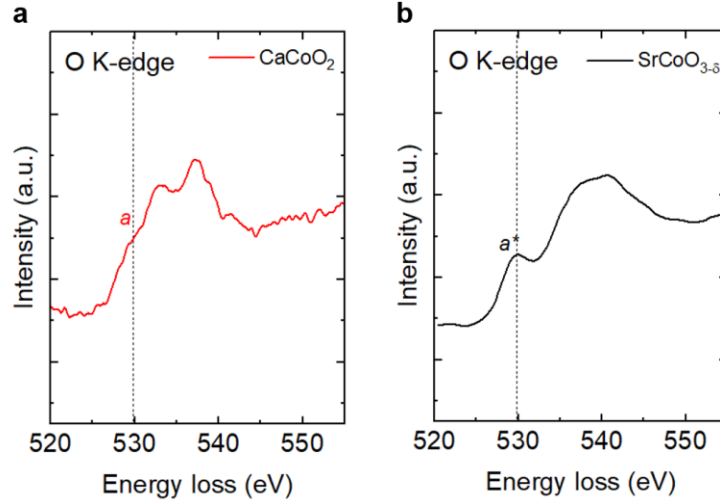
Fig. R1. O K-edges EELS spectra for CaCoO$_2$. a, Spatially averaged O K-edge EELS spectrum measured for the CaCoO$_2$ film. **b,** O K-edge EELS spectrum for SrCoO$_{3-\delta}$ taken from [ref.[49] in revised manuscript]. The peaks a (and a*) are attributed to O 2p – Co 3d hybridization.

As we discussed in the manuscript, unlike octahedrally coordinated d^4 systems, the Q$_2$-JT-distortion not only splits the $d_{xz/yz}$ orbitals but also draws the ligands along one direction inward, toward Co$_{(1)}$. This substantially increases the hybridization of the σ-bonded Co$_{(1)}$-O orbitals (Fig. 4a in the revised manuscript), encouraging a strong admixture of holes on the neighboring oxygen. Although the interpretation is complicated by the three distinct oxygen sites, the spatially averaged O K-edge EELS supports the existence of hybridized state and reflect the unusual electronic properties due to the JTE.

From the symmetry mode analysis (please see the response to referee #3 comment (2)), we found that there exists a Q$_2$-JT mode (or normal mode) in the distorted CaCoO$_2$ structure. Raman spectroscopy is one of the ways to observe this normal mode which we have attempted; however, due to large background signal from the SrTiO$_3$ substrate, we could not experimentally distinguish the Raman spectrum of CaCoO$_2$ thin film from the SrTiO$_3$ substrate. Although unsuccessful, we have added a coauthor Daniel Jost due to his significant efforts for Raman measurements, and contributions in interpreting the EELS data. We further note that the highly-distorted superstructure we observe, unique among the many materials in the infinite-layer structure, is a consequence of the geometric frustration of the JTE and Ca-cation displacements.

Finally, we have performed additional experiments and refinements on the oxygen positions (see response to Referee #2). We have thus added more details on the GIXRD refinement and ABF-STEM of the oxygen positions in the Methods section on page 14 (lines 4-18).

Referee #2 (Remarks to the Author):

1 Summary of the key results

The authors present a new infinite-layer structured material, CaCoO2, and show a complex displacement pattern that they attribute to Jahn-Teller (JT) distortions and local degeneracy of the Co 3d orbitals. The structure is characterized using a combination of aberration corrected scanning transmission electron microscopy (STEM) and X-ray diffraction (XRD). Density-functional-theory (DFT) is then used to provide understanding of the complex microstructure with relation to the complex electronic structure. The authors results suggest that the oxide results in cooperative JT distortions, local degeneracy of orbitals ordering at Co atoms, and increased hybridization in CoO2 planes giving rise to two-dimensional JT lattice.

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We thank the referee for their positive evaluation, extended references and discussion regarding the JTE in square planar geometry. Overall, we agree with the assessment and summary of the referee regarding the novelty here. To refine our presentation (and to enhance the appeal to chemistry and physics communities) we have make the following revisions:

- We have added a reference to Ref. #1 above, describing it as a nearly square planar molecular system. [Note that the molecule starts with tetrahedral coordination, making the d^6 high spin state JT active. As a result, the tetrahedron is distorted towards the square-planar geometry. Thus, we believe that this is related to our interests, but not technically a JT distortion originating within a starting square-planar configuration. We are in fact unaware of a purely square-planar anion coordinated JT molecular system.]

- We have added references to the layered perovskites (Ref. #3, #5, and #6 above). This together with our prior reference and discussion of the cuprates will hopefully clarify that this work is not a claim of a first demonstration of 2D layered oxides with JT effects. We have revised to emphasize that the four-fold anion coordination is what is unusual here, which also induces the strong coupling and frustration in the Ca lattice.

Additional experiments suggested by the referee are discussed below.

3 Data & methodology: validity of approach, quality of data, quality of presentation

(1) The figures and figure panels are well organized and visually appealing. The HAADF imaging are good quality images, especially for a beam sensitive material. The relation between STEM, XRD, and theory is well constructed. I very much like the style of using local, global, and theoretical experiments to understand the physics occurring in the material.

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We thank the reviewer for bringing our attention to this confusing point. It is true that if you project a single unit cell of this structure, one of the Co columns seems to be split into two. However, due to the orientation of the unit cell with respect to the $[100]_t$ projection, a second unit cell must be included to encompass all three Co atomic positions in the projection. This addition will show the Co columns are indeed split into three positions. To deliver a clearer representation of this aspect of the $CaCoO_2$ structure, we have modified Fig. 2h as shown in Fig. R2 in the revised manuscript. We believe that this will resolve the apparent discrepancy between Fig. 2h and Fig. 2f.
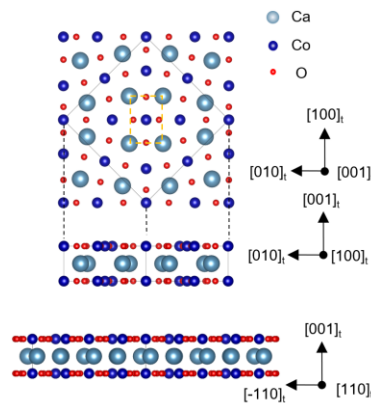
Fig. R2. Unit cell structure of $CaCoO_2$ based on HAADF-STEM and GIXRD refinement. Dark (bright) blue balls indicate Co (Ca) cations and red balls indicate oxygen.

We agree that the resolution in the original Fig. 2f is not sufficient for quantifying individual atomic positions, and it was not used to do so. We have extracted the atomic positions from images of the $[110]_t$ zone axis like that shown in the original Fig. 2g where the atoms are sufficiently well separated for this measurement, and subsequently projected the resulting cation model to images of the $[100]_t$ zone axis simply to show consistency. We also show a plan-view HAADF-STEM image which has sufficiently high resolution to verify the position of the cations clearly (Fig. 2e in the revised manuscript). This plan-view HAADF-STEM image was previously in Fig. 3 but now we have moved it to Fig. 2e in the revised manuscript following the referee's suggestion below (referee #2 comment 3-(3)).

We thank the referee for this suggestion regarding the presentation and we have revised the manuscript accordingly. We moved the previous Fig. 2d to Extended data Fig. 1 in the revised manuscript. We then replaced the previous Fig. 2h with the previous Fig. 3d with oxygen positions indicated to avoid redundancy. Overall, we agree this is a more effective presentation of the structure.

We thank the reviewer for their feedback on the quality of the ABF data and their encouragement to obtain higher signal-to-noise measurements. We first emphasize that by far the biggest challenge is not measurement limitations, but the extreme beam/air sensitivity of $CaCoO_2$. Within the thin film heterostructure, $CaCoO_2$ is remarkably stable (unchanged at least on the months scale) since the $CaCoO_2$

layer is encapsulated by $SrTiO_3$ – this enabled the synchrotron experiments in Pohang, for example. However, when samples are thinned to electron transparency, the $CaCoO_2$ is exposed and is very air sensitive, necessitating the great efforts we have described to optimize sample transfer from preparation directly into the microscope. We suspect that the beam sensitivity arises from the chemical sensitivity of the exposed surface. Preparing plan-view focused ion beam (FIB) lamellas suitable for measurement of oxygen positions is additionally challenging due to the geometry of the film, which is only at most ~30 nm thick. The area of sample where the substrate has been fully removed (necessary for unambiguous measurement of oxygen positions) is thus very small.

Nevertheless, we have taken considerable effort to address this comment, performing additional experiments. Individually, the newly acquired data are of similar quality to that included in the original manuscript, as we are working at the limit of what is currently achievable even with state-of-the-art instruments. However, by doing a series of multiple measurements we could perform unit cell averaging and improve the net signal-to-noise of the image (Fig. R3b), as compared to the original ABF image (Fig. R3a).

From these improvements (Fig. R3b), we can more clearly identify the $O_{(1)}$ and $O_{(2)}$ atomic positions from ABF-STEM. Note that previously we refined the oxygen positions purely based synchrotron x-ray measurements. With these new data, we have now also refined with respect to the ABF-STEM. While there are no qualitative changes to the refinement (only slight changes to the refined oxygen coordinates, and an x-ray refined *R*-factor equivalent to the original refinement), we find much improved agreement with the ABF-STEM data (Fig. R3b), particularly in the positions pointed out by the reviewer. We added a unit cell averaged ABF image with the new refined structure (Fig. R3b) in Fig. 3d in the revised manuscript. We have also added more details on the GIXRD refinement and ABF-STEM of the oxygen positions in the Methods section on page 14 (lines 4-18).
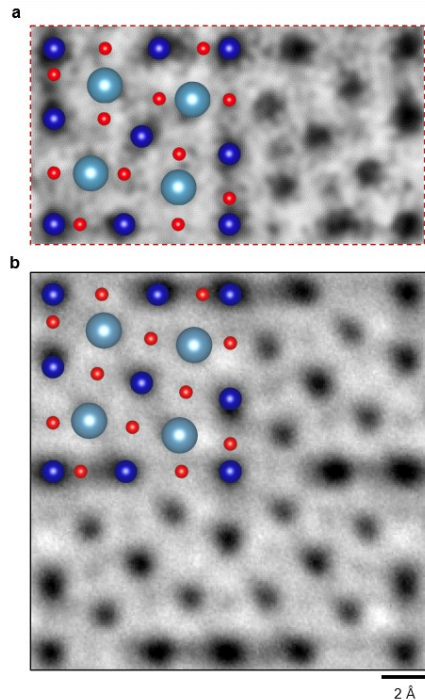
Fig. R3. Plan-view ABF-STEM image of $CaCoO_2$ with refined structure model. Dark areas indicate the atomic positions. **a**, ABF-STEM image without unit cell averaging and previous (in the original manuscript) refined structure model. **b,** The unit cell averaged ABF image with new refined structure model.

(5) Although the use of DFT to explain the orbital degeneracy and displacement structure works, I feel that the authors have methods available to them to experimentally understand the orbital ordering. Extended Data Fig. 3 presents electron energy-loss near edge fine structure (ELNES) analysis to confirm the valance state of Co. This data could equally be used to map the crystal field spitting with atomic to near atomic resolution. Such experiments should be feasible with the microscopes available to the authors and would provide a more direct comparison between experiments, theory, and the overall conclusions.

We fully agree that spatially-resolved EELS-mapping would be very interesting – indeed this is a core focus of research and expertise of Kourkoutis, and such experiments have been performed in collaborations between Kourkoutis and Hwang for example for materials which are more robust to beam exposure. As stated previously, the issue is not the instrumentation but the sample sensitivity. The beam sensitivity of these films does not allow sufficient signal to be acquired for atomic resolution chemical mapping of valence states or other electronic variations. The EEL spectra shown in Extended Data Fig. 3 (which becomes Extended Data Fig. 4 in the revised manuscript) were produced by aligning and summing several spectra, each acquired by continuously scanning over independent fields of view at low beam

current (~25 pA) and represent total acquisition times of 65 minutes for panel (a) and (b). These acquisition parameters are necessary to avoid subtle changes to the near-edge structure induced by the beam.

(6) In Figure 2(h), the atom legend does not match the image, specifically the Co.

Following referee #2 comment 3-(3), the current Fig. 2h has been replaced with the previous Fig. 3d and we put the full atom legend in the figure.

4 Appropriate use of statistics and treatment of uncertainties

The use of statistics and uncertainties is used where appropriate.

5 Conclusions: robustness, validity, reliability

The data and conclusions drawn from the data are reliable. Except for the structure inconsistencies mentioned in Figure 2, which is a vital component of the paper and could use clarification. It would also be more reliable to measure hybridization or electronic structure using experiments rather than simply stating hybridization must be included in the electronic structure calculations for structural agreement between theory and experiments.

We clarified the apparent inconsistencies in Fig. 2 and made relevant changes as we described in our response to referee #2 comment 3-(1). Following the referee's comments, we performed additional experiments (O K-edge EELS) to understand the relationship between structure and orbital hybridization and provide a better connection between theory and experiments. We provided the details of this discussion in our response to referee #1.

6 Suggested improvements: experiments, data for possible revision

(1) As suggest above, better light element STEM imaging is recommended and necessary for the quality expected of a *Nature* publication.

1. Eric R. Hoglund, De-Liang Bao, Andrew O'Hara, Sara Makarem, Zachary T. Piontkowski, Joseph R. Matson, Ajay K. Yadav, et al. "Emergent Interface Vibrational Structure of Oxide Superlattices." Nature 601, no. 7894 (January 27, 2022): 556–61. https://doi.org/10.1038/s41586-021-04238-z.

2. Yücelen, Emrah, Ivan Lazić, and Eric G. T. Bosch. "Phase Contrast Scanning Transmission Electron Microscopy Imaging of Light and Heavy Atoms at the Limit of Contrast and Resolution." Scientific Reports 8, no. 1 (December 2018): 2676. https://doi.org/10.1038/s41598-018-20377-2.

3. Lazić, Ivan, Eric G.T. Bosch, and Sorin Lazar. "Phase Contrast STEM for Thin Samples: Integrated Differential Phase Contrast." Ultramicroscopy 160 (January 2016): 265–

80. https://doi.org/10.1016/j.ultramic.2015.10.011.

4. Ohtsuka, Masahiro, Takashi Yamazaki, Yasutoshi Kotaka, Iwao Hashimoto, and Kazuto Watanabe. "Imaging of Light and Heavy Atomic Columns by Spherical Aberration Corrected Middle-Angle Bright-Field STEM." Ultramicroscopy 120 (September 2012): 48–55. https://doi.org/10.1016/j.ultramic.2012.06.006.

5. Findlay, S.D., Y. Kohno, L.A. Cardamone, Y. Ikuhara, and N. Shibata. "Enhanced Light Element Imaging in Atomic Resolution Scanning Transmission Electron Microscopy." Ultramicroscopy 136 (January 2014): 31–41. https://doi.org/10.1016/j.ultramic.2013.07.019.

6. Huang, Rong, and Yuichi Ikuhara. "STEM Characterization for Lithium-Ion Battery Cathode Materials." Current Opinion in Solid State and Materials Science 16, no. 1 (February 2012): 31–38. https://doi.org/10.1016/j.cossms.2011.08.002.

We have addressed above in our response to referee #2 comment 3-(4).

(2) I would suggest considering more ELNES analysis. The authors have suggested that spatially varying crystal field splitting, correlations effects, and Ca bonding are responsible for the highly distorted structure. They have the capabilities to understand the spatial changes in electronic structure using microscopes at their disposal. These suggested experiments would also help alleviate the differences between the STEM-HAADF – DFT structure and XRD electron density – DFT electron density differences. Rather than saying increased hybridization brings DFT predictions closer to the experimental predictions, the authors can through experiments show that hybridization is key and corroborate with DFT.

Likewise, it would be nice to see O-K edge data in either the main text or extend figures. The O-K edge is often equally or more telling as the metal L23 edges and are worth investigating to inform more about local bonding in the material.

Two key references are listed below, but there are many others out there.

1. Stoyanov, E., F. Langenhorst, and G. Steinle-Neumann. "The Effect of Valence State and Site Geometry on Ti L3,2 and O K Electron Energy-Loss Spectra of TixOy Phases." American Mineralogist 92, no. 4 (April 1, 2007): 577–86. https://doi.org/10.2138/am.2007.2344.

2. Varela, M., M. P. Oxley, W. Luo, J. Tao, M. Watanabe, A. R. Lupini, S. T. Pantelides, and S. J. Pennycook. "Atomic-Resolution Imaging of Oxidation States in Manganites." Physical Review B 79, no. 8 (February 23, 2009): 085117. https://doi.org/10.1103/PhysRevB.79.085117.

We have addressed above in our response to referee #2 comment 3-(5).

7 References: appropriate credit to previous work?

The manuscript appropriately references prior works in most places.

The authors reference a review that well summarizes oxide systems with octahedral and tetrahedral coordination, ref 5-6. It would be worth including references of other systems with orbital ordering of square planar JTE, then explain what makes this system unique or how this manuscript adds additional and significant understanding of the prior works.

Following to the reviewer's suggestions, we have added a reference to ref.[26] in the revised manuscript, describing it as a nearly square planar molecular system making its d^6 high spin state JT active. We also added relevant sentences on page 3 (lines 21-24) in the revised manuscript.

In addition, we added a paragraph on page 4 (lines 18-22) in the revised manuscript to emphasize what makes infinite layer structure special (or unique) for studying orbital degeneracy effects. We also included new sentences which emphasize how distinct 2D-JTE in infinite layer to other 2D-JTE in perovskite-based materials with relevant references [ref.[50-53] in the revised manuscript] on page 10 (lines 18-21; Conclusion section) in the revised manuscript.

8 Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

(1) The paper as a whole is well written. The statement "As we will demonstrate, the collective response is considerably richer." in the introduction might be meant to bait the audience to read more, however it would be a better use of space to emphasize what makes this system "richer" and unique.

Following the referee's suggestion, we have revised to emphasize the origin of the ordered distortion we find, namely that the absence of apical oxygen gives rise to strong electrostatic coupling between the CoO_2 and Ca layers – an interaction which is largely screened for octahedral coordination.

(2) On page 4 in the second paragraph, "square plane" should be "square planar"

We thank the reviewer for pointing out the typo, which has been corrected.

9 Final remarks

Just to emphasize, I do very much like this work and feel it should publish with changes. They have logical progression of the story and the story itself is exciting from a very fundamental and moderately broad perspective. The story just needs a few "guess and check" or "black box connections" fixed and the manuscript should be made self-consistent. The manuscript could easily go from a good manuscript to exceptional manuscript with a few more experiments. The story is predominantly of interest to the Material science community, but it could also be broadly of interest to physics and chemistry. This work is worthy of publication in a high impact journal, but I will leave the *Nature* worthiness decision to the Editor.

We thank the referee for their very positive review and constructive comments, which we have addressed with additional experiments and following suggested revisions.

Referee #3 (Remarks to the Author):

Following their observation of superconductivity in infinite-layer rare-earth nickelate, authors use a similar strategy in order to stabilize an infinite-layer CaCoO2 . Within this new phase, authors expect to achieve an unprecedented Jahn-Teller effect and subsequent orbital orders in infinite-layer transition metal oxides. This would be a breakthrough as JTE and JTD are at the core of several properties and applications.

The manuscript is well written, well presented and largely accessible for non-specialist. Nevertheless, the main motivation (getting a JTE) is finally not really reached at the end of the study, and the material prefers to adopt a different distorted structure following ice rules. Furthermore, even though authors explain that there is a competition between ice rules and JTE, there is no evidence of the existence of a JTE and JTD (see below). Thus, at the moment, I am not convinced that the manuscript warrants publication in Nature as its impact, beyond stabilizing the CaCoO2 phase, appears more limited.

We thank referee #3 for their strong endorsement of the importance of the claims of the manuscript. The technical question they raise is that, given the geometric frustration we observe, whether there is indeed a JTE and JTD, and in general a Jahn-Teller instability in competition with the geometric constraints of the distorted Ca lattice. We have performed additional calculations to address the analysis suggested in the responses below.

I explain below the different points:
1) Having a Jahn-Teller active ion in terms of electronic configuration is not a guarantee of having a JTE. It is a prerequisite but one also needs compact bands with limited hybridization between transition metal d and O p states. If the electronic structure is too hybridized, the Jahn-Teller force can be too weak and annihilate the JTE (Phys. Rev. B 21, 5662 (1980), Phys. Rev. Res. 1, 033131 (2019)). In the present case, the authors identify a hybridized Co d – O p state with the creation of a ligand hole. I suspect that it could prevent a JTE and promote the observed structural distortions.

The JTE should arise with spontaneous symmetry breaking and associated orbital order in the system where it has energetically degenerate orbitals [ref.[1] in the revised manuscript]. Our DFT+U calculations show that the total energy of $CaCoO_2$ structure with equivalent Q_2-JTD is lower than that without any distortion (please see the response below to referee #3 comment (3)). This indicates that $CaCoO_2$ is 'willing' to undergo spontaneous JTD as expected (Fig. 1e in the revised manuscript). However, unlike the cooperative JTE in perovskite compounds, interlayer coupling results in a $(2\sqrt{2},2\sqrt{2},1)$ tetragonal supercell structure with large hybridization at $Co_{(1)}O_4$. This arises because of the lack of apical anions, as emphasized by referee #2. We can conclude that the driving force for the observed distortion is the JTE,

and hybridization arises to accommodate the competition between JTD and geometric frustration of Ca layer. In addition, our cluster multiplet calculation support this idea by showing both d_{xz}/d_{yz} degeneracy lifting and ligand hole character in the highly JT-distorted $Co_{(1)}O_4$ (Fig. 4e in the revised manuscript). We added these discussions on page 9 (lines 9-15) and page 10 (lines 18-21) in the revised manuscript.

2) Looking at Co-O bond lengths is not necessarily a good indicator of a JTE as the coupling of several distortion can produce a virtual "JTE" (see Phys. Rev. B 101 214304 (2020), Nat. Comm. 10, 1658 (2019)). An appropriate manner to extract this propensity is to perform a symmetry mode analysis that identifies which eigen displacement of the high symmetry undistorted cell contributes to the global lattice distortion (each eigen displacement of the undistorted cell defines a precise lattice distortion, see amplimodes software for instance, https://www.cryst.ehu.es/cryst/amplimodes.html).

Assuming a ($\sqrt{2},\sqrt{2},1$) primitive P4/mmm supercell with only the oxygen motion of the Q2 mode as sketched in Figure 1.e, one would get a P4/mbm cell with a M3+ lattice distortion corresponding to expectation for a Q2 JTE in CaCoO2. Repeating the analysis but with the atomic coordinates reported in extended Table 4, we end up with a structure in which the M3+ amplitude is exactly zero from a symmetry mode analysis point of view. It means that there is no Q2 JTD (and so no JTE) in the material. Thus, what is stabilized in the compound is not associated with a Jahn-Teller effect.

We thank referee #3 for the comments on Q_2-JTE in $CaCoO_2$. As the referee mentioned, the distortion can be understood by the irreducible representation (or normal modes) of the parent structure (high symmetric structure). Here, we use the amplimodes software suggested by the referee to understand the distortion in $CaCoO_2$ structure using symmetry mode analysis. The distortion of the refined $CaCoO_2$ structure (Extended Data Table 4) with ($2\sqrt{2},2\sqrt{2},1$) tetragonal supercell can be decomposed into four normal modes: SM2, SM3, M1+, and X1+. Table R1 shows that the atomic displacement for all the atoms (O, Ca, and Co) can be explained by the superposition of these normal modes. Particularly, the atomic displacement at oxygen sites in the ($2\sqrt{2},2\sqrt{2},1$) tetragonal supercell can be described by SM2(1), SM2(2), SM3, M1+, and X1+ (there exist two sets of SM2 for different oxygen cites). We visualized each normal mode for all oxygen sites in Fig. R4. Note that SM2(1) and X1+ are responsible the for Q_2-JTD at $Co_{(1)}O_4$ and $Co_{(2)}O_4$, respectively. In addition, SM2(2) and M1+ are responsible for $Co_{(3)}O_4$ rotation and CoO_4 breathing mode, respectively. The SM3 mode gives out-of-plane (or [001]-direction) distortions.

Atoms	WP	Modes
O2	2f	SM2(2) SM3(1) M1+(1) X1+(1)
Ca1	1d	SM2(1) SM3(1) X1+(1)
Co1	1a	SM2(1) SM3(1)

Table R1. Summary of the allowed normal mode for each atom. WP is Wyckoff positions.
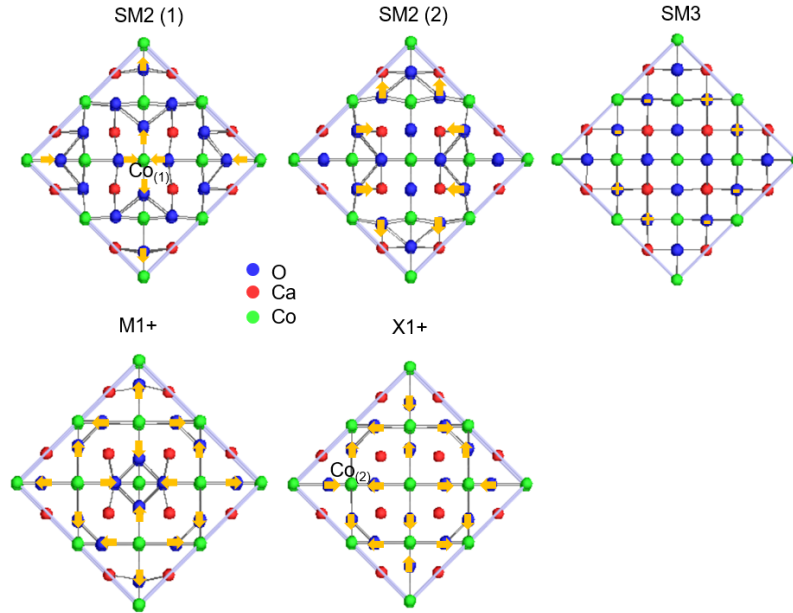
**Fig. R4.** Visualization of the allowed normal modes for oxygen atoms.

From the symmetry mode analysis, we obtained the amplitude of each normal mode in the $CaCoO_2$ structure (Table R2). All the existing normal modes for O, Ca and Co are summed and depicted in Table R2. We obtained finite-amplitude values for SM2, M1+, and X1+ but not SM3, since there is no atomic displacement along the [001]-direction. Since there is a finite amplitude for both SM2 and X1+ we can conclude that there exists a Q_2-JTD contribution for the refined $CaCoO_2$ structure.

Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
SM2	(a,-a,0,0)	P4/mbm (127)	4	2.5277
SM3	(a,-a,0,0)	P4/nmm (129)	3	0.0000
M1+	(a)	P4/mmm (123)	1	0.5284
X1+	(a,0)	P4/mmm (123)	2	0.5501

Table R2. Summary of the amplitudes for each normal mode that contribute to the refined $CaCoO_2$ structure.

Following the suggestion of referee #3, we have performed DFT+U calculations (U = 5 eV) to see whether the structure can be stabilized solely by Q_2-JTD. The initial structure was taken with all the atoms positioned at high symmetry points of the ($\sqrt{2},\sqrt{2},1$) primitive P4/mmm supercell (Fig. R5). We then applied the Q_2-JTD to this initial structure and compared total energies with different distortion amplitudes. Here we defined distortion amplitude by the ratio between long and short Co-O bonding length. The total energy for the non-distorted structure was – 184.44 eV while those for 10% distortion and 100% distortion are – 185.77 eV and – 172.28 eV, respectively (Fig. R5). Thus, we find that structure with 10% Q_2-JTD is more stable than a structure without any distortion. This suggests that CaCoO$_2$ with Co d^7 configuration is willing to undergo a JTD (or JT-active).

without distortion
-184.44 eV

With 10% distortion
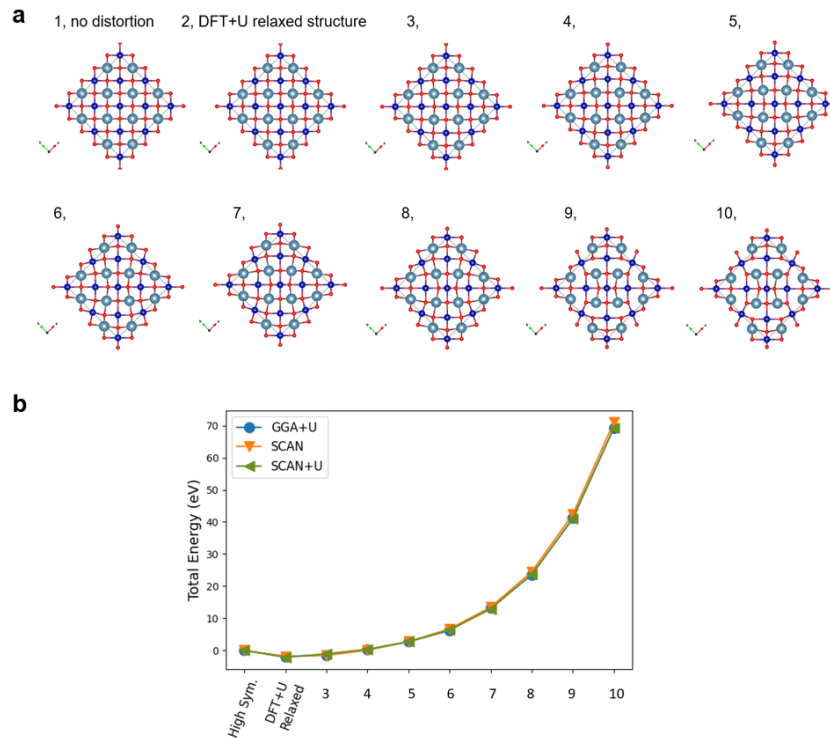-185.77 eV

With 100% distortion
-172.28 eV
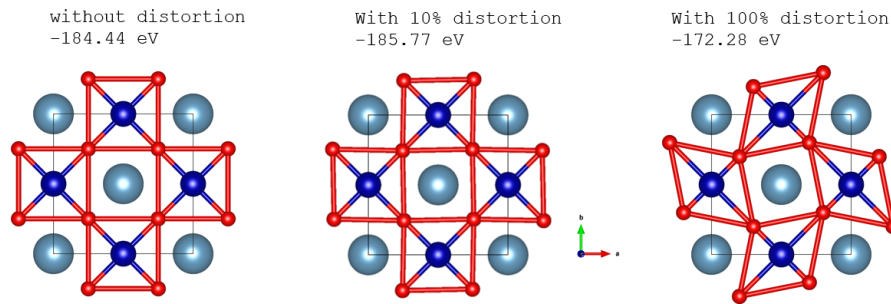
Fig. R5. DFT+U (U = 5 eV) calculation for total energy under equivalent Q_2-JT-distortion in $\sqrt{2} \times \sqrt{2} \times 1$ supercell.

Although the total energy with 10% JTD is lower than without any distortion in CaCoO$_2$, our DFT calculation shows that the structure always converged to the current DFT relaxed structure with lower total energy (Extended Data Fig. 14 in the revised manuscript). For example, the DFT relaxed structure (U = 5 eV) with ($2\sqrt{2},2\sqrt{2},1$) tetragonal supercell is -190.66 eV which is smaller than that of the ($\sqrt{2},\sqrt{2},1$) tetragonal supercell with equivalent Q_2-JTD (Fig. R5). This indicates that there is another factor competing with the JTE which is responsible for the final structure. Given the very close interlayer distance between the Ca layer and CoO$_4$ layer (lack of apical oxygen), the geometrically frustrated Ca layer strongly couples to the JTE in CoO$_4$ and results in a distorted structure that follows the "ice rules". We added this discussion on page 9 (lines 9-15) with new Extended data Fig. 13 and Fig. 14.

To address the referee's concerns, additional calculations were performed using three different first-principle calculations: GGA+U, SCAN, and SCAN+U (see Methods in revised manuscript). We performed these calculations with 10 different initial structures, e.g., structure #1 is without any distortion, structure #2 is the DFT relaxed one, and structure #10 is the experimental structure (Fig. R6a). Structures between #3 to #9 have the $(2\sqrt{2}, 2\sqrt{2}, 1)$ tetragonal supercell but with different distortion amplitudes. No matter where we start or which methods we used, the structure converged to the same DFT+U relaxed structure which gave the lowest total energy among the others (Fig. R6b). Therefore, we believe that this DFT relaxed structure is not a local minimum, but the global minimum along with this symmetry-breaking pathway. We added this discussion on page 9 (lines 13-15) with new Extended data Fig. 14.

Fig. R6. a, $2\sqrt{2} \times 2\sqrt{2} \times 1$ super cell with different distortion amplitude. Closer to #10, the structure approaches the experimentally refined structure. **b,** Normalized total energy for the structure depicted in **a**. Three different first-principle calculations are used.

The magnetic order used for DFT+U calculation was (pi, pi, 0) – antiferromagnetic (AFM) order (Fig. R7). To address the referee's question on the relationship between spin order and the JTD, we performed DFT+U calculations with various magnetic ground states. We started with four different magnetic grounds states, i.e., (pi, pi, 0), (pi, pi, pi), (0, 0, pi) and nonmagnetic. Our total energy calculation on the relaxed structure shows that (pi, pi, 0) – AFM structure is the most favorable magnetic ground state for $CaCoO_2$ (Table. R3). Note that the nonmagnetic structure does not give any converged relaxed structure. Moreover, the same distortion symmetry with refined $CaCoO_2$ has been captured only with the (pi, pi, 0) – AFM ground state. Our results indicate that there is indeed a strong coupling between structure and spin order as well as the associated orbital order.

(pi, pi, 0)	(pi, pi, pi)	(0, 0, pi)
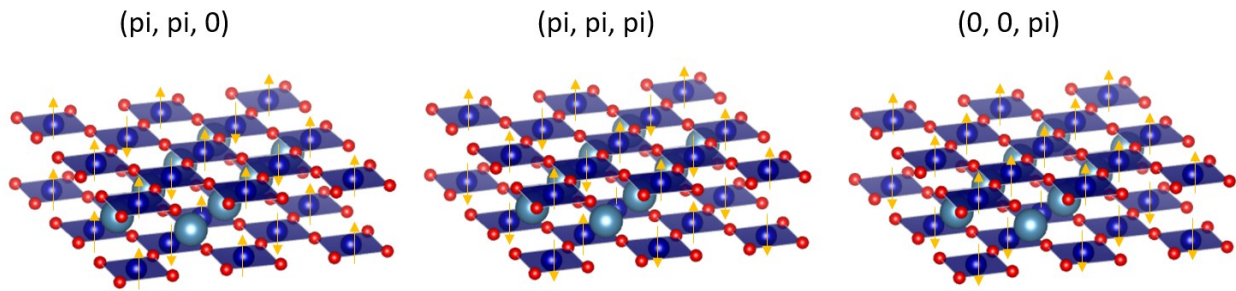
Fig. R7. Various AFM ground states in $CaCoO_2$.

Magnetic state	U=5eV
(pi,pi,0) AFM	-190.66 eV
(pi,pi,pi) AFM	-188.19 eV
(0,0,pi) AFM	-189.60 eV
Nonmagnetic	Not stable

Table R3. DFT+U total energy calculation for various magnetic ground states in $CaCoO_2$.

6) Do the authors have an explanation for the large difference of band gaps between DFT and experiments ? Usually, DFT gaps are underestimated with respect to experiment, which is not the case here. Are lower U values giving a similar trend ?

Firstly, we emphasize that the gap extracted from transport experiments is virtually always far lower than the band gap itself, as it is dominated by conductivity arising from processes such as variable range hoping. Secondly, we include our results on U-dependent band structure to address the referee's second question. As we lower the U values from 6 eV, the band gap starts to close at 4 eV (see in Fig. R8). Note that the band gap from U = 5 eV is ~ 0.67 eV and U = 6 eV is ~ 1.01 eV. These results indicate that a larger U value tends to increase the band gap.
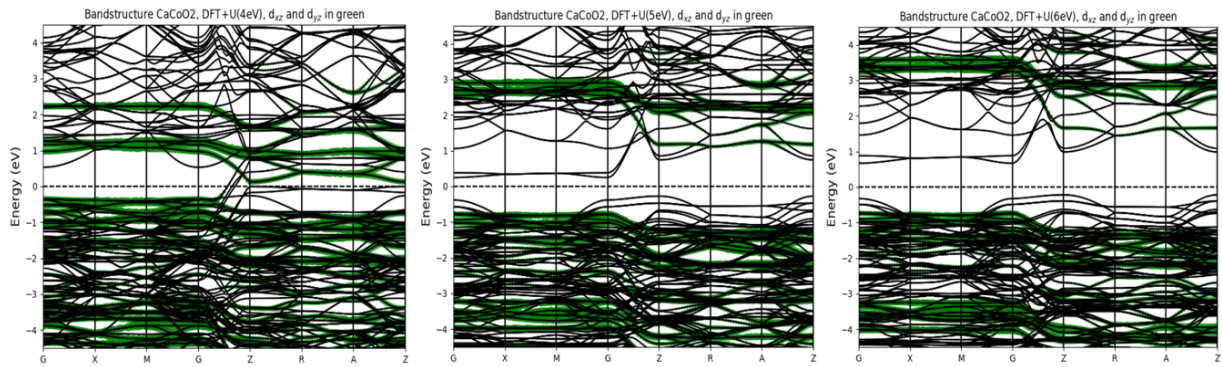
Fig. R8. DFT calculated band dispersion of $CaCoO_2$ with U = 4, 5, and 6 eV. Green lines highlight dxz (and dyz) projections.

7) I have also another minor comment: the data provided in extended table 3 yields a non-stoichiometric cell with 8 Ca, 12 Co, and 16 O ions. There might be a typo on some atomic coordinates.

We thank referee #3 for finding a typo in Extended table 3. The y-coordinate for $Co_{(2)}$ should be 0.205, not 0.200. We have made proper changes to Extended Data Table 3 in the revised manuscript. Corrected atomic coordinates yield stoichiometric unit cell with 8 Ca, 8 Co, and 16 O ions.

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

Authors changed their manuscript based on reviewer's comments. After minor revision, this work can be published in Nature. This is my comments on their replies.

1) Regarding EELS data, I expected the authors would focus on the spectra from CaCoOx with different oxygen contents. This is seen in Extended Data Fig. 6. Regarding the extended data Fig. 5, please consider to remove it, since suppression of the pre-peak is clearly seen in the extended data Fig. 6. I wonder if the comparing EELS data between CaCoO2 and SrCoOx are proper.

2) Regarding Raman approach, this is a natural choice to find the JT effect, however difficulty is also expected due to a huge STO contribution in Raman data. The authors tried to prove the existence of JTE with extensive sets of analysis suggested by other referee, at the same time 2D JTE is not uncommon. I think it is highly probable.

Referee #2 (Remarks to the Author):

The manuscript is now in much better shape. The authors did a great job addressing the other reviewers and my comments. The new ABF images are much higher quality (beautiful!), the newly refined structure matches the image adequately, and the figure presentation makes much more sense now. It would have been nice to have spatially resolved electron energy-loss experiments complementing the DFT, but those are hero experiments that may not be possible in these beam sensitive materials. The DFT, experimental structure, and O-K edge data is sufficient to prove the authors point. I am happy to say that this manuscrIpt is most definitely ready for publication in Nature.

Referee #3 (Remarks to the Author):

Authors have provided satisfying evidences of the existence of a Jahn-Teller effect (JTE) in these new 2D materials from total energy calculations. However, this JTE is overcome by other facts producing an hybrid distortion pattern, that include part of what is a local JTD (M1+ and X1+ shown in the reply are not pure JTD but a "breathing distortion" and "half breathing-half Jahn-Teller" distortion, respectively).

JT effect and JT distortions being at the core of several properties and applications, the identification of new potential materials showing a JT effect and/or JT distortion is a breakthrough in the field of material science. I thus recommand the publication of the manuscript.

Author Rebuttals to First Revision:

We thank the referees for their second reviews, and for their recommendation for publication. In the following, we attach each referee's comments (in blue), our responses (in black), and we indicate the associated changes in the revised manuscript (in red).

Referee #1 (Remarks to the Author):

Authors changed their manuscript based on reviewer's comments. After minor revision, this work can be published in Nature. This is my comments on their replies.

1) Regarding EELS data, I expected the authors would focus on the spectra from CaCoOx with different oxygen contents. This is seen in Extended Data Fig. 6. Regarding the extended data Fig. 5, please consider to remove it, since suppression of the pre-peak is clearly seen in the extended data Fig. 6. I wonder if the comparing EELS data between CaCoO2 and SrCoOx are proper.

We thank the referee for their positive evaluation of our work. Following the referee's suggestion, we removed Extended Data Fig. 5 from the manuscript, which avoids redundancy and a comparison with SrCoOx, rather than within the CaCoOx family.

2) Regarding Raman approach, this is a natural choice to find the JT effect, however difficulty is also expected due to a huge STO contribution in Raman data. The authors tried to prove the existence of JTE with extensive sets of analyses suggested by other referee, at the same time 2D JTE is not uncommon. I think it is highly probable.

We thank the referee for understanding the technical challenges we faced, and for accepting the computational analysis suggested by referee #3.

Referee #2 (Remarks to the Author):

The manuscript is now in much better shape. The authors did a great job addressing the other reviewers and my comments. The new ABF images are much higher quality (beautiful!), the newly refined structure matches the image adequately, and the figure presentation makes much more sense now. It would have been nice to have spatially resolved electron energy-loss experiments complementing the DFT, but those are hero experiments that may not be possible in these beam sensitive materials. The DFT, experimental structure, and O-K edge data is sufficient to prove the authors point. I am happy to say that this manuscript is most definitely ready for publication in Nature.

We thank the referee for their positive appraisal of our revisions and for their strong endorsement for publication.

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Authors have provided satisfying evidences of the existence of a Jahn-Teller effect (JTE) in these new 2D materials from total energy calculations. However, this JTE is overcome by other facts producing an hybrid distortion pattern, that include part of what is a local JTD (M1+ and X1+ shown in the reply are not pure JTD but a "breathing distortion" and "half breathing-half Jahn-Teller" distortion, respectively).

JT effect and JT distortions being at the core of several properties and applications, the identification of new potential materials showing a JT effect and/or JT distortion is a breakthrough in the field of material science. I thus recommend the publication of the manuscript.

We thank the referee for their positive appraisal of our revisions and for their recommendation for publication. In particular we are grateful for their suggestions for further analysis, to support the existence of an underlying JT instability. This not only improved our manuscript, but also addressed previous comments of referee #1 as well.