



STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Volume 75 (2019)

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Table S1: List of all pseudo-cubic to tetragonal permuted hkl with related peak positions and relative intensities of γ -CsCoO₂

h	k	l	Multiplicity	Peak position		Intensities
				d	2 theta	
0	0	4	2	2.08026	19.63188	0.89144
0	0	8	2	1.04013	39.87164	0.33778
1	0	1	8	4.79728	8.47917	0.16052
1	0	3	8	2.50791	16.25921	0.49352
1	0	5	8	1.60113	25.5943	0.13375
1	0	7	8	1.16508	35.44413	0.00078
1	0	9	8	0.9133	45.69941	0.01487
1	1	2	8	2.93877	13.86265	7.33735
1	1	6	8	1.31539	31.28287	2.16994
2	0	0	4	2.93563	13.87757	3.66545
2	0	2	8	2.39864	17.00522	0.17586
2	0	4	8	1.69731	24.12147	3.708
2	0	6	8	1.25395	32.85783	0.02884
2	0	8	8	0.98041	42.41379	0.89891
2	1	1	16	2.504	16.28475	0.98417
2	1	3	16	1.90682	21.43774	0.06052
2	1	5	16	1.40565	29.22772	0.00555
2	1	7	16	1.08291	38.23381	0.0088
2	2	0	4	2.0758	19.67443	1.77837
2	2	4	8	1.46939	27.93354	3.61118
2	2	8	8	0.92992	44.83799	0.60152
3	0	1	8	1.9051	21.4573	0.03014

3	0	3	8	1.59909	25.62741	0.13301
3	0	5	8	1.26781	32.48881	0.033
3	0	7	8	1.01599	40.86071	0.00697
3	1	2	16	1.69549	24.14772	7.40206
3	1	4	16	1.38519	29.66931	0
3	1	6	16	1.11109	37.22794	2.71891
3	1	8	16	0.90743	46.01192	0
3	2	1	16	1.59808	25.64394	0.26529
3	2	3	16	1.40427	29.25701	0.00547
3	2	5	16	1.1639	35.48112	0.00162
3	2	7	16	0.96012	43.35511	0.0003
3	3	2	8	1.31313	31.33794	2.16078
3	3	6	8	0.97959	42.45091	0.89628
4	0	0	4	1.46781	27.96407	1.8012
4	0	2	8	1.3842	29.69099	0
4	0	4	8	1.19932	34.40011	1.32125
4	0	6	8	1.00805	41.19689	0
4	1	1	16	1.40359	29.27165	0.00542
4	1	3	16	1.2668	32.51544	0.06557
4	1	5	16	1.08197	38.26848	0.00864
4	1	7	16	0.91255	45.73938	0.02987
4	2	0	8	1.31285	31.34481	2.15964
4	2	2	16	1.252	32.91054	0.05734
4	2	4	16	1.11024	37.25749	2.71255
4	2	6	16	0.95341	43.67561	0.01688
4	3	1	16	1.16273	35.51808	0.00166
4	3	3	16	1.08134	38.29157	0.00854
4	3	5	16	0.95946	43.38636	0.00032
4	4	0	4	1.0379	39.96084	0.67061
4	4	4	8	0.92872	44.89883	0.59879
5	0	1	8	1.16273	35.51808	0.00083
5	0	3	8	1.08134	38.29157	0.00427
5	0	5	8	0.95946	43.38636	0.00016
5	1	2	16	1.10973	37.27521	2.70875
5	1	4	16	1.00742	41.22403	0
5	1	6	16	0.8859	47.19723	1.23555

5	2	1	16	1.08103	38.30312	0.00848
5	2	3	16	1.01469	40.91536	0.01411
5	2	5	16	0.91198	45.76934	0.02997
5	3	2	16	0.97866	42.49329	1.78657
5	3	4	16	0.90632	46.07156	0
5	4	1	16	0.91142	45.79929	0.03007
6	0	0	4	0.97854	42.49859	0.44646
6	0	2	8	0.95255	43.71704	0.0084
6	0	4	8	0.88547	47.2216	0.61663
6	1	1	16	0.9588	43.4176	0.00034
6	1	3	16	0.91161	45.78931	0.03004
6	2	0	8	0.92833	44.9191	0.59788
6	2	2	16	0.90605	46.08646	0

*The observed Miller indices indicated that the true symmetry of the compound is $I4_1/amd$. Moreover, the reflection conditions for all permuted hkl Bragg peaks generated by a compound with $I4_1/amd$ symmetry satisfies the extinction rule of the Bragg reflections having hkl values where $h + k + l = 2n$. There is no evidence of extra reflections that violate the extinction conditions as depicted in Table S1.

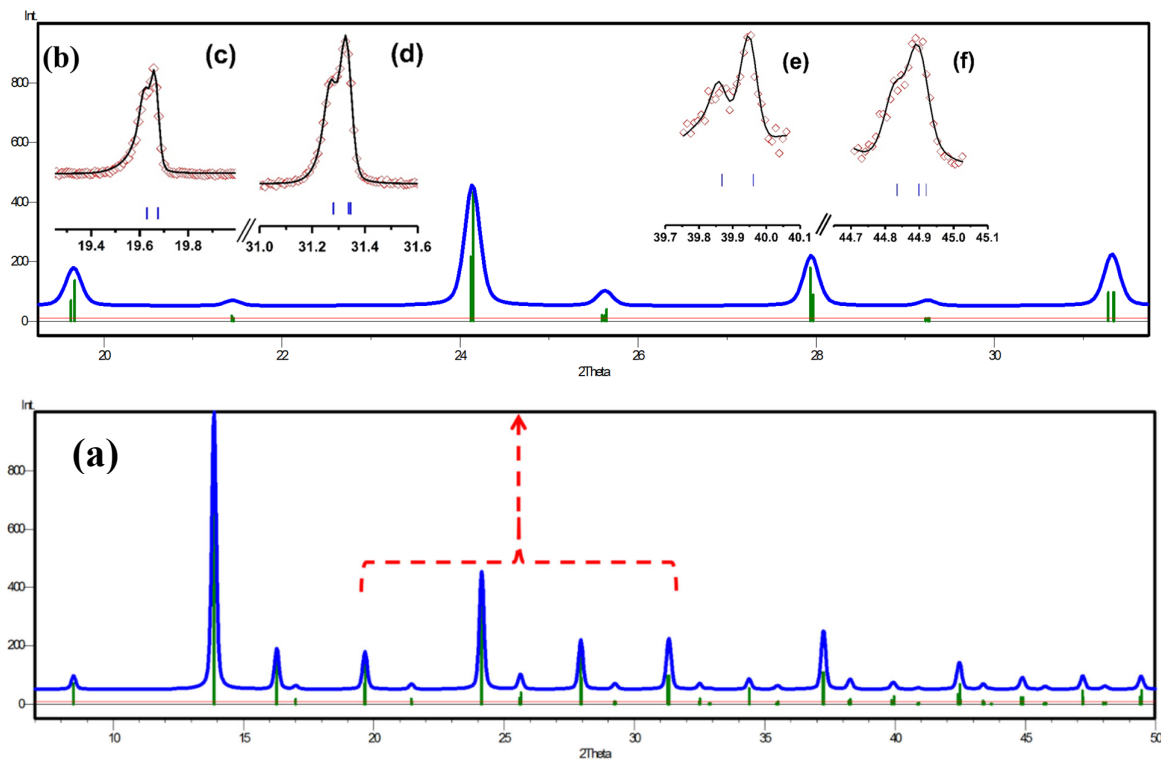


Figure S1 (a) Theoretical powder pattern of high pressure γ -CsCoO₂ phase (*I4₁/amd.*) plotted in linear scale as a function of diffraction angle 2θ ($\lambda=0.7093$ Å). (b-f) The enlarged region shows the cubic pseudosymmetry is violated slightly as indicated by subtle peak splittings both in expanded b) simulated pattern and c-f), into the pairs of *hkl* indices as seen in the observed powder diffractogram.

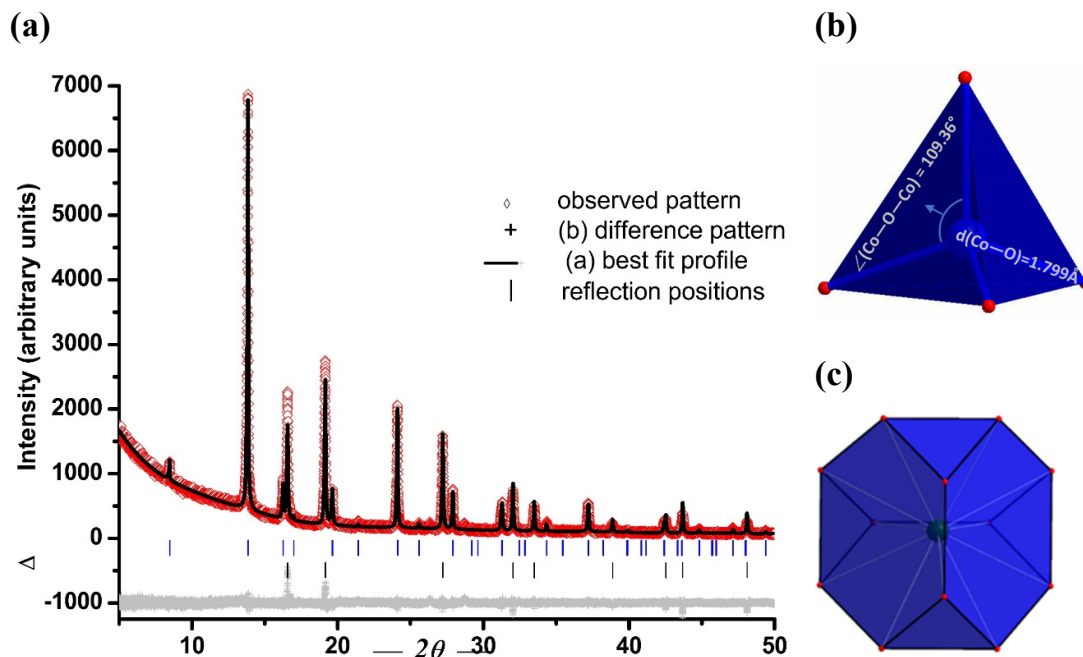


Figure S2 (a) Rietveld refinement fit of the powder data of high pressure γ -CsCoO₂, reproduced synthesis at 6GPa, plotted in square root scale as a function of diffraction angle 2θ ($\lambda=0.7093$ Å) showing the observed pattern (diamonds), the best Rietveld-fit profile (black line), reflection mark (vertical bars: blue; HP-CsCoO₂ black; CoO), and difference plot $\Delta=I_{\text{obs}} - I_{\text{calc}}$ (gray line). (b) CoO₄ tetrahedron emphasizing the refined bond lengths and angles. (c) The truncated tetrahedron of 12 oxygen atoms formed around Cs.

Demonstration of Phase Transition Pathways

Find below the methodology to interactively visualize and self-explore the symmetry modes that contribute to the gamma-beta transition in CsCoO₂ using the ISOTROPY Software Suite (iso.byu.edu).

i) CsCoO2_cubic-orth29_goodmatch_anim.avi

The movie file contains an animation of the gamma-beta phase transition in CsCoO₂, which highlights the unique structural order parameters belonging to distinct parent-space-group irreps. This animation was generated via real-time screen capture of the ISOVIZ software utility, which allows one to interactively explore the structural order parameters associated with a phase transition. The ISODISTORT software was used to parameterize the child (beta-phase) structure in terms of irrep symmetry modes of the parent (gamma-phase) structure, and thereby generate the input file for ISOVIZ. Both ISODISTORT and ISOVIZ are components of the ISOTROPY Software Suite (iso.byu.edu).

In the animation, observe that the large tetrahedral-tilt associated with irrep GM5⁻ does much of the work needed to deliver tetrahedral edge sharing, but can't complete this work by itself. The large contributions of GM4⁻ and X3, which act primarily to split the three-dimensional corner-sharing cristobalite network into layers, are also critical to the formation of edge sharing. The smaller displacive contributions of X1 and GM5⁺, and also the lattice strains belonging to GM1⁺/GM3⁺/GM5⁺, are further needed to achieve chemically-sensible bond lengths and coordinations. Notice the very distinct role that irrep SM2 plays in shearing the alternating layers in opposite directions.

ii) CsCoO2_cubic-orth29_goodmatch.isoviz

To interactively explore the symmetry modes that contribute to the gamma-beta phase transition in CsCoO₂, open this input file (generated by ISODISTORT) with ISOVIZ; resize the window if needed. Each interactive slider in the ISOVIZ control panel (at the right-hand side) corresponds to a symmetry-mode of the child structure, which belongs to a specific instance or "order parameter" of a specific irrep of the parent space group. The sliders are initially preset to the values that correspond to the experimentally-determined beta-phase structure. The master slider at the top of the control panel simultaneously multiplies every symmetry-mode amplitude by a common factor between 0 and 1, so as to continuously evolve the structure between parent (0) and child (1), thereby animating the phase transition. The "animate" button near the bottom of the window causes the master slider to oscillate between 0 (parent) and 1 (child).

The gray sliders near the bottom control panel are irrep-specific submasters -- they simultaneously multiply all symmetry-mode amplitudes of a given irrep by a common factor between 0 and 1, allowing one to explore irrep-specific structural components. Useful keyboard toggles include "i" (resets all modes to their initial values), "z" (sets all modes to 0), "r" (resets all viewer parameters, including the modes), "s" (toggles all irrep-submaster sliders between 0 and 1). To see how individual irreps contribute to the overall transition, use "s" to toggle all irrep sliders to zero, and then manually turn them back on again (drag their sliders to 1) one at a time. The ISOVIZ utility can be downloaded and installed from the ISOTROPY Software Suite site (iso.byu.edu).

iii) CsCoO₂ cubic-orth29 goodmatch dist.txt

If desired, one can recreate the ISOVIZ input file from within ISODISTORT. Use the "Import an ISODISTORT distortion *file*" link on the ISODISTORT home page to import the CsCoO₂ distortion file, which takes you directly to the "distortion" page of ISODISTORT, where you then select "Save interactive distortion", and click "OK" to generate and save the ISOVIZ input file to your computer. It might be helpful to first change the child-cell "Viewing range" to $x=\{0,1\},y=\{-0.2,1.25\},z=\{0,2\}$ and the "Maximum bond length" to 2.3 Angstroms; both options are available near the bottom of the "distortion" page.

The distortion file was created via a symmetry-mode decomposition (ISODISTORT's Method 4) of the child structure relative to the parent structure, using CIF structure files as input for both phases. For the case of CsCoO₂, this process is not entirely automatic. Due to the very large atomic displacements involved, ISODISTORT matches up the atoms of the distorted and undistorted child structures in a mathematically correct but rather inconvenient fashion -- each atom in the undistorted structure gets automatically matched to the nearest-neighbor atom in the distorted structure which has the same type and local symmetry. Thus, following the symmetry-mode decomposition, the distortion file had to be carefully modified by hand in order to match the atoms up properly.