Supporting Information

Pressure-induced abnormal insulating state in the triangular layered cobaltite Li_xCoO_2 (x = 0.9)

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1. Preparation of Delithiated Positive Electrode Materials.

Chemical delithiation of the $LiCoO_2$ materials was achieved by stirring the powder $LiCoO_2$ in acetonitrile solutions containing NO_2BF_4 oxidizer in excess. The molar ratio of $LiCoO_2$ and NO_2BF_4 is 5:1 for preparing $Li_{0.9}CoO_2$ samples. After 24 h of lithium extraction at room temperature, the $LiCoO_2$ powder was washed with acetonitrile several times, and the solution was removed by centrifugation. The resulting materials were then dried at 80 °C.

Table S1. ICP-AES results of $LiCoO_2$ and the chemically delithiated $LiCoO_2$. The values in the table are normalized with the cobalt content in the $LiCoO_2$ and delithiated $LiCoO_2$ samples.

samples	Li content	Co content
$LiCoO_2$	1.02	1.00
delithiated $LiCoO_2$	0.89	1.00

2. The typical Rietveld refinement results.

The typical Rietveld refinement results of $Li_{0.9}CoO_2$ at pressure 0.3 GPa and 19.8 GPa are summarized in Table 2.

TABLE S2. Structural parameters obtained from full Rietveld refinements of the diffraction diagrams for $Li_{0.9}CoO_2$ collected at pressure 0.3 GPa and 19.8 GPa: lattice parameters; and volume of the unit cell.

Parameter	R-3m phase at 0.3 GPa	R-3m phase at 19.8 GPa
a (Å)	2.8071(5)	2.7409(3)
c (Å)	13.9849(1)	13.3378(7)
z (O)	0.24039(8)	0.24039(8)
V (Å^3)	95.4381(4)	86.7784(9)

Note: The relative atomic positions for Co , O and Li were fixed. The Li atoms occupy 3 a Wyckoff positions at (0, 0, 0), Co atoms occupy 3 b Wyckoff positions at (0, 0, 1/2) and O atoms occupy 6 c Wyckoff positions at (0, 0, 0.24039).

3. Structure optimization

Ferromagnetically spin-polarized, anti-ferromagnetically spin-polarized, as well as non-spin-polarized DFT were used to optimize the structure, respectively, at various values of external pressure.

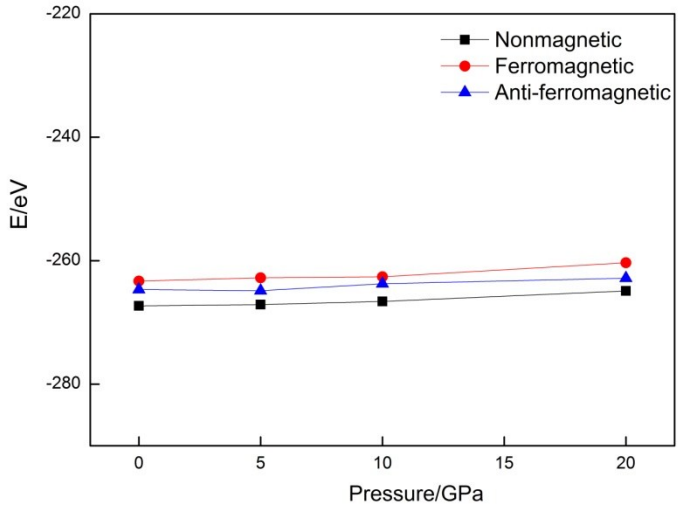


Figure S1. Energy differences between different magnetic structures at various external pressures.

4. Structure parameters of supercell of $Li_{0.9}CoO_2$ obtained from DFT calculations.

Table S3. Structure parameters of supercell of $Li_{0.9}CoO_2$ obtained from DFT calculations at various external pressures.

Pressure (GPa)	*a* (Å)	*c* (Å)	Average Co-O bond length (Å)	Average CoO_6 octahedral volume (Å^3)	Average distortion parameter Δ_d of ^{CoO_6} octahedron (10^{-4})
0	5.6556(0)	14.1272(2)	1.9257(0)	9.4224(9)	0.3731(1)

5	5.6092(9)	13.8726(4)	1.9131(3)	9.2519(2)	0.3572(2)
10	5.5689(5)	13.6558(5)	1.9028(1)	9.1116(7)	0.3353(6)
20	5.5016(7)	13.299797)	1.8846(8)	8.8639(5)	0.3204(7)
40	5.3977(6)	12.7782(2)	1.8574(9)	8.5029(3)	0.2939(0)

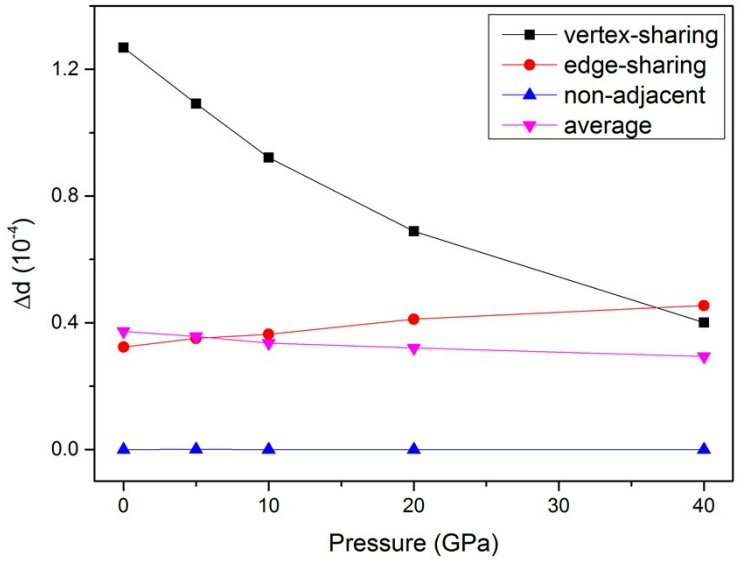


Figure S2. Distortion parameter Δ_d of all CoO_6 octahedrons in the supercell of $Li_{0.9}CoO_2$ versus pressure. There are 12 CoO_6 octahedra in the 2 x 2 x 1 supercell, of which 2 are vertex-sharing with the vacancy-O octahedron (i.e. the O_6 octahedron containing the Li vacancy), 6 are edge-sharing with the vacancy-O octahedron, and 4 are non-adjacent to the vacancy-O octahedron.

5.

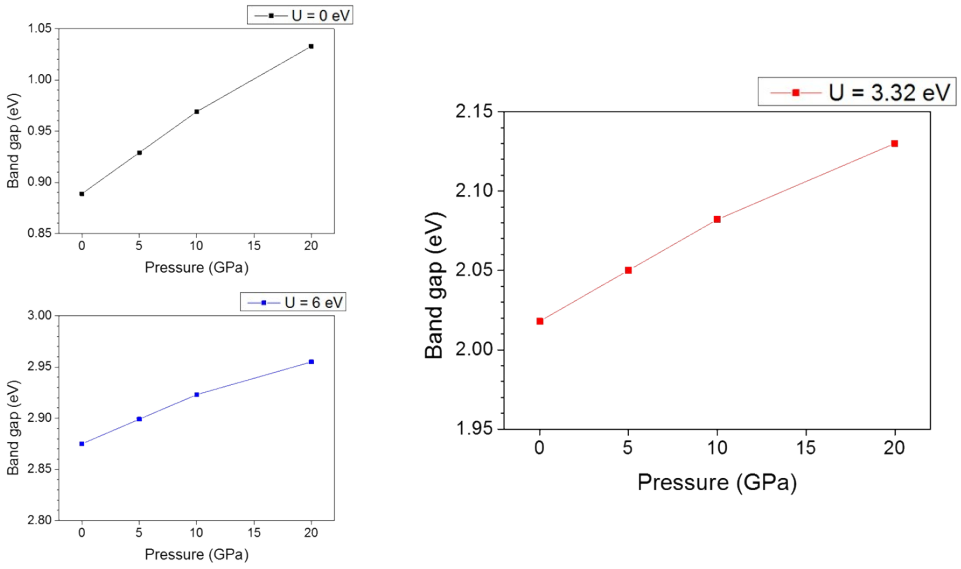
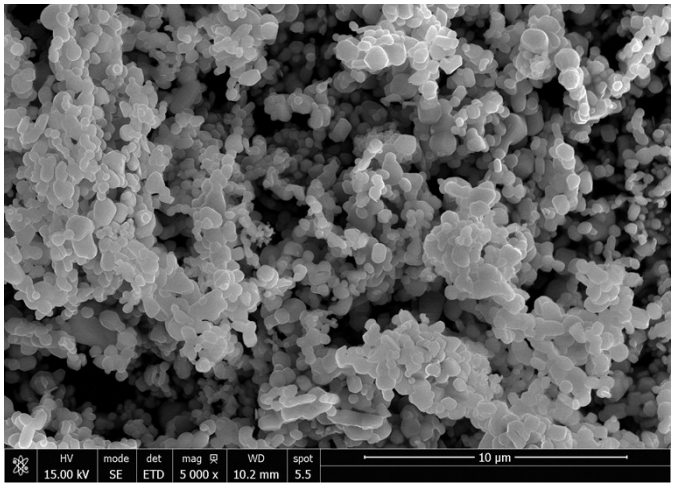
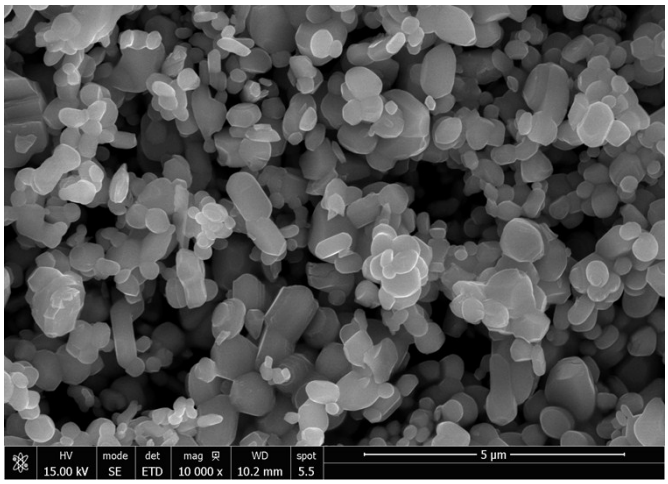


Figure S3. Calculated band gap under various external pressures with different Hubbard U.

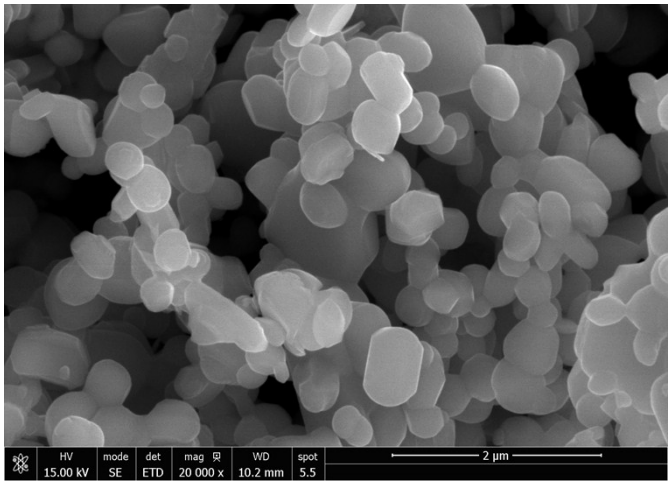
6. High magnification scanning electron micrograghs of $Li_{0.9}CoO_2$ sample before and after high pressure process (up to 20 GPa).



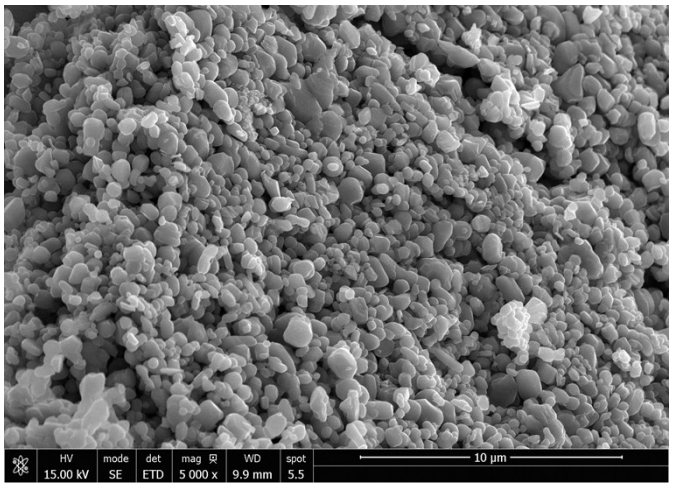
(a)



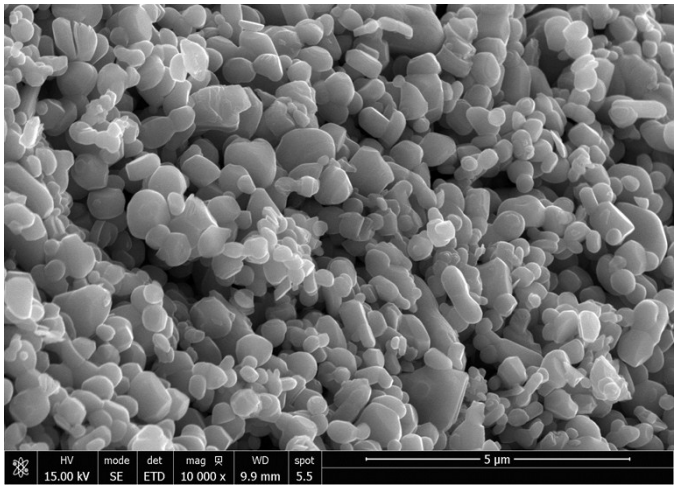
(b)



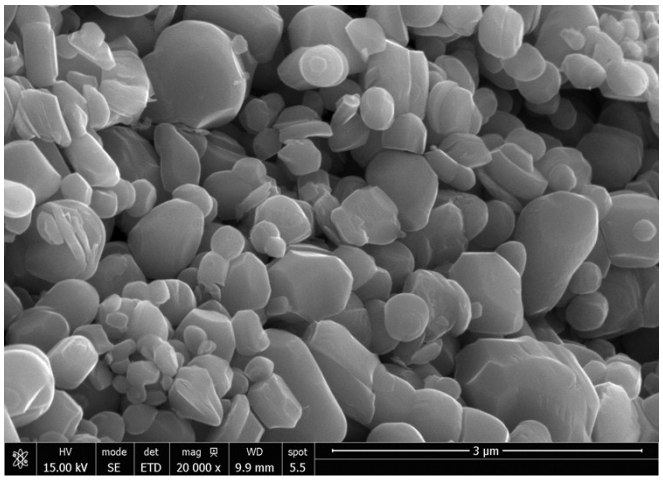
(c)



(d)



(e)



(f)

Fig. S4. High magnification scanning electron micrograghs of $Li_{0.9}CoO_2$ sample before and after high

pressure process (up to 20 GPa). (a-c) photomicrograghs of $Li_{0.9}CoO_2$ before high pressure process with different magnifications ×5000 (a), ×10000 (b), ×20000 (c); (d-f) micrograghs of $Li_{0.9}CoO_2$ after high pressure process with different magnifications ×5000 (d), ×10000 (e), ×20000 (f).