Supplementary Materials for Publication

Sequential Spin State Transition and Intermetallic Charge Transfer in $PbCoO_3$

Zhehong Liu[⊥,〃], Yuki Sakai[§,▲], Junye Yang[⊥], Wenmin Li[⊥,〃], Ying Liu[⊥,〃], Xubin Ye[⊥,〃], Shijun Qin[⊥,〃], Jinming Chen[*,○], Stefano Agrestini[∞], Kai Chen[∞], Sheng-Chieh Liao[∞], Shu-Chih Haw[○], Francois Baudelet[◇], Hirofumi Ishii[○], Takumi Nishikubo[▲], Hayato Ishizaki[▲], Tatsuru Yamamoto[▲], Zhao Pan[▲], Masayuki Fukuda[▲], Kotaro Ohashi[▲], Kana Matsuno[▲], Akihiko Machida[◆], Tetsu Watanuki[◆], Saori I. Kawaguchi,[⊕] Angel M. Arevalo-Lopez[●,#], Changqing Jin[⊥,〃], Zhiwei Hu[∞], J. Paul Attfield[●], Masaki Azuma[*,▲,§] & Youwen Long[*,⊥,〃,⊕]

[⊥]Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

[〃]School of Physics, University of Chinese Academy of Sciences, Beijing 100049, China

[§]Kanagawa Institute of Industrial Science and Technology, 705-1 Shimoimaizumi, Ebina 243-0435, Japan

[▲]Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan

[○]National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30076, Taiwan, R.O.C

[∞]Max-Planck Institute for Chemical Physics of Solids, NöthnitzerStraße 40, 01187 Dresden, Germany

[◇]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin-BP48, 91192 GIF-sur-YVETTE CEDEX, France

[◆]Quantum Beam Science Research Directorate, National Institutes for Quantum and Radiological Science and Technology, Sayo, Hyogo 679-5148, Japan

[●]Centre for Science at Extreme Conditions and School of Chemistry, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, United Kingdom

[⊕]Japan Synchrotron Radiation Research Institute, SPring-8, 1-1-1 Kouto, Sayo, Hyogo 679-5198, Japan

[⊕]Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China

Present addresses

[#]Université Lille, CNRS, Centrale Lille, ENSCL, Université Artois, UMR 8181–UCCS–Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

Corresponding Authors*

*jmchen@nsrrc.org.tw

*mazuma@msl.titech.ac.jp

*ywlong@iphy.ac.cn.

Supplementary Tables

Table S1 Refined Structural Parameters[a] for $PbCoO_3$ at 290 K under Various Pressures Based on the Neutron Powder Diffraction.

P (GPa)	0.093	1.512	2.239	4.684
a (Å)	7.64791(10)	7.61416(9)	7.61391(9)	7.57567(9)
y(Pb2)	0.0277(6)	0.0257(4)	0.0245(5)	0.0288(5)
x(O)	0.5079(6)	0.5089(5)	0.5087(5)	0.5033(23)
y(O)	0.3058(3)	0.3064(2)	0.3047(2)	0.3053(3)
z(O)	0.1997(3)	0.2014(3)	0.1999(2)	0.2007(3)
U_{iso} (Pb1) ($\times10^{-2}$ Å^2)	0.54(16)	1.11(13)	0.70(12)	0.52(22)
U_{iso} (Pb2) ($\times10^{-2}$ Å^2)	0.48(8)	0.75(5)	0.76(5)	0.54(10)
U_{iso} (O) ($\times10^{-2}$ Å^2)	0.69(4)	0.79(3)	0.72(3)	1.13(5)
R_{WP}	0.0265	0.0264	0.0253	0.0297
R_P	0.0248	0.0243	0.0232	0.0240
χ^2	1.173	1.045	1.198	0.009

[a] Atomic sites: Pb1 2a (0, 0, 0), Pb2 12g (1/2, y, 0), Co1 4b (1/4, 1/4, 1/4), Co2 4c (1/4, 1/4, 3/4), O 24h (x, y, z); The occupancy factor was fixed at 1; Atomic displacement parameters U_{iso} for Co1 and Co2 sites were fixed at 0.60×10^{-2} Å^2. Split site model was used for Pb2 site.

Supplementary Figures

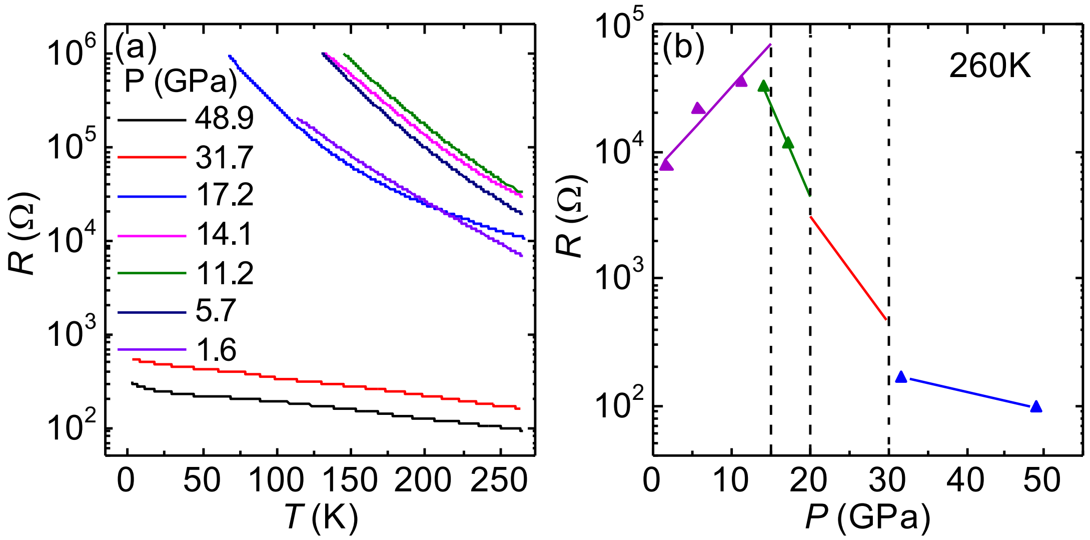

Figure S1 Electrical transport properties of $PbCoO_3$ during pressure release from 48.9 to 1.6 GPa. (a) Temperature dependence of resistance at different pressures. (b) Resistance values under various pressures at 260 K. The triangles show the measurement data, and the lines display the linear fitting results. The red line between 20 and 30 GPa is a guide for eyes since no data was collected in this pressure region during pressure release.

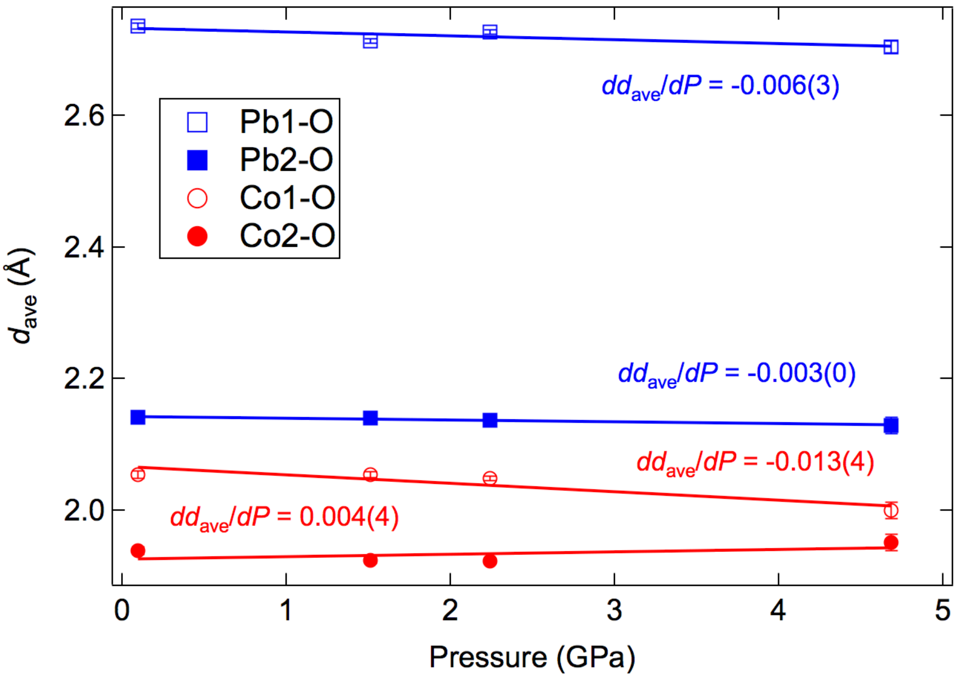

Figure S2 Pressure dependence of the average bond length (d_{ave}) calculated from the structural parameters determined by Rietveld analysis of neutron diffraction data. Pb1, Pb2, Co1, and Co2 represent the sites occupied by Pb^{2+}, Pb^{4+}, Co^{2+}, and Co^{3+}, respectively. Co1-O bond length decreases significantly compared to the other bonds, strongly supporting the continuous HS-LS transition of Co^{2+}.

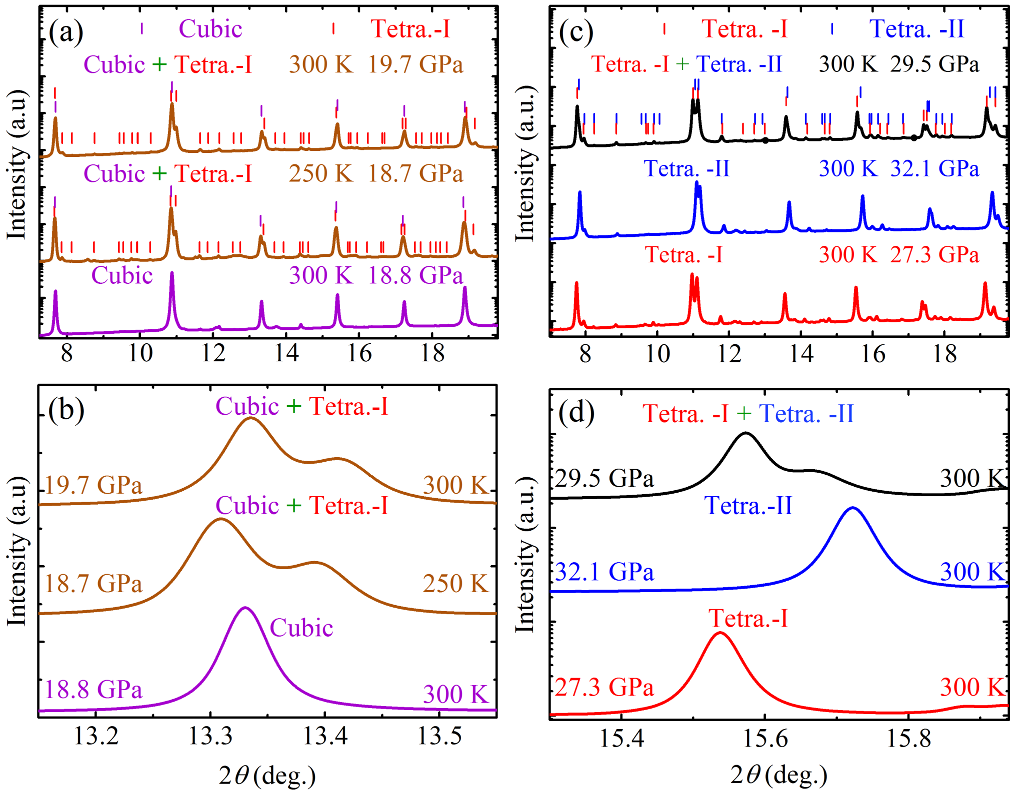

Figure S3 (a) and (c) show the synchrotron X-ray diffraction patterns measured at different temperatures and pressures. The purple, red and blue ticks show the cubic, Tetra.-I and Tetra.-II phases, respectively. (b) and (d) show the enlarged view for SXRD patterns.

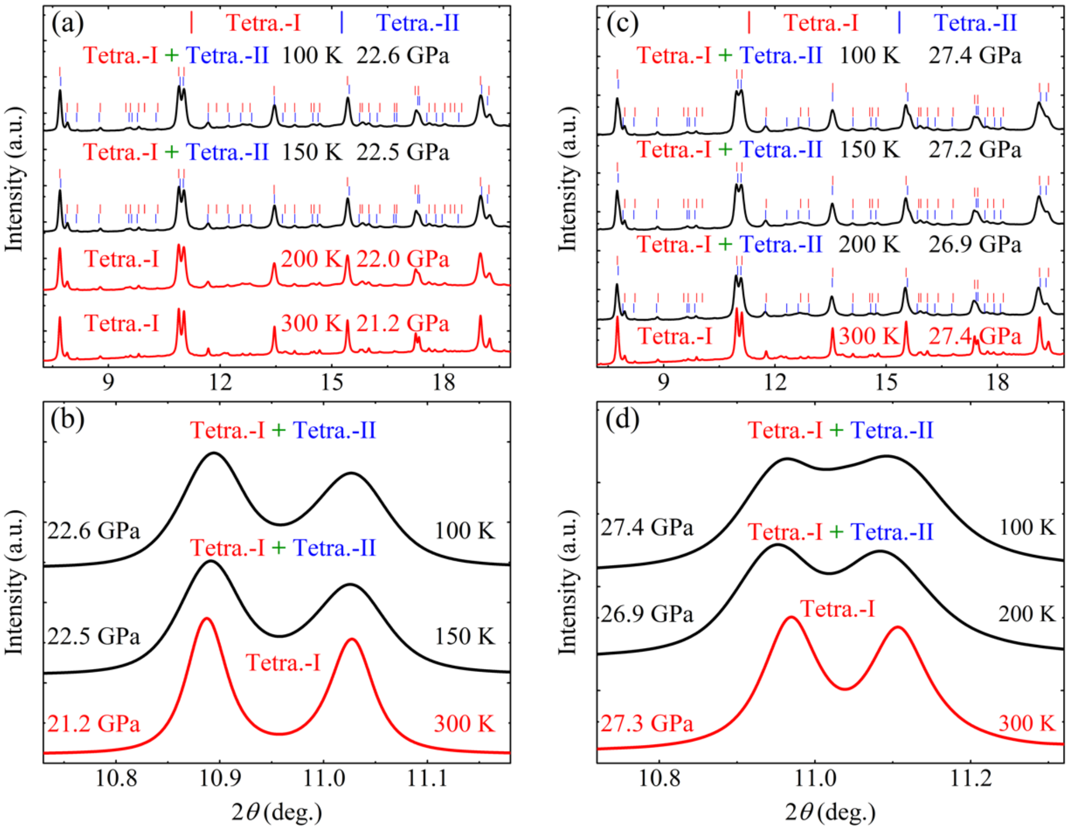

Figure S4 Synchrotron X-ray diffraction patterns measured at different pressures and temperatures. The red and blue ticks in (a) and (c) show the Tetra.-I and Tetra.-II phases, respectively. These two phases coexist on cooling to 150 K at a pressure near 22 GPa, while 200 K near 27 GPa. (b) and (d) show the enlarged view for the main peaks between 10.8° and 11.2°. The remarkable broadening at lower temperatures is indicative of two-phase coexistence.