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Pressure-induced abnormal insulating state in triangular layered cobaltite Li$_x$CoO$_2$ (x = 0.9)

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Lithium cobaltite oxides (LiCoO$_2$) have been serving as an important rechargeable battery material with reversible extraction and insertion of lithium ions. During the charge-discharge process, the lithium amount can be extracted out 50% or more, and the layered structure remains stable with a semiconductor to metal transition at around x=0.7. Static high pressure, as an effective tool to tune crystal and electronic structure, was utilized to the most studied layered Li$_{0.9}$CoO$_2$ compound to investigate the effects on the structural stability and transport properties by synchrotron X-ray diffraction (XRD), electric resistivity, UV-vis absorption spectroscopy, and ab initio calculations. Up to 19.8 GPa, no structural phase transition was observed, but surprisingly its electric transport behavior changed from a semiconductor to an insulating state. The detail XRD and UV-vis spectroscopy analysis reveals that the pressure-induced Co-O bond length shrinkage in the CoO$_6$ octahedron enhances the crystal field splitting, which leads to band gap opening and the decreasing Co-Co distance causes the t$_{2g}$ bands to overlap and the electron holes to be localized. The profoundly different response of the ground state to high pressure indicates an unusual, delicate interplay between the crystal structure and the electronic structure in LiCoO$_2$ and may provide a new route for the development of lithium-ion battery performance with assistance of pressure.

Introduction

With its high voltage, high energy density and excellent cycling stability, lithium cobaltite oxides (LiCoO$_2$) have been widely served as the cathode material for rechargeable lithium-ion batteries (LIBs), stimulating many investigations on the relationships between its structure and properties.\textsuperscript{1,2,3,4} Li$_x$CoO$_2$ forms into a layered structure with Lithium ions inserting between the Co-O layers, where the CoO$_2$ octahedra share their edges and the cobalt ions form a triangular lattice. Li$_{0.9}$CoO$_2$ with a layered α- NaFeO$_2$ structure belongs to the rhombohedral system (space group R-3m) and has Co-O layers and interlayers of Li ions that are alternately stacked along the c axis. The Co-O triangular lattice layer consists of edge-sharing CoO$_6$ octahedra. It is believed that most of the physical properties have a strong connection with the electronic structure of the Co-O layers.\textsuperscript{5,6} X-ray absorption spectroscopy (XAS) studies\textsuperscript{7,8} and angle-resolved photoemission spectroscopy (ARPES) studies\textsuperscript{9} on the delithiated Li$_x$CoO$_2$ (x < 1) revealed that Co is in the 3+/4+ mixed valence state. Both Co$^{3+}$ and Co$^{4+}$ ions stay in their low spin configuration $S = 0$ (t$^{6}e^{0}_{g}$) and $S = 1/2$ (t$^{5}e^{1}_{g}$), respectively. The five Co 3d orbitals split into a lower manifold containing three t$_{2g}$ states and a higher manifold containing two e$_{g}$ states under the octahedral ligand field, and the three t$_{2g}$ orbitals are further split into one a$_{1g}$ orbital and two e$_{g}$ orbitals under the distorted octahedral field. The ligand field splitting is mainly due to anisotropic hybridization between the Co 3d orbitals and the O 2p orbitals and, therefore, the O 2p components are mixed with the Co 3d states. The electronic band structure of Li$_{0.9}$CoO$_2$ (x < 1) shows that the top valence and bottom conduction bands are formed mainly by the hybridized d states of Co and the p states of O, and the Fermi level is located near the top of the Co 3d t$_{2g}$ bands.\textsuperscript{10,11} In delithiated samples, extra electron holes are created in the upper t$_{2g}$ valence bands formed by the overlapping t$_{2g}$ orbitals of Co in the CoO$_2$ octahedral sharing edges, which implies that the geometry of the CoO$_2$ octahedron is strongly connected to the band structure around the Fermi level.

A fundamental understanding of the complicated relationship between the structural and electronic properties of Li$_x$CoO$_2$ is needed to improve battery performance because Li$_{0.9}$CoO$_2$ is a reference compound for a whole family of layered materials obtained by the substitution of other metals for cobalt. Earlier investigations of the Li$_x$CoO$_2$ system showed that the lithium deintercalation process can cause complicated successive crystal phase transitions.\textsuperscript{12-14} For Li$_{0.9}$CoO$_2$, with 0.93 ≤ x ≤ 1\textsuperscript{14,15}, it is a one-phase solid solution domain with a hexagonal structure (Li-rich hex-I); for 0.5 ≤ x < 0.75, there is another one-phase region (Li-poor hex-II); and for 0.75 ≤ x < 0.93, Li-rich hex-I and Li-poor hex-II phases can coexist, which is attributed to an insulator-metal transition upon Li extraction.\textsuperscript{16}

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Electronic Supplementary Information (ESI) available: Text and figures give details of the sample preparation, ICP-AES results, typical Rietveld refinement results, structure optimization, structure parameters of supercell of Li$_x$CoO$_2$ from DFT calculations, distorted parameter $\Delta d$, calculated band gap under various external pressures with different Hubbard $U$, high magnification scanning electron micrographs of Li$_{0.9}$CoO$_2$ before and after high pressure process. See DOI: 10.1039/x0xx00000x
These two phases have the same crystal symmetry (R-3m) and only a small variation in the lattice constants, mainly in the c axis. As highlighted by Menetrier et al., the Li-rich hex-I phase behaves like a semiconductor, while the Li-poor hex-II phase is metallic, implying that an insulator-metal transition occurs at intermediate Li concentrations. Marianetti et al. proposed that this insulator-metal transition is a first-order Mott transition due to the impurities-Li vacancy. A monoclinic phase also appears in a narrow range around x = 0.5, which can be attributed to an interlayer lithium/vacancy ordering. As for the magnetic properties of the Li$_x$CoO$_2$ system, both Li-rich hex-I and Li-poor hex-II phases show Curie-Weiss behavior. Notably, a magnetic anomaly is observed near 175 K at x = 0.67. All these observations suggest that Li$_x$CoO$_2$ exhibits various interesting electronic, magnetic, and thermoelectric properties, depending on the lithium content x.

In this respect, high-pressure can be a very effective, clean tool compared to chemical doping, e.g., modifying the effective bandwidth (W) of the transition metal by changing the M-O bond length and/or the M-O-M bond angle and thereby tuning the electronic and magnetic properties of materials. High-pressure driven transformations of several other electrode materials have been reported, for example, Li$_x$FePO$_4$, Na$_x$CoO$_2$, V$_2$O$_5$, and Li[LixNi$_{1-x}$]O$_2$. As one of the fundamental state parameters, pressure can vary electrochemical properties dramatically compared to the ambient pressure state. Nonetheless, little experimental and theoretical work has investigated the behavior of the layered Li$_x$CoO$_2$ materials at high pressure so far. Wang et al. compared experimental high-pressure structural and vibrational properties to ab initio calculations for pristine LiCoO$_2$ and found that the structure remained layered up to at least 26 GPa at room temperature with a large inhomogeneous compression rate (the c/a ratio decreases by about 5%). To date, less attention has been paid to the electronic properties of LiCoO$_2$, especially the defective cobaltites Li$_x$CoO$_2$ (x < 1) under pressure.

In this work, we report the effect of pressure on the structural and electronic properties of the semiconductor Li$_x$CoO$_2$ with x = 0.90, by synchrotron X-ray diffraction, electric resistivity, UV-vis absorption spectroscopy and first-principles calculations. We found a dramatic increase of electrical resistivity (~ 3 orders of magnitude) and blue shift in the UV-vis absorption spectrum with pressure from 1 bar to 19.8 GPa, while the structural symmetry remained unchanged, which is quite unusual. In most correlated oxides, pressure usually broadens the 3d bandwidth and thereby leads to a transition towards a more conducting state. The opposite effect observed in this work is unique and is apparently connected with different physical mechanisms. We explain this behavior as a consequence of larger crystal field splitting induced by the decreasing Co-O bond length and the $t_{2g}$ bands overlapping due to the decreasing Co-Co distance. Our first principles calculations also provide solid support for this interpretation. The findings uncovered by the comprehensive high pressure investigations provide deep insights into the complex relationship of the crystal structure and electronic performance in this important cathode material, which may be used for guiding the future lithium metal oxides battery industry for better performance.

**Experimental**

Sample Preparation.

The Li-deficient sample Li$_{0.9}$CoO$_2$ was obtained by a two-step approach. The pure LiCoO$_2$ was first synthesized by a previously established method and then the Li-deintercalated sample was obtained via a chemical extraction process from LiCoO$_2$. Chemical delithiation of the Li$_x$CoO$_2$ materials was achieved by stirring the powder in acetonitrile solutions containing NO$_3$BF$_4$ oxidizer in excess. The molar ratio of LiCoO$_2$ and NO$_3$BF$_4$ is 5:1 for preparing Li$_{0.9}$CoO$_2$ samples. After 24 h of lithium extraction at room temperature, the Li$_x$CoO$_2$ powder was washed with acetonitrile several times, and the solutions were removed by centrifugation. The resulting materials were then dried at 80°C. The Li content value x was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The results of the Li content determination are in the Supporting Information Part 1.

**In Situ High-Pressure XRD.**

In situ high-pressure UV-vis absorption spectroscopy

The powdered sample was pressed into a pellet and loaded into a Mao-Bell symmetric diamond anvil cell (DAC) with a pair of 300 µm culet diamonds. The rhenium gasket was pre-indented from a thickness of 250 µm to 40 µm and a sample chamber 160 µm in diameter was drilled in the center of the indented area. Silicone oil was used as a nearly hydrostatic pressure transmitting medium and small ruby spheres were placed in the sample chamber to monitor the pressure. In situ high-pressure X-ray diffraction experiments were performed at the 16BM-D beamline of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL). A focused monochromatic X-ray beam with about 4 µm in diameter (fwhm) and wavelengths of 0.3100 Å was used for the diffraction experiments. The XRD patterns were collected with a MAR 3450 image plate detector. The one-dimensional XRD profiles were analyzed using Rietveld refinements using the GSAS + EXPGUI software packages to obtain the lattice parameters and coordinations of all atoms.

**In Situ High-Pressure Electrical Measurement.**

The electrical resistance measurements under high pressure were performed in a DAC using the standard four-probe method with temperature ranging from 300 K to 80 K cooled with liquid nitrogen. A T301 stainless steel gasket was pre-indented from a thickness of 250 µm to 40 µm and a hole was drilled at the center with a diameter of 250 µm. A fine cubic boron nitride (c-BN) powder was used to cover the gasket to keep the electrode leads insulated from the metallic gasket. The c-BN powder was pressed and further drilled into a central chamber with a diameter of 160 µm, in which the Li$_{0.9}$CoO$_2$ powder sample was loaded. Platinum foils with a thickness of 5 µm were cut into several microns in width and used as electrodes. Four Platinum leads were arranged to contact the sample in the chamber. Ruby spheres were placed around the sample for pressure calibration.

**In Situ High-Pressure UV-vis absorption spectroscopy.**

In situ high-pressure UV-vis absorption spectroscopy measurements were performed on an UV-vis absorption spectrophotometer with a response time of 1 s. The wavelength...
ranged from 400 nm to 800 nm. The intercept of the absorption edge onto the energy axis from a plot $(\alpha h\nu)^2$ versus photon energy ($h\nu$) gives a good approximation of the Li$_{0.9}$CoO$_2$ band gap energy.

**Density Function Theory Calculations.**

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP)$^{34,35}$ based on a generalized gradient approximation with Hubbard U correction (GGA+U)$^{36}$ to the DFT. The PBE$^{37}$ exchange correlation and a plane wave representation for the wave-function with a cut-off of 500 eV were used. Li$_{0.9}$CoO$_2$ calculations were performed with a 2×2×1 supercell (Figure 1 (c)). The Brillouin zone was sampled by 4×4×2 special k-points using the Monkhorst-Pack scheme$^{38}$ for structural optimization, and 7×7×3 for the density of states (DOS) calculation. Because the d orbital plays an important role in transition metals, the U (on-site coulomb term) value for Co-3d was set at 3.32 eV, which is advised by the Materials Project$^{39}$. Ferromagnetically spin-polarized, antiferromagnetically spin-polarized, as well as non-spin-polarized DFT were used to optimize the structures at various values of external pressure, respectively. According to the small energy differences between these magnetic structures, we assumed that Li$_{0.9}$CoO$_2$ was nonmagnetic in our further calculations (Figure S1, Supporting Information).

**Results**

The powder XRD patterns of Li$_{0.9}$CoO$_2$ at various high pressures up to 19.8 GPa are presented in Figure 1 (a). In these patterns, no trace of a new phase was observed, and the original hexagonal structure was preserved to the highest pressure in this research. No disappearance or splitting/broadening of peaks was observed, indicating that the sample was single phase.$^{12,14,18}$ Further detailed investigations were conducted on these XRD patterns with Rietveld refinements to study the atomic positions as a function of pressure. The starting atomic model was based on the pure LiCoO$_2$ structure with space group R-3m. Figure 1 (b) shows the representative Rietveld fittings for Li$_{0.9}$CoO$_2$ with R-3m space group at 0.3 GPa and 14.4 GPa. (c) The atomic model of 2×2×1 Li$_{0.9}$CoO$_2$ supercell.

Figure 1. Crystal structure probed by XRD under pressure up to 20 GPa. (a) Integrated one-dimensional X-ray powder diffraction patterns of Li$_{0.9}$CoO$_2$ at various pressures and room temperature. The incident X-ray wavelength was λ = 0.3100 Å. (b) Representative Rietveld refinements for Li$_{0.9}$CoO$_2$ with R-3m space group at 0.3 GPa and 14.4 GPa. (c) The atomic model of 2×2×1 Li$_{0.9}$CoO$_2$ supercell.
pressure up to 19.8 GPa. The fitting of the pressure-volume data with the third-order Birch-Murnaghan equation of state\(^\text{40}\) yielded the values for the bulk modulus \(B_0\) and its pressure derivative \(B'_0\) as \(B_0=159.4(9)\) GPa and \(B'_0=5.8(4)\). The values of the bulk modulus \(B_0\) and its derivative \(B'_0\) are close to the values of LiCoO\(_2\) \((x=1)\) with \(B_0=149(2)\) GPa and \(B'_0=4.1(3)\).\(^\text{26}\) The obtained value of the ambient pressure unit cell volume \(V_0\) was 95.45 Å\(^3\).

Figure 2 (c) shows the Co-O bond length as a function of pressure. With increasing pressure, the Co-O bond length decreased. Figure 2 (d) describes the volume compression of the CoO\(_6\) octahedron. Upon compression, the Co-O bond length decreased and the interactions between the central Co atom and the O ligands enhanced further, inducing larger crystal field splitting in the CoO\(_6\) octahedron. From a structural perspective, the CoO\(_6\) octahedron in Li\(_{0.9}\)CoO\(_2\) distorted as pressure increased. In the lithium cobaltite oxides family, electrical transport properties have an important connection with the Co-O layers, so we expected pressure to have a significant impact on the electronic properties of Li\(_{0.9}\)CoO\(_2\).

Figure 3 (a) illustrates the temperature dependence of the electrical resistivity \(\rho(P,T)\) of Li\(_{0.9}\)CoO\(_2\) at different pressures up to 15.9 GPa. The data shown in the figure were collected during heating after slowly cooling down to ~80 k in a diamond anvil cell (DAC) using the standard four-probe method. Li\(_{0.9}\)CoO\(_2\) is reported as a narrow-band semiconductor at ambient pressure in earlier studies.\(^\text{3} \) As shown in Figure 3 (a), with increasing pressure to 15.9 GPa, the sample Li\(_{0.9}\)CoO\(_2\) still exhibited a semiconductor behavior in the measured temperature range with an electrical resistivity \((\rho)\) increase of 3 orders of magnitude in the low-temperature region. This means that the electronic charge hopping was significantly reduced with increasing pressure.

As this material belongs to a Li-rich solid solution, the electronic conductivity is thermally activated. We examined the activation energy from the intrinsic region of electrical conductivity \((\sigma)\) in a polycrystalline Li\(_{0.9}\)CoO\(_2\) sample. The \(\sigma\) (in Napierian logarithmic coordinate) vs the 1/T Arrhenius plot in Figure 3 (b) exhibits a linear region in the high-temperature region. The high-T linear region should be attributed to the intrinsic region of \(\sigma\) and can be expressed by \(\sigma = \sigma_0 \exp(-E_a/k_BT)\), where \(\sigma_0\) is the pre-exponential constant, \(k_B\) is the Boltzmann constant, and \(E_a\) is the activation energy. The fit at various pressures gives the intrinsic \(E_a\) values of Li\(_{0.9}\)CoO\(_2\) as a function of pressure, which is plotted in the inset of Figure 3 (b), demonstrating that the activation energy exhibits a nearly linear increase with pressure.

The dramatic increase in the electrical resistivity \((\rho)\) indicates band gap opening under pressure. To confirm this, we utilized UV-vis absorption spectroscopy to measure the pressure dependence of the band gap. As a crystalline semiconductor, the optical absorption near the band edge follows the formula \(\alpha h\nu = A(h\nu-E_g)^n\),\(^\text{41}\) where \(\alpha, h, E_g\) and \(A\) are the absorption coefficient, light frequency, band gap, and a constant, respectively. The value \(n\) depends on the characteristics of the transition in the semiconductor, i.e. \(n = 1\) for direct transition or \(n = 4\) for indirect transition. For Li\(_{0.9}\)CoO\(_2\), the value of \(n\) is 1. The band gap energy \((E_g)\) of Li\(_{0.9}\)CoO\(_2\) can be thus estimated from a plot \((\alpha h\nu)^2\) versus photon energy \((h\nu)\). The intercept of the plot to the X-axis gives a good estimation of the band gap energy.

Figure 4 displays the band gap result from the UV-vis absorption study with pressures up to 19.1 GPa. (a-f) give the
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(ahυ)² versus photon energy (hυ) of the Li0.9CoO2 powder under pressures from 1.7 GPa to 19.1 GPa at room temperature. The red fitted lines give the corresponding band gap estimation shown in Figure 4 (g). We found that the band gap energy of the R-3m Li0.9CoO2 blue shifts with an increase of pressure. The estimated band gap energies of the sample were about 1.29, 1.39, 1.48, 1.49, 1.53, and 1.67 eV for Li0.9CoO2 at room temperature and pressures of 1.7, 7.2, 13.6, 15.6, 18.3, and 19.1 GPa, respectively. This trend is consistent with the electrical resistivity increasing by several orders of magnitude with pressure.

Density functional theory (DFT) calculations were also employed for insight into the main experimental results of Li0.9CoO2. The calculations were extended to volumes corresponding to a pressure of about 40 GPa to see how the structural changes would extrapolate if the layered structure were assumed to be stable over the whole range. Table S3 (Supporting Information) summarizes the calculated structural parameters of the supercell at various pressures. We can see that both lattice parameters (a and c) decreased with increasing external pressure, while lattice parameter c was more sensitive to pressure variation. At 20 GPa, c shrunk by 5.85% while a dropped 2.72%, which is in good agreement with our Rietveld refinement results. The average Co-O bond length and CoO₆ octahedral volume also decreased with increasing pressure, consistent with our experiments. To describe the distortion degree of a CoO₆ octahedron, the distortion parameter Δd is defined as

\[ \Delta d = \frac{1}{6} \sum_{i=1}^{6} \left( \frac{d_i - \bar{d}}{\bar{d}} \right), \]

where \( d_i \) is the length of the \( i \)th Co-O bond and \( \bar{d} \) is the average length of all six Co-O bonds inside the octahedron. 42,43 As shown in Table S3 (Supporting Information), the average Δd is around 3.0 x 10⁻⁵ and varies little with pressure, thus the decreasing Co-O bond length rather than distortion is responsible for the difference of electronic structure under various pressures. The detailed Δd of all CoO₆ octahedrons in the supercell is shown in Figure S2, Supporting Information.

The density of states (DOS) for LiₓCoO₂ under different external pressures is displayed in Figure 5. The projected density of states (PDOS) of Li is not shown here because the contribution of Li to the valence band and the conduction band is notably very small compared to Co and O. As Figure 5 (a) shows, LiCoO₂ is a band insulator with a Fermi level between the filled \( t_{2g} \) states and the unfilled \( e_g \) states. This result is consistent with the reported literature. 6 As Li is partially removed, the electrostatic potential of the Li vacancy will bind the hole, resulting in an impurity band that breaks away from the top of the conduction band.

Figure 4. UV-Vis absorption study of the Li₀.₉CoO₂ band gap under high pressure. (a-f) UV-Vis absorption spectra of Li₀.₉CoO₂ at various pressures from 1.7 GPa to 19.1 GPa. The fitted absorption edges (red lines) provide good estimations of the band gaps. (g) The evolution of the band gap at different pressures from the fitting (a-f).

Figure 5. Density of states (DOS) of LiₓCoO₂ (a) LiCoO₂ at ambient pressure, (b) Li₀.₉CoO₂ at ambient pressure, and (c) Li₀.₉CoO₂ at 20 GPa (d) Li₀.₉CoO₂ at 40 GPa.

(ahυ)² versus photon energy (hυ) of the Li₀.₉CoO₂ powder under pressures from 1.7 GPa to 19.1 GPa at room temperature. The red fitted lines give the corresponding band gap estimation shown in Figure 4 (g). We found that the band gap energy of the R-3m Li₀.₉CoO₂ blue shifts with an increase of pressure.

The estimated band gap energies of the sample were about 1.29, 1.39, 1.49, 1.53, 1.67, and 1.77 eV for Li₀.₉CoO₂ at room temperature and pressures of 1.7, 7.2, 13.6, 15.6, 18.3, and 19.1 GPa, respectively. This trend is consistent with the electrical resistivity increasing by several orders of magnitude with pressure.
the valence band. Consequently, the Fermi level moves down to the edge of the valence band and the band gap decreases, which is shown in Figure 5 (b). Therefore, the band gap of the Li0.9CoO2 is lower than that of LiCoO2 at ambient pressure. With increased external pressure, the conduction band minimum (CBM) moved up while the valence band maximum (VBM) remained still, leading to the band gap opening shown in Figure 5 (c) and (d), which agrees with the trend from our UV-Vis absorption study. It should be noted that the calculated band gap is closely related to the Hubbard U; thus the specific values of the calculated band gap might be quite different from those from experiments. The calculated band gap under various external pressures with different Hubbard U is shown in Figure S3, Supporting Information.

To gain further insight into the microscopic origin of the semiconducting to insulating state transition, it is necessary to characterize the difference of the hole at various pressures. As shown in Figure 6, we plotted the hole density by subtracting the charge density of the partially delithiated structure from that of stoichiometric LiCoO2 while holding all structural parameters constant. The valleys (red) indicate electron accumulation while the hills (blue) denote electron depletion, i.e., hole concentration. It is obvious that the contour lines around the hole move closer together with increasing pressure, indicating that the hole becomes more localized. Both the hole localization and band gap opening induced by high pressure contributed to the insulating state.

**Discussion and Conclusions**

The observation of a strong increase of the electrical resistivity in layered cobalt oxide Li0.9CoO2 $\rho$ (i.e., suppression of electron hopping) with increasing pressure is unexpected and opposes to the results reported on most TMO. There is no structure phase transition in the investigated pressure range up to 20 GPa. The five Co 3$d$ orbitals split into a lower manifold containing three $t_{2g}$ states and a higher manifold containing two $e_g$ states under the distorted octahedral field. Earlier XPS and valence-band UPS studies on the electronic band structure of LiCoO2 and our DFT calculations showed that the Fermi level is located near the top of the Co 3$d$ $t_{2g}$ bands and the electronic states at the Fermi level are dominated by the $a_{1g}$ band. Our calculations also showed that the conduction band minimum (CBM) was dominated by the $e_g$ band. The positions of the $a_{1g}$ and $e_g$ can be largely affected by high pressure through a change of the lattice parameter. The length of Co-O bond decreased with increased pressure, which causes the crystal field splitting to increase, i.e., the unoccupied $e_g$ level shifted upwards and the $a_{1g}$ level shifted downwards; thus the band gap increased. Moreover, the decrease of the Co-Co distance ($d_{Co-Co}$) enhanced the direct $t_{2g}$-$t_{2g}$ orbital overlapping, ensuring the electron holes created in the $t_{2g}$ bands were localized. Therefore, under the effect of band gap opening and electron hole localization, the material exhibited a dramatic increase in electrical resistivity. This interpretation is supported by the experimental observation of blue shift in the UV-vis absorbance spectroscopy with increasing pressure.

In summary, we investigated the effect of pressure on the electronic and structural properties of Li0.9CoO2. We observed an abnormal pressure effect: a transition from a semiconducting state to an insulating state, contrary to our original expectations. This finding is a consequence of a pressure-induced crystal field splitting and $t_{2g}$ band overlapping. The pressure-induced semiconducting to insulating state transition was further confirmed by blue shift in the UV-Vis absorption spectra and $ab$ initio calculations. Our results provide a comprehensive understanding of this type of layered structure material from the lattice, bond length, and electronic configuration perspectives. We expect that the mechanism uncovered here will provide a guideline for finding a strategy to improve lithium ion battery performance.

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**Notes and references**

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