



Revealing the Electronic Origin of Pressure-Induced Isostructural Transformations in $\text{Ca}_3\text{Co}_2\text{O}_6$

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Abstract

Structural peculiarities of $\text{Ca}_3\text{Co}_2\text{O}_6$, including its low dimensionality and inherent geometric frustration, are the main sources of the exotic physical properties observed for this material. Exploring the interplay between the lattice and other electronic degrees of freedom is crucial for understanding the mechanism governing its physical behavior. In this study, we present a comprehensive analysis of the structural features of $\text{Ca}_3\text{Co}_2\text{O}_6$ in a large pressure range of 0–30 GPa, utilizing a combination of x-ray diffraction and Raman spectroscopy, complemented by density functional theory calculations. Notably, we observe several isostructural modifications at 3 GPa, 10 GPa, and 22 GPa, which have not been detected elsewhere. These phase transitions are accompanied by anomalies in the pressure-dependent variation in Ca and O atomic positions and Co–O interatomic bonds. Bader charge analysis also reveals changes in charge redistribution trends among Co, Ca, and O across the phase transitions, suggesting an electronic origin for the pressure-induced isostructural transitions in $\text{Ca}_3\text{Co}_2\text{O}_6$.

Keywords $\text{Ca}_3\text{Co}_2\text{O}_6$ · isostructural transformations · high pressure · Raman spectroscopy · x-ray diffraction · DFT calculations

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Introduction

Spin-chain cobaltite $\text{Ca}_3\text{Co}_2\text{O}_6$ is of great interest due to the emergence of exotic magnetic phenomena resulting from a combination of geometric magnetic frustration and intrinsic low dimensionality in its crystal structure.^{1–5} This material is crystallized in the rhombohedral crystal structure of the $R\bar{3}c$ space group, consisting of chains of alternating oxygen cage faces sharing $\text{Co}^{\text{I}}\text{O}_6$ trigonal prisms and $\text{Co}^{\text{O}}\text{O}_6$ octahedra along the c -axis.^{1–5} Due to the different crystal coordination of cobalt ions, the Co^{O} ions are in the low-spin (LS) state ($S=0$), whereas the Co^{I} ions are in the high-spin (HS) state ($S=5/2$). Moreover, the chains of face-sharing polyhedra are separated by non-magnetic Ca atoms and arranged in a triangular lattice in the ab plane, with strong ferromagnetic (FM) intra-chain interactions that are much stronger than the antiferromagnetic (AFM) inter-chain ones. The competition between the intra-chain and inter-chain interaction, combined with a triangular lattice, leads to complex magnetic ground states in $\text{Ca}_3\text{Co}_2\text{O}_6$.

It is important to note that in geometrically frustrated systems, many different magnetic states are close in energy

and compete for the ground state, making these systems extremely susceptible to small changes in temperature, magnetic field, or pressure. It was established that the ferromagnetic ordering inside the chains of $\text{Ca}_3\text{Co}_2\text{O}_6$ was formed around $T_N \approx 100$ K. As the temperature is lowered, a long-range magnetic order develops below $T_{N1} \approx 25$ K, with peculiar magnetic transitions near 10 K and 7 K.^{6–9} Below T_{N1} , the coexistence of short-range and long-range spin-density-wave (SDW) incommensurate AFM orders with a wave propagation vector $\mathbf{k} = (0, 0, k_z \sim 1.01)$ has been observed.^{6–9} The short-range magnetic order is believed to be due to defects in the long-range SDW structure propagation with stacking faults along the c -axis.² Below $T_{N2} \approx 10$ K, a metastable long-range collinear commensurate AFM order (CAFM) with a propagation vector $\mathbf{k} = (0.5, -0.5, 0)$ emerges, followed by the appearance of an exotic spin-freezing state at 7 K.¹⁰

Furthermore, a sequence of magnetic-field-induced magnetic transitions was observed in these systems.^{6,8,9} The initial SDW state was suppressed under a small magnetic field, accompanied by a phase transition from the incommensurate magnetic structure to the commensurate one. As the magnetic field increases, the commensurate structure transforms to a ferrimagnetic structure having an up-up-down-down configuration among the chains and then transforms to the FM state. A noteworthy field-induced phenomenon in these systems is the appearance of regularly spaced magnetization steps at low temperatures, accompanied by an increase in magnetic hysteresis, which has been ascribed to the quantum tunneling of magnetization.⁹ Each magnetic phase transition, induced by T or H , is accompanied by dielectric anomalies, clearly signaling a magnetoelectric coupling effect and multiferroic behavior.^{6,8,9}

Interestingly, high-pressure neutron diffraction experiments¹¹ revealed that at pressures above 2 GPa, both the long-range SDW and short-range orders are completely suppressed, while the CAFM phase is stabilized. These observed magnetic phenomena are attributed to pressure-induced changes in the balance between intra- and inter-chain magnetic interactions in $\text{Ca}_3\text{Co}_2\text{O}_6$. The rhombohedral crystal structure was reported to remain unchanged across the magnetic phase transition and under pressures up to of 32 GPa.¹¹ However, pressure-induced isostructural transitions without changes in crystal structure symmetry have often been observed in many complex oxides, such as Mn_3O_4 ,¹² RMn_2O_5 ,^{13,14} and BiOCl .¹⁵ Notably, the transitions in these compounds were found to be of electronic origin, related to charge redistribution among ions.^{12–15}

Motivated by these findings, and to gain a deeper understanding of the pressure effect on the structural properties of $\text{Ca}_3\text{Co}_2\text{O}_6$, we performed detailed studies on the pressure-induced behavior of the crystal structure and vibrational features of this frustrated magnetic material in a pressure range

of 0–30 GPa using x-ray diffraction (XRD) and Raman spectroscopy (RS) measurements. The experimentally obtained results were supplemented with density functional theory (DFT) calculations of the structural and electronic properties. As expected, several pressure-induced isostructural transformations were discovered in $\text{Ca}_3\text{Co}_2\text{O}_6$.

Experimental and Computational Methods

The powder $\text{Ca}_3\text{Co}_2\text{O}_6$ sample was synthesized using the sol–gel method as described previously.¹¹ RS experiments were performed using a LabRAM HR Evolution spectrometer with wavelength excitation of 632.8 nm (Horiba, France). The XRD measurements at high pressure were performed utilizing the Xeuss SAXS/WAXS 3.0 system (Xenocs SAS, Grenoble, France) with a Dectris EIGER2 R 500K detector. An x-ray source with Mo K_α radiation of $\lambda = 0.7115$ Å was used. The FIT2D program was utilized to convert two-dimensional XRD images to one-dimensional diffraction patterns.¹³ The XRD data were analyzed using the FullProf software package.¹⁴

The XRD and RS data were collected at room temperature in a pressure range of 0–30 GPa using the Boehler-Almax Plate type diamond anvil cell (DAC). Diamond anvils with culets of 300 μm were used. The sample was loaded into a hole made in a 150- μm -diameter rhenium gasket, which was indented to a thickness of about 30 μm . No pressure-transmitting medium was used. The pressure was measured using the ruby fluorescence method, with an error that typically did not exceed 0.1 GPa. Two-dimensional XRD images were converted into one-dimensional diffraction patterns using the FIT2D software.¹⁶

DFT calculations were performed in a non-spin-polarized framework, utilizing the Quantum ESPRESSO software package.¹⁸ The interaction between core and valence electrons was treated using fully relativistic pseudopotentials, which inherently account for the effects of spin–orbit coupling (SOC) and provide an implicit consideration of the Hubbard U correction.^{19,20} Exchange–correlation interactions were managed using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).²¹ Kohn–Sham wave functions and corresponding potentials were represented by plane wave expansions, with kinetic energy cutoffs set to 50 Ry (680.28 eV) for the wave functions and 500 Ry (6802.85 eV) for the potentials, ensuring computational accuracy. The Brillouin zone was sampled using a uniform $5 \times 5 \times 5$ k -point grid centered at the Γ point, allowing for adequate coverage of reciprocal space. For the structural optimizations, both ionic positions and cell parameters were relaxed with strict convergence thresholds, specifically 10^{-5} Ry/Bohr (2.57×10^{-4} eV/Å) for atomic forces and 10^{-6} Ry (1.36×10^{-5} eV) for total

energy, ensuring that the system reached its ground state configuration.

Results and Discussion

The crystalline properties of the synthesized sample were examined by Rietveld analysis of the XRD pattern collected at ambient conditions. As shown in Fig. 1, the pattern was satisfactorily fitted with a single rhombohedral $R\bar{3}c$ phase. The lattice constants obtained at ambient conditions are $a = 9.0778(4)$ Å and $c = 10.3818(5)$ Å (in a hexagonal system), which are comparable to those reported in previous studies.^{11,22} Furthermore, the Rietveld analysis of XRD data showed that the rhombohedral crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ remained stable under compression across the entire pressure range up to 28 GPa, similar to that observed by Kozlenko et al.¹¹

The pressure-dependent evolution of the lattice parameters and unit cell volume of $\text{Ca}_3\text{Co}_2\text{O}_6$ is displayed in Fig. 2a and b, respectively. Generally, lattice compressibility can

be examined by fitting the lattice compression data to the Birch–Murnaghan (BM) equation of state²³:

$$P = \frac{3}{2}B_0(x^{-7/3} - x^{-5/3}) \left[1 + \frac{3}{2}(B' - 4)(x^{-2/3} - 1) \right], \quad (1)$$

where $B_0 = -V(dP/dV)_T$ and $B' = (dB_0/dP)_T$ are the bulk modulus and its derivative with respect to pressure, respectively, $x = V/V_0$ is the relative change in unit cell volume, and V_0 is the ambient pressure volume. Meanwhile, for the unit cell parameters, in the BM equation, x stands for the cube of the relative change in the lattice parameter $x = (a/a_0)^3$. It is noteworthy that there is a strong correlation between B_0 and its derivative B' , which is the primary reason for the large variation in the reported values of these parameters for many oxides across different measurements.^{13,23,24} Generally, an approach that fixes B' at 4, i.e., the second-order BM equation of state, is commonly used to properly compare compressibility data and monitor phase transitions, which works well for many oxides.^{13,23–26} In addition, the experimental and DFT-calculated lattice compression data for $\text{Ca}_3\text{Co}_2\text{O}_6$ of this study are well fitted with the second-order

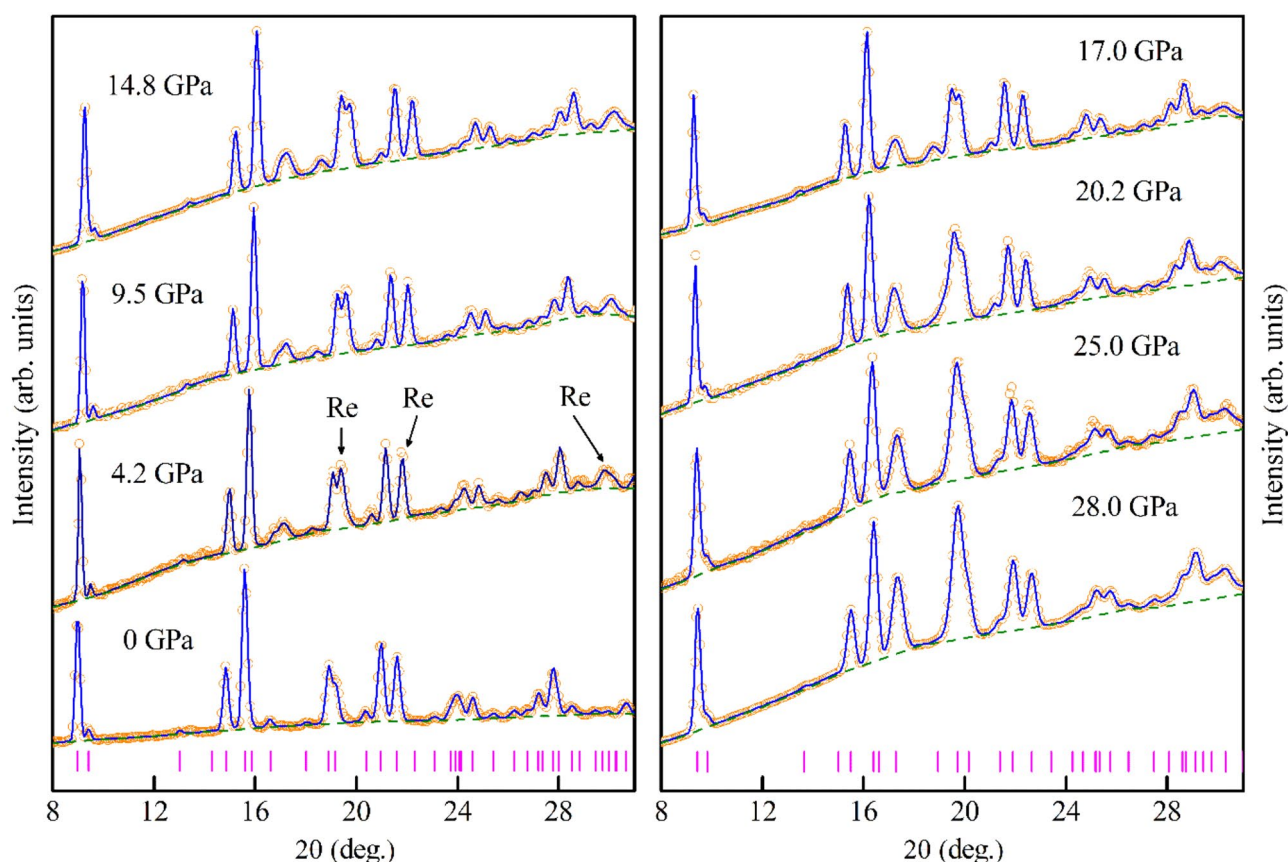


Fig. 1 XRD data of $\text{Ca}_3\text{Co}_2\text{O}_6$ collected at representative pressures and room temperature along with the corresponding Rietveld-fitted curves. The dashed lines indicate the selected background. The struc-

tural peaks for the rhombohedral $R\bar{3}c$ phase of $\text{Ca}_3\text{Co}_2\text{O}_6$ are positioned by vertical ticks. Intense peaks from the rhenium gasket are denoted by *Re*.

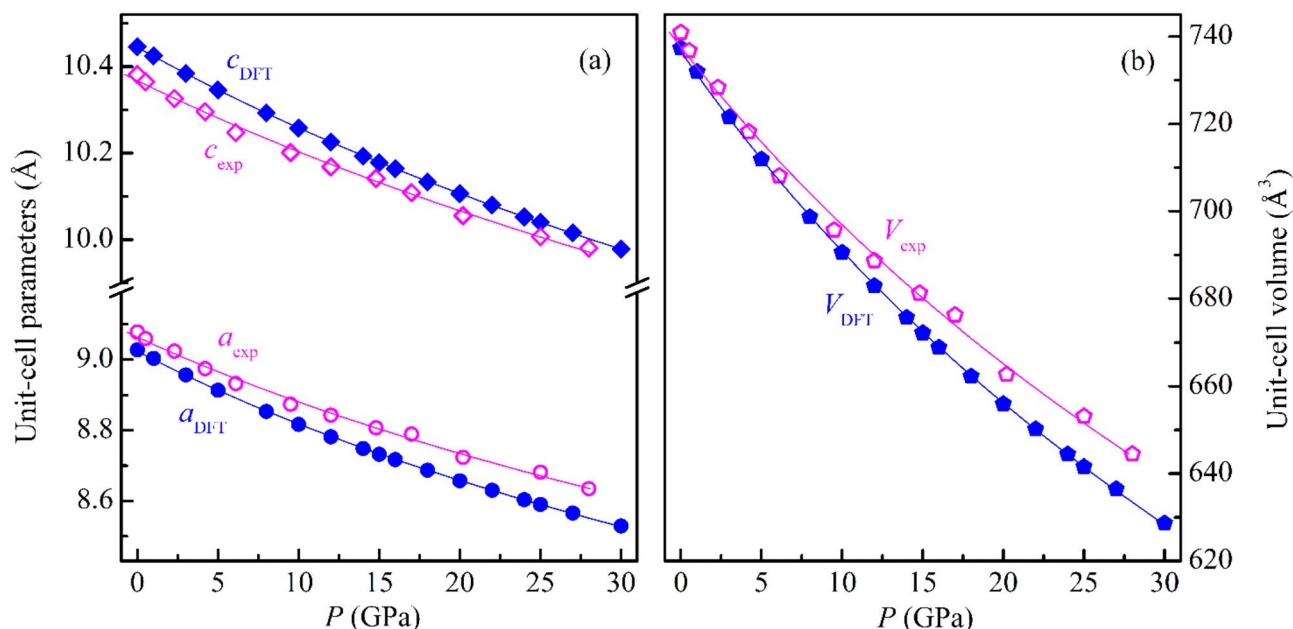


Fig. 2 Pressure-dependent variation in unit cell parameters (a) and volume (b) with their interpolation using the BM equation of state as a function of the pressure. The experimental values are represented

by pink open symbols, while the DFT-calculated values are shown by blue solid symbols (Color figure online).

BM equation of state. Therefore, a similar approach was applied to fit all the available data in this study.

As a fitting result, the bulk modulus B_0 of the studied sample is 157(4) GPa, which is close to that previously reported.¹¹ Similarly, the calculated value of B_0 is $B_{0a} = 144(4)$ GPa for the parameter a and $B_{0c} = 190(5)$ GPa for the parameter c . According to previous studies,^{23,26} the axial compressibility is calculated as follows:

$$k_x = -x \frac{dx}{dP} = \frac{1}{3(B_{0x} + B_x \cdot P)}. \quad (2)$$

The obtained zero-pressure value k_a is 0.0023 GPa⁻¹, which is 1.3 times larger than k_c of 0.0018 GPa⁻¹. Moreover, it is evident from Fig. 4 that there is a gradual increase in the ratio c/a with increasing pressure. The observations imply a significantly anisotropic lattice compression, with compressibility along the c -axis (i.e., along the chains of face-sharing CoO₆ polyhedra) being much weaker than the compressibility in the directions perpendicular to the chains, i.e., along the a and b axes. This can be attributed to the quasi-one-dimensional crystal structure feature of Ca₃Co₂O₆, particularly the lower atomic density in the ab plane.¹¹

Furthermore, to gain a deeper understanding of the evolution of the local atomic structure in Ca₃Co₂O₆ under compression, the RS spectra were recorded at high pressures up to 30 GPa and room temperature, as illustrated in Fig. 3. The RS spectrum of Ca₃Co₂O₆ at ambient conditions exhibits

nine vibrational modes located at 126, 184, 194, 440, 470, 540, 570, 616, and 633 cm⁻¹, which are labeled by their numbers in this order, as depicted in Fig. 3. On the other hand, for the rhombohedral crystal structure with $R\bar{3}c$ symmetry, the group theory predicts 24 Raman-active modes, including 4 A_{1g} and 10 doubly generated E_g modes.²⁷ The A_{1g} modes primarily involve the vibrations of oxygen ions, while the E_g modes involve the vibrations of Co^I ions at the trigonal prismatic sites, and calcium and oxygen ions.^{27,28} The Co⁰ ions at the octahedral sites remain stationary for all Raman-active modes, whereas the Co^I ions participate only in the E_g modes.^{27,28} According to previous Raman studies of Ca₃Co₂O₆-based materials,^{27–29} the lowest frequency modes at 126, 184, and 194 cm⁻¹ can be assigned to the rotational vibration of CoO₆ polyhedra, the bending vibration of Co⁰-Co^I bonds, and the stretching vibration of Ca–O bonds, respectively.²⁹ However, the symmetry assignment of these modes remains unclear. The A_{1g} mode at 470 cm⁻¹ involves bending vibrational modes of the CoO₆ octahedra, while the E_g modes at 540 and 616 cm⁻¹ and the A_{1g} modes of 440, 570, and 633 correspond to the anti-stretching vibrations of the CoO₆ octahedra.^{27–29}

As depicted in Fig. 3a, upon compression, the aforementioned Raman modes shift toward higher frequencies. Notably, the soft mode at $\nu_{10} = 616$ cm⁻¹ displays a sudden shift and then merges with the neighboring higher-frequency mode at $P > 3$ GPa. Additionally, the weak modes at $\nu_{10} = 184$ and 194 cm⁻¹ tend to merge under compression

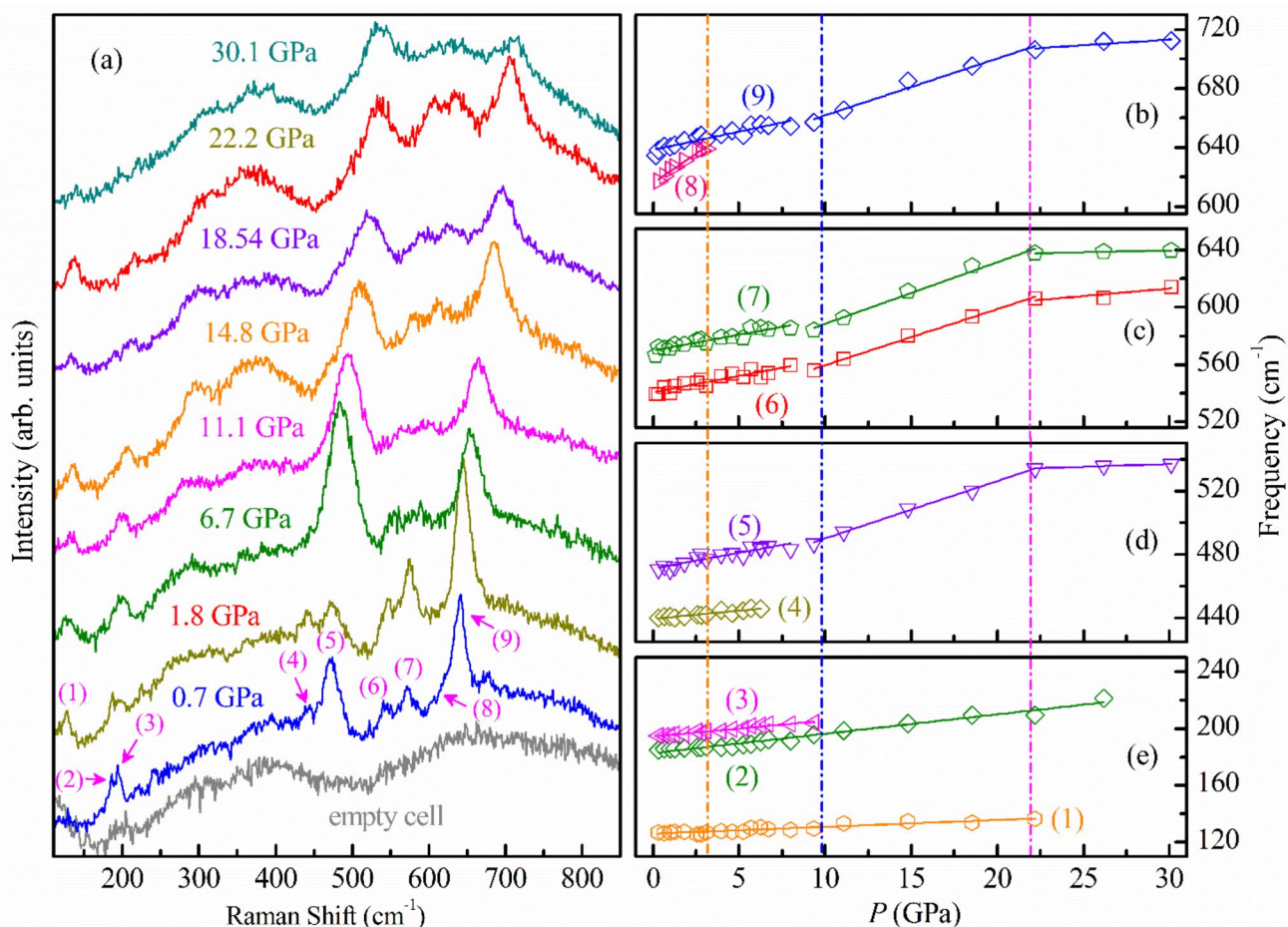


Fig. 3 (a) Raman spectra of $\text{Ca}_3\text{Co}_2\text{O}_6$ measured at selected pressures, with the spectrum from an empty DAC included for comparison of the background conditions in the high-pressure experiment.

(b–e) Vibrational mode frequencies of $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of pressure and their linear interpolations.

and become indistinct above 9.25 GPa. An important feature is the pressure-induced suppression of the intensity of the mode at 440 cm^{-1} , which then disappears at 6.27 GPa. Moreover, as shown in Fig. 3b–e, all the bending and anti-stretching modes exhibit pronounced changes in $d\nu/dP$ around 10 GPa and 22 GPa, while the frequencies of the lower-frequency modes related to the rotational vibration of CoO_6 polyhedra and cationic vibrations increase almost linearly with respect to pressure. As evident from Table I, the bending and stretching modes demonstrate larger shifts than the modes involving the CoO_6 rotations and Ca/Co vibrations. In particular, the pressure coefficient $k_{\nu_i} = (1/\nu_{i0})d\nu_i/dP$ of the mode at $\nu_{i0} = 616\text{ cm}^{-1}$ is 0.0130 GPa^{-1} , which is significantly higher than the $0.0037\text{--}0.0042\text{ cm}^{-1}\text{ GPa}^{-1}$ observed for other bending and stretching modes. The lower pressure coefficient of $0.0032\text{ cm}^{-1}\text{ GPa}^{-1}$ was observed for the rotational mode of CoO_6 polyhedra, a phenomenon usually observed in rare-earth transition metal oxides.¹⁴ It is noteworthy that the pressure coefficient of the mode at 440 cm^{-1} is 0.0023 GPa^{-1} , much smaller than those

Table I Pressure coefficients $(1/\nu_{i0})d\nu_i/dP$ of Raman modes in the different pressure ranges of $\text{Ca}_3\text{Co}_2\text{O}_6$

Mode frequency at 0 GPa (cm^{-1})	$(1/\nu_{i0})d\nu_i/dP\text{ (GPa}^{-1}\text{)}$		
	$P < 10\text{ GPa}$	$10 < P < 22\text{ GPa}$	$P > 22\text{ GPa}$
634	0.0039	0.0061	0.0012
616	0.0130	–	–
570	0.0039	0.0076	0.0004
540	0.0037	0.0073	0.0012
470	0.0042	0.0077	0.0007
440	0.0023	–	–
195	0.0057	–	–
184	0.0047	0.0076	–
126	0.0032	0.0031	–

observed for other anti-stretching and bending modes, yet close to the value obtained for the rotation mode. Therefore, we think this mode is more likely related to rotational vibrations rather than the oxygen anti-stretching vibration, which

was assigned by Gong et al.²⁹ Apart from the anomalous variations in mode frequencies, the characteristic features of the Raman spectra of $\text{Ca}_3\text{Co}_2\text{O}_6$ remain unchanged up

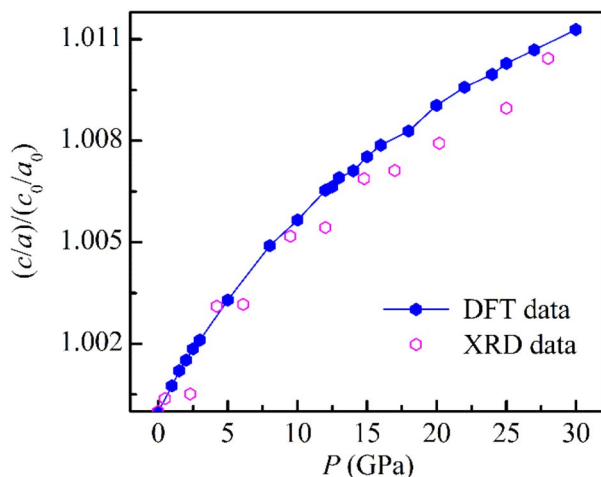


Fig. 4 Relative change in the c/a ratio as a function of pressure, with experimental and DFT-calculated values denoted by pink open and blue solid symbols, respectively (Color figure online).

to 30 GPa, suggesting the occurrence of pressure-induced isostructural transformations in $\text{Ca}_3\text{Co}_2\text{O}_6$.

To gain a deeper understanding of the mechanisms underlying the observed phenomena, we performed *ab initio* DFT calculations of the structural properties. Based on these results, we confirm that the initial rhombohedral crystal symmetry of $\text{Ca}_3\text{Co}_2\text{O}_6$ is preserved under high pressures up to 30 GPa, consistent with the XRD results. The pressure dependencies of the lattice parameters and unit cell volume, calculated from DFT calculations, were added in Fig. 2 for better comparison. It is evident that the calculated values and trends for the lattice parameters are in good agreement with the experimental data. Fitting the DFT lattice compression data yields a bulk modulus B_0 value of 137.0(4) GPa, comparable to the experimentally observed value. Notably, the pressure-dependent variation in the experimental c/a ratio with pressure is also well reproduced by the DFT calculations, as illustrated in Fig. 4.

It is important to note that, in addition to lattice parameters, information on the pressure-induced evolution of atomic coordinates is crucial for understanding the nature of the isostructural transformations observed in $\text{Ca}_3\text{Co}_2\text{O}_6$. However, while XRD can accurately determine lattice constants, the precise refinement of atomic fractional

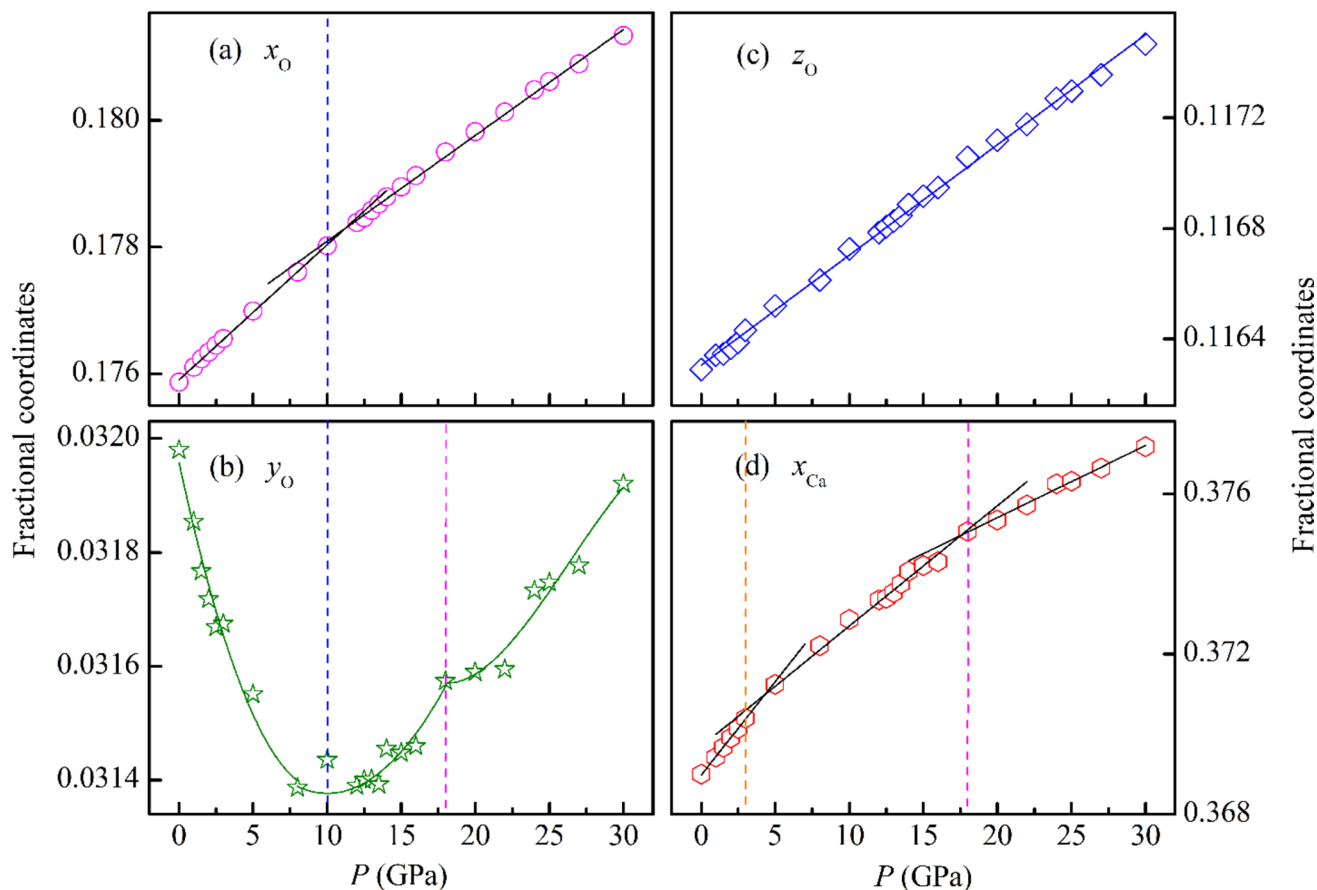


Fig. 5 DFT-calculated fractional coordinates of O and Ca atoms in the rhombohedral structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of pressure.

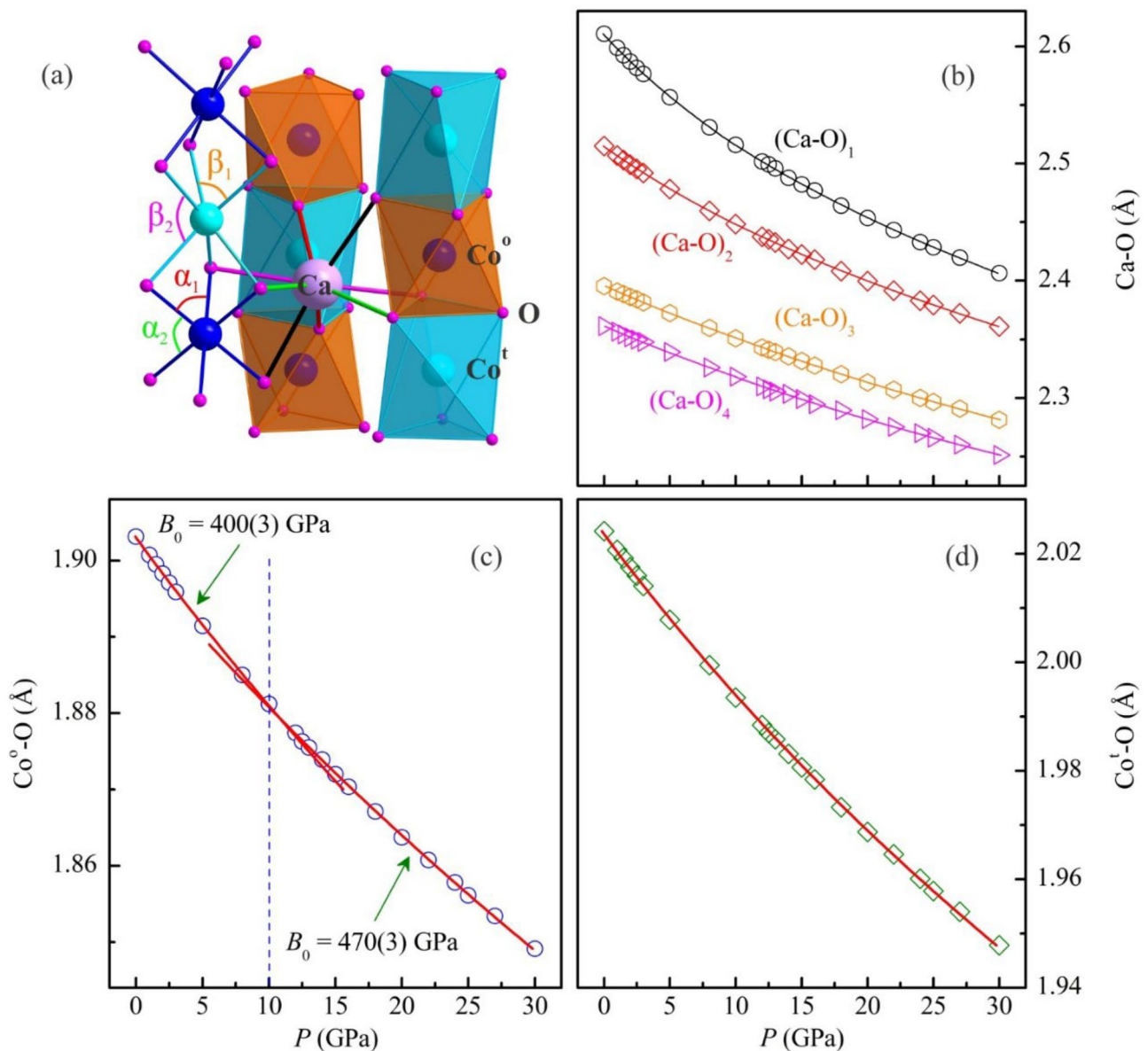


Fig. 6 (a) Structural arrangement of $\text{Ca}_3\text{Co}_2\text{O}_6$ showing three neighboring chains of CoO_6 polyhedra connected by CaO_8 polyhedra. (b–d) Ca–O, $\text{Co}^{\text{O}}\text{–O}$, and $\text{Co}^{\text{I}}\text{–O}$ bond lengths of $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of pressure.

coordinates, particularly for oxygen atoms, is extremely challenging due to the dominant scattering from heavier atoms and suboptimal data quality, especially in high-pressure measurements. Therefore, this information was carefully examined through DFT calculations in this study, and the results are presented in Fig. 5.

As depicted in Fig. 5, the pressure-dependent variations in the atomic coordinates of Ca and O in the rhombohedral crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ demonstrate significant changes around 3.5 GPa, 10 GPa, and 18 GPa, confirming the existence of isostructural transformations, as observed in Raman investigations. Most notable is the non-monotonic

variation in the oxygen fractional coordinate y_{O} (Fig. 5b). This parameter decreases sharply upon compression up to 10 GPa. As the pressure further increases to 30 GPa, it tends to rise, displaying a remarkable change in trend at 18 GPa. In contrast, the oxygen fractional coordinate x_{O} exhibits an obvious change in the slope of its P -dependent curve only near the first transition point at 10 GPa, while z_{O} increases almost linearly under compression without any anomalies. On the other hand, the x fractional coordinate of the Ca atom x_{Ca} increases upon compression, also showing remarkable changes in the slope of its P -dependent curve at the transition points. These observations likely indicate the

pressure-induced alterations in the crystal field environment or shifts in the bonding interactions between Ca, Co, and O atoms. The isostructural transformations might indicate subtle changes in the electronic or magnetic properties of the studied sample. However, it is worth mentioning here that the computations were performed in the spin-unpolarized state, suggesting an electronic origin of the observed isostructural transformations.

Furthermore, the characteristic interatomic distances Co–O and Ca–O and the bond angles O–Co–O were calculated, as illustrated in Fig. 6a, and their pressure-dependent curves are presented in Fig. 6b–f. It is worth noting that all

Table II Compressive modulus B_0 (GPa) for interatomic bonds and polyhedral units of $\text{Ca}_3\text{Co}_2\text{O}_6$, obtained by fitting the second-order BM equation of state to different data ranges

	$0 \leq P \leq 30$ GPa	$P \leq 10$ GPa	$10 \leq P \leq 30$ GPa
Co ^o –O	–	401(3)	470(3)
Co ^t –O	206.8(8)	200(3)	212.2(9)
(Ca–O) ₁	76.1(5)	72.5(5)	78.8(7)
(Ca–O) ₂	109.0(3)	106.0(5)	111.0(5)
(Ca–O) ₃	151.7(7)	158(1)	147.5(6)
(Ca–O) ₄	157.0(7)	161(1)	156(1)
Co ^o O ₆	–	276(2)	326(2)
Co ^t O ₆	–	205(2)	247(1)
CaO ₈	129.8(3)	126.8(4)	132.1(3)
Unit cell	137.0(4)	133.6(3)	139.6(3)

these interatomic distances except Co^o–O exhibit smooth variations in the entire studied range of pressure, which can be fully fitted to the second-order BM equation (1) (Fig. 6). Meanwhile, the Co^o–O distance in the CoO₆ octahedra demonstrates a sharp change in the slope of its P -dependent curve across 10 GPa. The compressive modulus B_0 for this bond was found to sharply increase from 401(3) GPa for $P \leq 10$ GPa to 470(3) GPa for $P \geq 10$ GPa. For comparison, the compressive modulus in each pressure range, below and above 10 GPa, was determined for other interatomic bonds. As can be seen in Table II, the changes in the compressive modulus of other bonds are much smaller than that of the Co^o–O bond. Moreover, the O–Co^o–O bond angles in the CoO₆ octahedra α_1 (α_2), $\alpha_1 + \alpha_2 = 180^\circ$, tend to increase (decrease) toward 90° , indicating that the Co^oO₆ octahedra become more regular under compression (Fig. 7a). Similarly, opposite behaviors of O–Co^t–O bond angles are also observed in the Co^tO₆ trigonal prisms: the bond angle β_1 increases and β_2 decreases with increasing P (Fig. 7b and c). It is worth noting that the magnitude of the pressure-induced changes in O–Co^o–O bond angles β_1 and β_2 are 2.8 and 3.3 times greater, respectively, than other O–Co^o–O bond angles, indicating a significantly larger pressure-induced distortion within the Co^tO₆ prisms. Additionally, as shown in Fig. 7d, the Co^t–O–Co^o bond angle tends to decrease upon compression, with an anomalous change in its slope around 10 GPa.

We also determined the pressure-induced behavior of the volume of CaO₆, Co^oO₆, and Co^tO₆ polyhedra. As shown in Fig. 8, similar to the unit cell volume, the compression

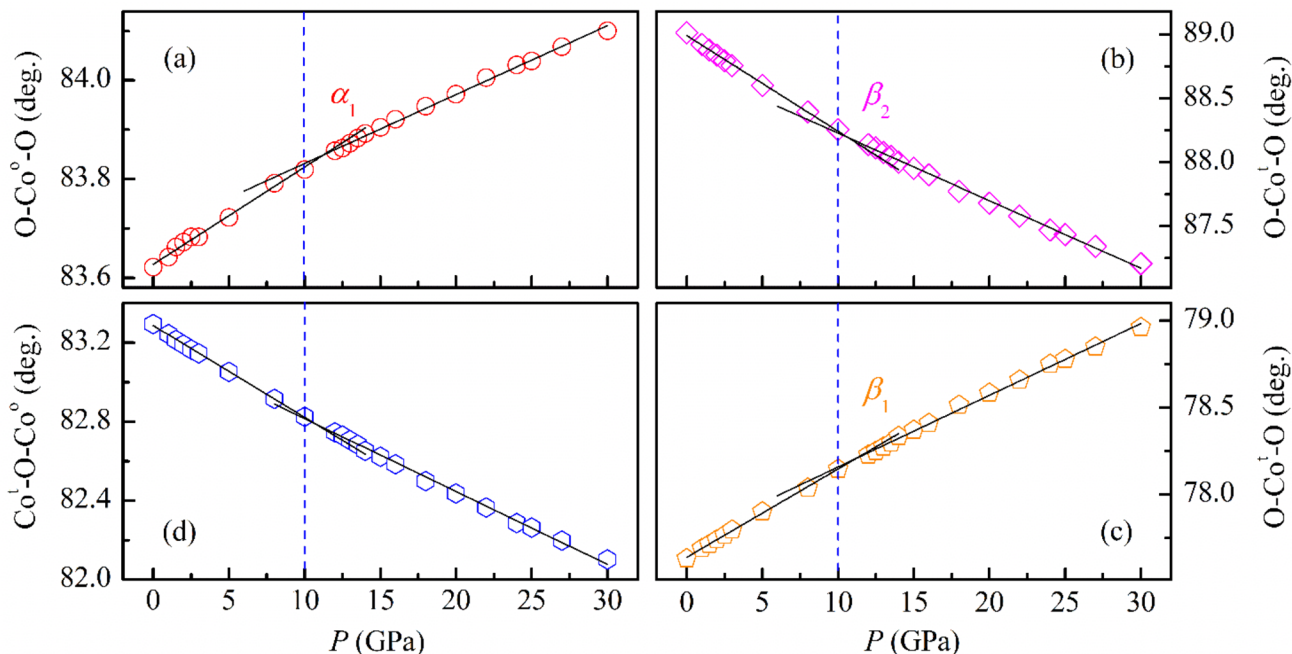


Fig. 7 Pressure-induced variation in characteristic O–Co–O (a–c) and Co–O–Co (d) bond angles of $\text{Ca}_3\text{Co}_2\text{O}_6$.

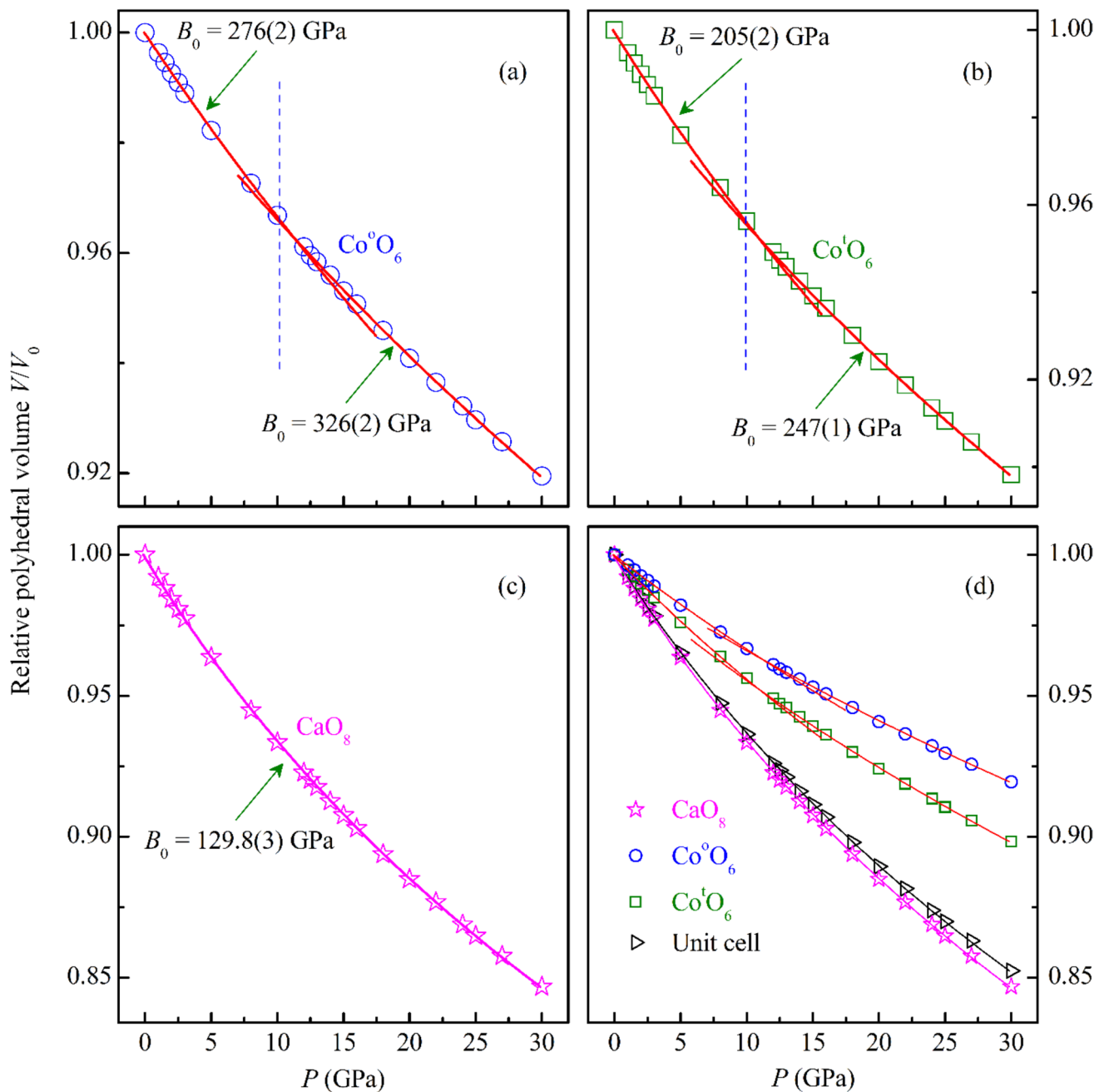


Fig. 8 Normalized volume of CaO_8 , $\text{Co}^\circ\text{O}_6$, and $\text{Co}^\dagger\text{O}_6$ polyhedra as a function of pressure.

data for the CaO_8 polyhedra can be described by a single second-order BM curve with a bulk modulus of $129.8(3)$ GPa, close to that of the unit cell volume (see Table II). This contrasts with the behaviors of the $\text{Co}^\circ\text{O}_6$ octahedra and $\text{Co}^\dagger\text{O}_6$ trigonal prisms (Fig. 8). Across the phase transition at 10 GPa, $\text{Co}^\circ\text{O}_6$ and $\text{Co}^\dagger\text{O}_6$ demonstrate a sharp increase in B_0 of 17.9% and 20.2%, respectively. The largest change in B_0 observed for the $\text{Co}^\dagger\text{O}_6$ trigonal prisms is particularly

noteworthy because the $\text{Co}^\dagger\text{--O}$ bond length did not show any significant changes around 10 GPa. This suggests a pressure-enhanced distortion related to modifications in the $\text{O--Co}^\dagger\text{--O}$ bond angles. Moreover, the close values of the compressive modulus for the unit cell and CaO_8 polyhedra indicates that the compressibility of the quasi-dimensional crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ is primarily due to the compressibility

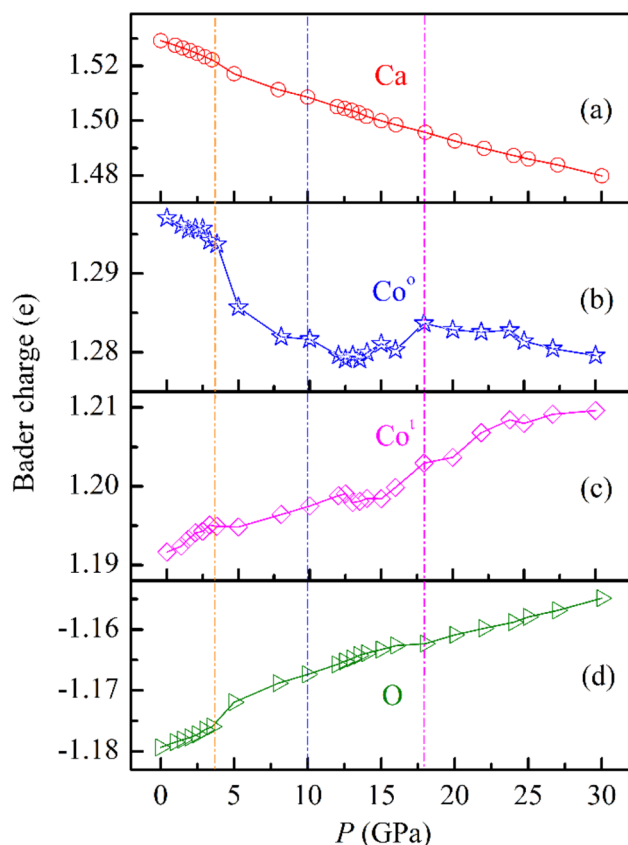


Fig. 9 Evolution of average Bader charge of Ca, Co, and O atoms in $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of pressure.

of the CaO_8 polyhedra, situated between the face-sharing CoO_6 chains.

To clarify the nature of the pressure-induced isostructural transformations of $\text{Ca}_3\text{Co}_2\text{O}_6$, the evolution of Bader charges on each constituent atom in the rhombohedral unit cell of $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of pressure was examined. Figure 9 clearly shows notable anomalies in the pressure-dependent Bader charge curves for Co and O atoms around 3.5 GPa, 10 GPa, and 18 GPa, confirming the electronic origin of the observed isostructural transformations. As depicted in Fig. 9, the Bader charge of Ca ions decreases throughout the entire pressure range, opposite to the behavior observed for O ions. On contrary, the Bader charge on Co^0 and Co^I ions exhibit complex and non-monotonous variations with pressure (Fig. 9).

To gain a deeper understanding of the charge transfer process, the variation in the total pressure-induced change in the Bader charge for each atom type as a function of pressure was examined (Fig. 10). This value is calculated by multiplying the difference between the Bader charge per atom at a given pressure (q_p) and at zero pressure (q_0) by the total number of such atoms in the unit cell (m): $\Delta q = m \cdot (q_p - q_0)$. As seen in Fig. 10, in the pressure

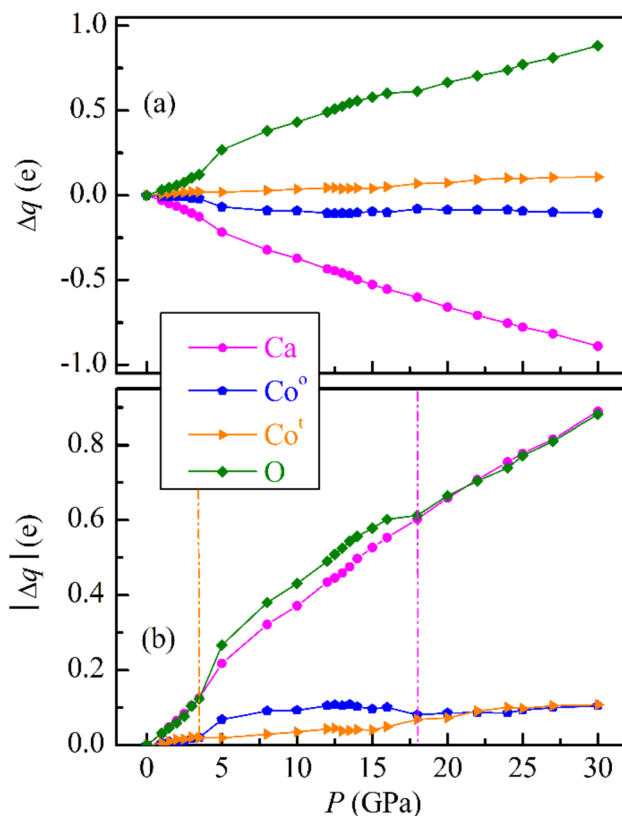


Fig. 10 Total pressure-induced change in Bader charge on Ca, Co, and O atoms Δq (a) and its absolute value $|\Delta q|$ (b) in $\text{Ca}_3\text{Co}_2\text{O}_6$ as a function of pressure.

ranges of $P \leq 3.5$ GPa and $P \geq 18$ GPa, the decreased Bader charge on Ca and Co^0 atoms is balanced by the increased Bader charge on O and Co^I atoms, respectively, which indicates the negative charge transfer from Co^0 to Co^I and from Ca to O upon compression. Notably, in the intermediate pressure range, there is observed evidence of additional charge transfer from Co^0 to O. The change in Bader charge likely alters the configuration of bonding electrons, leading to modifications of interatomic interactions and structural parameters.^{12–15,30} This mechanism may be responsible for the observed anomalous variation in the oxygen fraction coordinates and the isostructural transformations under compression observed in this study.

Conclusions

In summary, the pressure behavior of the structural features of $\text{Ca}_3\text{Co}_2\text{O}_6$ was investigated by means of x-ray diffraction and Raman spectroscopy, complemented by *ab initio* DFT calculations. The results of the x-ray diffraction measurements and DFT calculations indicate that

the initial $R\text{-}3c$ rhombohedral structure is preserved under compression up to 30 GPa. The lattice compression was found to be strongly anisotropic, with more pronounced compressibility within the ab plane, i.e., perpendicular to the spin-chain direction, due to the lower in-plane atomic density. However, Raman vibrational mode spectra demonstrated significant anomalies around 3 GPa, 10 GPa, and 22 GPa. The DFT calculations revealed that these transitions are related to sharp changes in the pressure-induced variation in the O and Ca atomic positions of atoms, as well as Co–O and Ca–O interatomic distances, implying the occurrence of isostructural transformations. Moreover, Bader charge analysis showed a change in the charge transfer trend at these transition points: the charge transfer likely occurs directly from Co^0 to Co^{I} and from Ca to O in the pressure ranges $P \leq 3.5$ GPa and $P \geq 18$ GPa, while an additional charge transfer from Co^0 to O appears in the intermediate pressure range. The observations indicate the electronic origin of the observed isostructural transformations in $\text{Ca}_3\text{Co}_2\text{O}_6$. These pressure-induced effects may also lead to changes in the magnetic properties of this geometrically frustrated magnetic material.

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Conflict of interest The authors declare that they have no conflict of interest.

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