



Investigation of multi-mode spin–phonon coupling and local B-site disorder in $\text{Pr}_2\text{CoFeO}_6$ by Raman spectroscopy and correlation with its electronic structure by XPS and XAS studies

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Abstract

Electronic structure of $\text{Pr}_2\text{CoFeO}_6$ (at 300 K) was investigated by x-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy techniques. All three cations, i.e. Pr, Co and Fe were found to be trivalent in nature. XPS valance band analysis suggested the system to be insulating in nature. The analysis suggested that Co^{3+} ions exist in low spin state in the system. Moreover, Raman spectroscopy study indicated the random distribution of the B-site ions (Co/Fe) triggered by same charge states. In temperature-dependent Raman study, the relative heights of the two observed phonon modes exhibited anomalous behaviour near magnetic transition temperature $T_N \sim 270$ K, thus indicating towards interplay between spin and phonon degrees of freedom in the system. Furthermore, clear anomalous softening was observed below T_N which confirmed the existence of strong spin–phonon coupling occurring for at least two phonon modes of the system. The line width analysis of the phonon modes essentially ruled out the role of magnetostriction effect in the observed phonon anomaly. The investigation of the lattice parameter variation across T_N (obtained from the temperature-dependent neutron diffraction measurements) further confirmed the existence of the spin–phonon coupling.

Keywords: Raman spectroscopy, x-ray photo-emission spectroscopy, neutron diffraction, spin–phonon coupling, x-ray photo-absorption spectroscopy

(Some figures may appear in colour only in the online journal)

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Introduction

To meet the increasing need for the next generation spintronic devices, multi-functional materials which respond to various external stimuli, e.g. magnetic field, electric field, pressure, etc are required. Particular attention has been given to look for the materials showing strongly coupled magnetism and electrical behaviours [1–4]. In this regard, the materials with double perovskite (DP) structure i.e. $R_2BB'O_6$ (R = rare earth and B and B' = transition metal) are of particular importance owing to their diverse fundamental and fascinating physical properties including near room temperature ferromagnetism, large magneto-dielectric effect, giant magneto-resistance, giant exchange bias, magneto-caloric effect etc [3–6]. Hence, such compounds have provided new frontier in material research and opened up ample opportunities for a broad spectrum of potential applications including sensors, spin filter junctions, memory devices, etc [7, 8]. Depending upon the B/B' -site ordering, the DPs are found to crystallize mainly into two types of structures: (1) the ordered monoclinic structure with $P_{21/n}$ symmetry (2) the B -site disordered orthorhombic structure with $Pnma$ symmetry [9, 10]. Eventually, the ordered DPs show the ferromagnetic (FM) behaviour owing to 180° super-exchange interactions $B^{2+}-O^{2-}-B'^{4+}$ (typically $B = \text{Co/Ni}$ and $B' = \text{Mn}$) but co-existence of B^{3+}/B'^{3+} ions (as a disorder) introduces the competing anti-ferromagnetic (AFM) interactions [5, 11]. However, despite the intense research interests and meticulous investigations on such DPs, complete understanding of its electronic structure is still far from well understood. Again, the self-ordering of the B/B' site ions in ordered DP occurs when these two ions have significant difference in their ionic radii and the charge states [9, 10]. Conversely, B -site disorder occurs for same charge states of B -site ions. Eventually, site disorder of a system is known to have profound effects on its physical properties which offered a fertile ground for theoretical research and called for rigorous experimental investigations world-wide [5, 11–16]. Moreover, few members of the ordered FM DPs exhibit spin–phonon coupling due to existence of competing nature of spin and phonon degrees of freedom [6, 9, 16, 17]. In fact, coupling between the magnetism (spin) and lattice (phonon) is one of the crucial mechanisms for the coupling between magnetic and electric orders in solids. Thus, to elucidate the magneto-electric coupling phenomena, probing the spin–phonon coupling can be an effective tool. For the strongly correlated oxide systems in which multi-functional properties are observed due to the presence of coupling between different properties, e.g. spin–phonon coupling, electron–phonon coupling etc, Raman spectroscopy can be a sensitive gauge for monitoring such coupled degrees of freedom [17–20].

Eventually, the Co/Ni/Mn -based ordered FM insulating DPs have been extensively studied in the past few years [5, 10, 11, 15]. On the other hand, the studies on the Fe based DPs are relatively limited, and hence much more possibilities are there to explore its physical properties [21–24]. In our previous work in a Fe based DP $\text{Pr}_2\text{CoFeO}_6$ (PCFO), the B -site disorder was seen to play a crucial role in bringing out a number of interesting phenomena including Griffiths like

phase in G -type anti-ferromagnetic background ($T_N \sim 269 \text{ K}$), re-entrant cluster glass behaviour, exchange bias, etc [25].

However, a comprehensive study deciphering the existence of spin–phonon coupling in such disordered AFM DP system PCFO is hitherto unreported, thus it can be interesting to study its temperature-dependent Raman spectra to unravel how magnetic ordering affects phonon modes in PCFO. Besides, Raman study is also helpful in getting an insight into the B -site cationic ordering in the system.

The local valance states of the B/B' site ions are strongly correlated to its cationic ordering; thus a prior understanding of its electronic structure can eventually help in further explorations of the origins of its different properties. On the other hand, both the x -ray photoemission spectroscopy (XPS) and x -ray absorption spectroscopy (XAS) are the widely used versatile and powerful techniques to probe the elemental composition and their nominal chemical states of a compound. In XPS study of a system having open-shell ions, the coupling between the open-shell and a core electron vacancy bring out multiplet structure which can effectively reveal the electronic structure of it. Apart from the main photoelectron spectral lines in XPS, the accompanying satellite shake-up peaks, chemical shifts and relative intensities of the core level peaks can be used to get precise information of nominal valance states, ligand co-ordinations and other electronic structure considerations. In XAS, the incident x -ray photon excites an electron in the core level to an unoccupied conduction level following the intra-atomic dipole selection rule. Like XPS, the XAS is used for the analysis of the oxidation states of the elements of a material. However, additionally, XAS has an intrinsic capability to sense the spin-states of ions precisely. This information of spin state remains embedded in the same multiplet structure which is used to specify the presence of different charge states. Eventually, in the present PCFO system, one end member is PrCoO_3 belonging to the cobaltite RCoO_3 family which have drawn considerable attention due to its inherent spin degree of freedom in addition to the other degrees of freedom viz., charge, orbital and lattice [26–28]. This emerges due to the three different energetically (merely) degenerate possible spin configurations of the Co^{3+} ions i.e. low (LS $t_{2g}^6 e_g^0$), intermediate (IS $t_{2g}^5 e_g^1$) and high (HS $t_{2g}^4 e_g^2$) spin states. For PrCoO_3 , it is still under debate whether the spin state remains in the low spin state (LS) or goes to higher spin states (high or intermediate) up to 300 K [28]. Although extensive studies on the electronic structure of the system LaCoO_3 can be found in literature, works on the PrCoO_3 system are particularly limited and needs much more efforts to understand its electronic structure. Unlike LaCoO_3 (absence of $4f$ electrons), PrCoO_3 contains two $4f$ electrons which effectively contribute in its valance band structure. Again, in LaCoO_3 , the crystal field splitting is found to be of the order of exchange interactions. However, for PrCoO_3 system, substituting smaller ions Pr^{3+} in the place of La^{3+} essentially increases the chemical pressure and this in turn transforms the structure from rhombohedral to orthorhombic symmetry leading to the lattice distortion. This is expected to have a direct effect on the hybridization process near Fermi level and thus affecting the bandwidth of the

valance band. Also, the effective Co–O bond length in PrCoO_3 gets decreased and thus it is expected to enhance the crystal field splitting. This altered crystal field splitting energy competing with the Hund's coupling energy can also affect the spin states of the Co^{3+} ions. However, to date no report on the electronic structure of $\text{Pr}_2\text{CoFeO}_6$ is available in literature; this provoked us for investigating its electronic structure.

In the present work with PCFO, we have thoroughly investigated its room temperature electronic structure by XPS as well as XAS studies and phonon behaviour by temperature dependent Raman measurements.

Experimental details

The polycrystalline sample of PCFO was synthesized by the conventional solid-state reaction route which was described elsewhere [25]. The structural analysis yielded a distorted orthorhombic structure (Pnma) [25]. The XPS data was recorded by an Omicron multi-probe surface science system which is well-equipped with a hemispherical electron energy analyzer (EA 125) along with a monochromatic x-ray source Al-K_α line with photon energy 1486.70 eV. The average base pressure was maintained at a value of $\sim 2.8 \times 10^{-11}$ Torr. The total energy resolution as calculated from the width of Fermi edge was about 0.25 eV. The XAS measurements were performed at the BL14 beamline of Hiroshima Synchrotron Radiation Centre, Hiroshima University, Japan. The total electron yield mode has been used as it requires relatively easy experimental setup and gives high signal to noise ratio. Raman spectra were recorded in a Renishaw inVia Raman spectrometer with 532 nm line of a diode pumped solid state laser delivering power of 5 mW mm^{-2} . To control the temperature of the sample, it was kept on a quartz sample holder which was put on the heating/cooling sample cell (THMS-600) connected to temperature control stage (TMS94). The incident laser beam was focused on the sample through the transparent window of the THMS-600 by a $50 \times$ short distance objective attached to the Leica DM 2500 M microscope. Backscattering geometry was used to collect the scattered beam through the same objective, and a 2400 grooves mm^{-1} grating was used as the dispersion element. The spectra were recorded with a spectral resolution of $\sim 1 \text{ cm}^{-1}$.

Results and discussions

X-ray photoemission spectroscopy study

We have investigated the electronic states near the Fermi level of PCFO by XPS study at 300 K. Figure 1(a) shows the survey spectrum of PCFO system, wherein specifications of the all peaks have been assigned according to the National Institute of Standards and Technology (NIST) database. It reveals that Pr, Co, Fe, and O are present at the surface of PCFO. However, the presence of any other elements except C was not detected from the spectrum, thus confirming the purity of the sample. The presence of C can be attributed to the adventitious molecules absorbed at the surface from the air. We have analyzed the XPS data by correcting the observed

binding energies of the elements by referencing the C 1s line at 284.8 eV to eradicate the charging effect. Figure 1(b) depicts the core level XPS spectrum of Pr3d region which comprises of two main (spin–orbit coupling) peaks $\text{Pr}(3d_{5/2})$ and $\text{Pr}(3d_{3/2})$ at $\sim 933.3 \text{ eV}$ and $\sim 953.7 \text{ eV}$ respectively. Two additional exchange splitting peaks ($\Delta E \sim 4.8 \text{ eV}$) are also observed at energies $\sim 928.5 \text{ eV}$ and $\sim 948.9 \text{ eV}$ [29]. These two exchange splitting peaks are produced due to the strong mixing of the final states (although in its ground state, Pr^{3+} has $4f^2$ configuration) $3d^0 4f^2$ and $3d^9 4f^3 h$ (h represents hole in $O2p$ valance band) through the co-valency hybridization [29]. Another clear feature denoted by m can be clearly observed above $\text{Pr}3d_{3/2}$ main peak (such feature is absent in $\text{La}3d$ XPS spectra). This feature m is seemingly associated to the multiplet effect [29]. All the above features strongly suggest the trivalent oxidation state of Pr ions. Moreover, for neutral Co atoms, Co 2s peak appears at 925.1 eV which should lie at slightly higher energy for Co^{3+} ions [30]. However, the states $\text{Pr} 3d_{5/2}$ and Co 2s have a theoretical cross-sectional area ratio of ~ 8 [30]. Whereas, the integrated areas under the experimental XPS peaks at $\sim 933.3 \text{ eV}$ and $\sim 928.5 \text{ eV}$ have a ratio of ~ 2.59 . Thus, if we assume that 933.3 eV peak is arising due to the $\text{Pr}3d_{3/2}$ while 927.5 eV peak is due to the Co 2s state, the area ratio of these two curves (~ 2.59) is in sharp contrast to the theoretically expected ratio (~ 8). Additionally, the theoretical area ratio of the main Pr3d and its exchange splitting peaks is 2:1 which is close to our observed value (2.59:1). Hence, the observed feature can be ascribed to the predominant contribution from Pr3d states.

Even though the XPS analysis is a surface sensitive technique but due to having the large mean free path of photoelectrons coming from cobalt ($\sim 1.5 \text{ nm}$ for $E_K^{\text{in}} = 700 \text{ eV}$), the Co2p XPS spectra has the ability to provide multiple information viz., charge and spin states, etc. Figure 1(c) depicts the core level Co2p XPS spectrum mainly consisting of two spin–orbit splitting peaks centered at $\sim 779.6 \text{ eV}$ ($2p_{3/2}$) and $\sim 794.7 \text{ eV}$ ($2p_{1/2}$). For Co-based compounds, the study of the XPS spectra is important since it contains shake-up satellite peaks which are highly sensitive to cation valency, ligand coordination etc [31–33]. The underlying physics of the shake-up satellite process in the 2p core level XPS spectra involves the screening of a core-hole through charge transfer from the ligand or sp orbitals. In its process, of the two competing channels leading to the final (excited) states: one is associated to the screening of the core-hole via charge transfer from ligands to the 3d orbitals leading to the well-screened state i.e. the main photoelectron peak. The other channel leading to the poorly-screened state corresponds to the shake-up satellite peaks (here the charge compensation occurs via sp orbitals instead of ligands). Eventually, the Co2p XPS spectra for high spin Co^{2+} ions in CoO exhibit such strong satellite structures positioned at $\sim 7 \text{ eV}$ above main peaks [31–33]. On the contrary, the low-spin Co^{3+} ions in octahedral co-ordination viz., Co_2O_3 , LiCoO_2 etc typically do not show any charge-transfer satellite or show it with very low intensity (compared to the Co^{2+} in CoO) [32, 33]. This happens for Co^{3+} due to the reduced charge transfer energy and enhanced Co3d- $O2p$ hopping strength as compared to the Co^{2+} case. Hence,

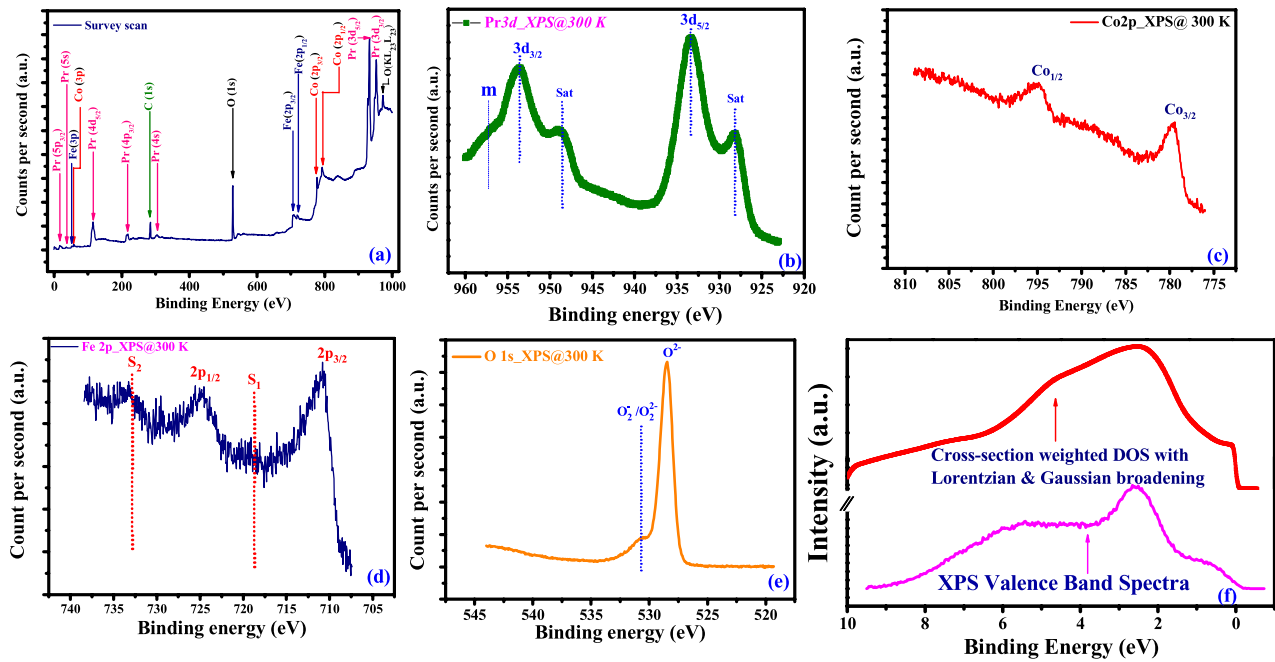


Figure 1. (a) XPS survey scan of PCFO. Core level spectra of Pr3d, Co2p, Fe2p, O1s are depicted in figures (b)–(e) respectively. Figure (f) represents the theoretical cross-section weighted DOS with Lorentzian and Gaussian broadening (upper panel) and XPS valence band spectra of PCFO (bottom panel).

observation of the mere absence or very weak feature of such satellite peaks in our Co2p XPS spectrum further suggests the presence of octahedrally coordinated Co³⁺ ions [32, 33]. Again, the spin–orbit coupling of the observed spectra ($\Delta E \sim 15.1$ eV) is also found to be consistent for Co³⁺ ions (as for Co²⁺ ions, it is ≥ 16 eV) [33].

In figure 1(d), the Fe 2p XPS spectra of PCFO are shown. It comprises two main peaks, positioned at ~ 710.9 eV ($2p_{3/2}$) and ~ 724.6 eV ($2p_{1/2}$) with $\Delta E \sim 13.7$ eV which are consistent with Fe ions with nominal valance state +3 [34]. Two shake-up satellite peaks marked as S_1 and S_2 are observed at positions ~ 718.8 eV and ~ 732.9 eV respectively. In principle, these satellite peaks appear due to charge transfer between the ligand site (O^{2-}) and metal ion Fe^{3+}/Fe^{2+} site. Since, different Fe ions viz., Fe^{2+} and Fe^{3+} have different electronic configurations (d^6 and d^5), it raises the satellite peaks at different positions (thus treated as hallmark). The Fe2p XPS spectra containing Fe^{2+} ions always show satellite peaks at ~ 6 eV higher than the main peaks whereas that containing Fe^{3+} ions show satellites at ~ 8 eV higher than main peaks [34]. Hence, trivalent Fe ions in PCFO can be inferred.

The core level O 1s spectra are shown in figure 1(e). The spectra consist of a strong peak at ~ 528.5 eV and a weak feature at ~ 530.8 eV. The first sharp peak at ~ 528.5 eV is the characteristic feature of the lattice oxygen ' O^{2-} '. However, the small peak at ~ 530.8 eV is ascribed to the oxygen species that contain fewer electrons due to the adsorption of oxygen leading to the formation of reduced electron rich species O_2^{2-} , O_2^- or O^- [35].

To get more insights into the electronic structure of Pr_2CoFeO_6 , we have also recorded valance band (VB) spectra near the Fermi level (figure 1(f)). Furthermore, we have also simulated the experimental VB spectra with the theoretically obtained partial density of states (by DFT calculations)

weighted by the atomic photoemission cross-section followed by binding energy dependent Lorentzian (accounting for the photo-hole lifetime broadening) and Gaussian (to account for the experimental resolution broadening) broadening which have been shown in figure 1(f) [30]. Both the experimental and the theoretical spectra showed the presence of weak spectral weight near the Fermi level indicating the insulating nature of the sample. Below Fermi level, the occupied spectral weight shows the most intense feature around ~ 2 eV for both of the spectra. This most intense feature is then followed by a shoulder like tail extending upto ~ 10 eV. The contrast between the most intense feature and its adjacent shoulder is conspicuous in the experimental spectra as compared to the theoretical one. This may be due to the errors incurred in the simulation of the experimental spectra which use the atomic values for the photoemission cross-sections which is a bad approximation for the photoemission matrix elements relevant for the itinerant valance states. As a matter of fact, the main contribution in forming the valance band is coming from O2p, Co3d, Fe3d and Pr4f orbitals. The most intense feature around ~ 2 eV is arising mainly due to the hybridization of Co3d, Fe3d and Pr4f with O-2p orbitals with significant proportion being from the Pr4f. On the other hand, the feature near the Fermi level (0–1 eV) is mainly associated with the extended Co/Fe3d orbitals. While the broad shoulder like feature above the most intense feature can be mainly ascribed to the hybridization of O2p and Co/Fe3d states and other contributions, e.g. O2p-Co/Fe 4sp and O2p-Pr 5sd oxygen bonding states.

X-ray absorption spectroscopy study

Figure 2(a) demonstrates the Co 2p XAS spectrum (at 300 K) related to the photo-absorption from Co2p core level to the Co 3d unoccupied level. The spectrum is comprised of two

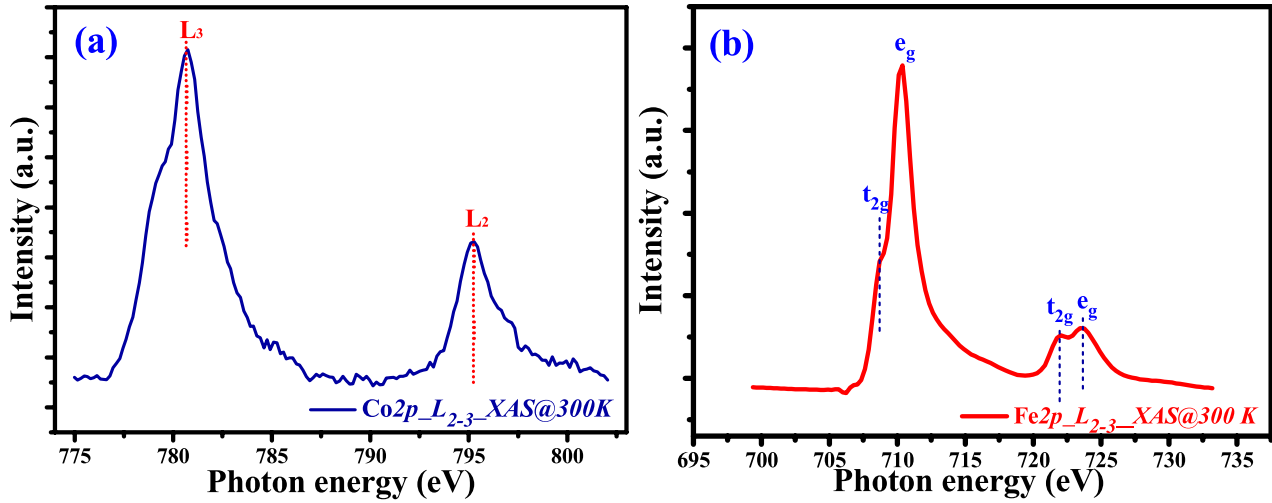


Figure 2. (a) and (b) show the room temperature XAS spectra at Co L_{2-3} and Fe L_{2-3} edges respectively.

main peaks $CoL_3(2p_{3/2})$ and $CoL_2(2p_{1/2})$ at ~ 780.7 eV and ~ 795.2 eV, respectively. The separation of these two peaks is associated to the spin-orbit (SO) coupling ($\Delta E \sim 14.5$ eV). The line shape and the peak positions of the observed $Co2p$ XAS spectra clearly suggest presence of trivalent Co ions in PCFO which is consistent with XPS data analysis [27]. No trace of a pronounced peak at ~ 777 eV corresponding to Co^{2+} ions can be observed from figure 2(a). This directly rules out any possibility of presence of any divalent Co ions in PCFO. Factually, the $Co2p$ XAS spectra recorded at L_{2-3} edge is extremely sensitive to the spin states since it involves the relevant valence shells directly. On looking at the L_2 edge of the $Co2p$ XAS spectra, a narrow and relatively sharp peak can be observed which is similar to the feature observed in $Co2p$ XAS for $LaCoO_3$ at 20 K [27]. This narrow and sharp L_2 peak at $Co2p$ XAS is a hallmark for low-spin state (LS) of Co^{3+} ions, so it undoubtedly confirms the presence of LS Co^{3+} ions in PCFO at room temperature, thus supporting our earlier results of neutron diffraction study [25, 27]. Factually, LS Co^{3+} state was also observed in another DP Ho_2CoFeO_6 [23].

Figure 2(b) depicts the $Fe2p$ XAS spectrum recorded at 300 K. The $Fe2p$ XAS spectrum is ascribed to the transition of electrons from $Fe2p$ to $Fe3d$ states. The $Fe 2p$ XAS spectrum can be broadly divided into two peaks $FeL_3(2p_{3/2})$ and $FeL_2(2p_{1/2})$ positioned at ~ 710.2 eV and ~ 723.6 eV, respectively, the corresponding spin-orbit splitting energy is $\Delta E \sim 13.4$ eV. Due to crystal field splitting, each of the main L_3 and L_2 peaks is further split into e_g and t_{2g} doublet. These t_{2g} features can be observed in the form of a prominent shoulder and a peak just 1.6 eV below the main L_3 and L_2 peaks respectively. The formation of this t_{2g} and e_g splitting can be attributed to the localized nature of Fe 3d electrons. Essentially, the spectral features are similar to the $Fe2p$ XAS spectra of the extensively studied Fe_2O_3 system, where the nominal valency of the Fe ions is +3 [36]. The $Fe2p$ XAS spectral feature excludes similarities from the spectral features as typically seen in metallic Fe, FeO or Fe_3O_4 , suggesting absence of any mixed-valence states [36]. It can be further noted that for Fe^{3+} ions sitting in

the tetrahedral co-ordination, the L_3 and L_2 peaks are not split into $e_g - t_{2g}$ doublet [37]. On the other hand, for the Fe^{3+} ions sitting in the octahedral co-ordination, it splits into e_g and t_{2g} which are separated by 1.6 eV [37]. Hence, the octahedral co-ordination of Fe^{3+} ions can be inferred for PCFO. Thus, the XAS data is in well-agreement with XPS results.

Temperature-dependent Raman study

The diffraction techniques are helpful for probing the basic crystal structure and its symmetry while the Raman spectroscopy is a unique tool to examine the changes in the local or/and dynamic structural symmetry, local disorder, cationic ordering, etc [9, 10, 17–19]. However, for the simple cubic $Pm\bar{3}m$ structure of ideal perovskites, all the atoms are centro-symmetrically positioned, and hence no Raman-active phonon modes are found in their Raman spectra. In contrast for the $Pnma$ structure, the distortion caused by the motion of the oxygen atoms around the B-site ions (in BO_6) or shifts in R lifts the degeneracy of the Raman modes, and few additional Γ -point phonons become Raman allowed [38]. The symmetry analysis by group theory predicts that there are 60 possible Γ -point phonon modes in such compounds with orthorhombic structure ($Pnma$). Of these possible modes, only 24 are found to be Raman allowed while among the rest, 25 are infrared allowed, three are acoustic translational and 8 are inactive silent modes. The Raman active modes are written in irreducible representation as $\Gamma_g = (7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g})$, where A_g modes correspond to the stretching vibrations of BO_6 octahedra and B_g modes refer to the anti-stretching modes of vibration from the same source.

In the figure 3(a), we have shown the experimental Raman spectra (i.e. the scattering intensity variation with the Raman shift) recorded at different temperatures ranging from 300 K to 80 K for Pr_2CoFeO_6 . It can be seen from the figure 3(a) that of many weak Raman bands, two prominent bands positioned at $\omega_1 \sim 435$ cm^{-1} and $\omega_2 \sim 650$ cm^{-1} are observed for all the temperatures. Typically, the phonon modes arising due to the motion of the heavy rare earth ions appear below the

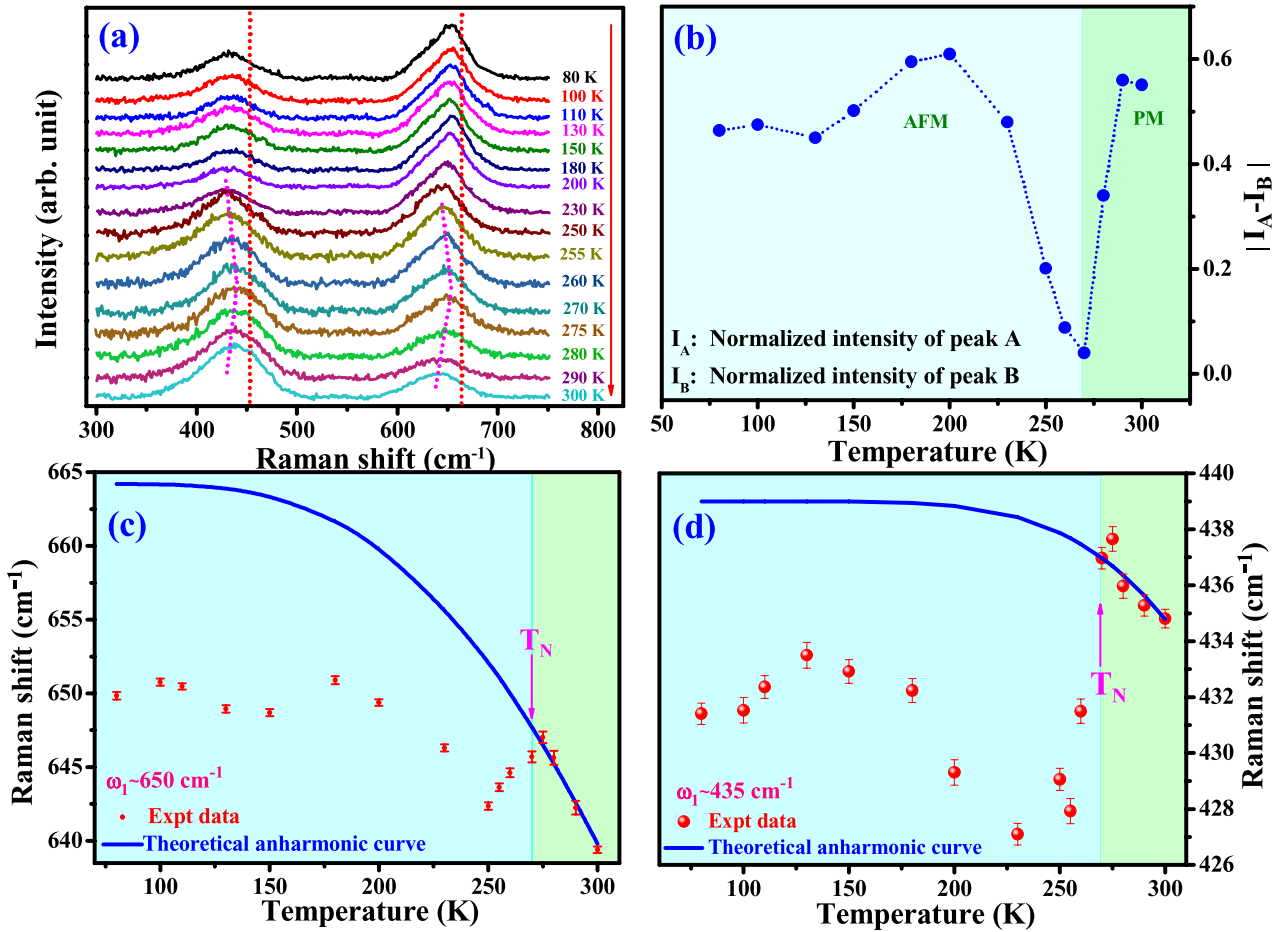


Figure 3. (a) Raman spectra at different temperatures. (b) Relative height variation of two modes with temperature. Anharmonic fit to the ‘thermal variation of Raman shift’ for stretching (c) and anti-stretching (d) modes respectively.

200 cm^{-1} , and the modes observed above 300 cm^{-1} are solely due to the motion of light oxygen ions. As already stated the Co/Fe (B-site) ions are centrosymmetric hence they do not contribute to these modes. Thus, both of the observed peaks are associated to the oxygen motion in Co/FeO₆ octahedra. Observing the similarities between the observed Raman spectra of PCFO to that of the other earlier reported spectra of perovskites and double perovskites oxides, bands observed at $\sim 435\text{ cm}^{-1}$ and $\sim 650\text{ cm}^{-1}$ can be attributed to the anti-stretching and stretching (or breathing) vibrations of the Co/FeO₆ octahedra respectively [9, 10, 16, 19, 38–41]. Illiev *et al* have explicitly shown by the lattice dynamical calculations that the lower energy band ω_1 involves both the bending and anti-stretching vibrations whereas the higher energy band ω_2 arises purely due to the stretching vibrations [40]. It is a comprehensible fact that for the fully disordered DPs; the number of Raman excitation peaks should remain the same as for the single perovskite, i.e. RBO₃ or RB’O₃. However, the only noticeable change that can be observed is the change in the phonon frequency, and their peak widths arising due to the changes occurred in the average force constants (due to random B–O/B’–O bonds) and their phonon lifetimes [39, 41]. As PCFO has B-site disordered orthorhombic structure, the observed broadness in both of the bands ω_1 and ω_2 can be ascribed to the random site distribution of the Co/Fe ions.

Moreover, another feature that can be noted in the peaks (figure 3(a)) is the asymmetry in its shapes. Eventually, due to the presence of cationic disorder in PCFO, the different B/B’–O vibrations (these unresolved contributions originating from different B/B’–O₆ octahedral co-ordinations) will lie close in energy leading to the formation of an asymmetric band envelope.

As a matter of fact, ordered DP systems (P2₁/n) e.g. La₂CoMnO₆, Pr₂CoMnO₆, Nd₂CoMnO₆, Y₂CoMnO₆, and Y₂NiMnO₆ etc exhibit additional number of low intensity Raman modes (along with the two main intense stretching and anti-stretching modes) which are attributed to the B-site cationic ordering in the system [6, 42, 43]. Factually, in the ordered DPs, the effective lattice parameter increases due to the cationic ordering leading to a Brillouin zone folding which essentially gives rise to additional new Γ -point Raman modes [39]. Moreover, for the epitaxial thin film of the DP compounds, a clear peak splitting (which is typically considered as a hallmark for cationic B-site ordering) is observed in both of the stretching and anti-stretching modes [9, 10, 39]. On the contrary, for the compounds with disordered orthorhombic (Pnma) structures show less number of Raman modes as compared to that for ordered monoclinic (P2₁/n) structures [19, 42]. As a matter of fact, we could identify only two main broad peaks $\omega_1 \sim 435\text{ cm}^{-1}$ and $\omega_2 \sim 650\text{ cm}^{-1}$ for PCFO,

suggesting towards the random site distribution of the Co/Fe atoms which well accord to our previous work [25].

On the other hand, the DPs containing R-site ions of large ionic radii usually show smaller number of Raman modes. This is because large R-ions cause smaller octahedral tilts and relatively small distortions which lead to the rise of Raman modes at low wave numbers but of weaker intensities as compared to that of DPs with smaller R-ions (causing large octahedral distortions). Thus, for DPs with smaller R-ionic radii show more resolvable Raman modes as compared to the DPs with large ionic radii [42, 43]. Hence, the absence of such additional Raman modes for PCFO can also be elucidated based on the large ionic radii of the Pr-ions.

Raman spectra at different temperatures ranging from 300 K down to 80 K have been recorded to study the effect of magnetic ordering upon the lattice vibration (figure 3(a)). To explore the impact of the temperature on the relative intensities of the two Raman modes (stretching and anti-stretching), we have normalized each of the Raman spectra concerning the most intense peak. Interestingly, the intensities of the two bands ω_1 and ω_2 vary differently with temperature. The intensity of the most intense peak at room temperature, i.e. the anti-stretching mode (ω_1) remains almost constant throughout the temperature range whereas that of stretching mode (ω_2) keeps increasing with decreasing temperature. This behaviour is scarce and interesting since the Raman intensity usually increases with decreasing temperatures owing to the reduced phonon scattering at low temperatures. Figure 3(b) shows the plot of relative intensity $|I_{\omega_1} - I_{\omega_2}|$ as a function of temperature. Interestingly, as the temperature reaches $T_N \sim 269$ K, the intensities of both the Raman modes ω_1 and ω_2 become merely equal. Below 269 K, the intensity of ω_2 peak starts dominating over that of the ω_1 peak. Hence, it indicates that the onset of magnetic ordering is affecting the phonon modes, thus leading to the observed anomalous behaviour of their thermal intensity variations.

To further confirm whether the magnetic spin ordering affects the lattice vibrations, we have investigated the ‘temperature variation of the Raman excitation frequencies for both the modes i.e. ω_1 and ω_2 ’ (figures 3(c) and (d)). Since, for the whole temperature range, no additional Raman mode could be observed, it undoubtedly ruled out the possibility of any global structural transition. Under such condition, the temperature variation of the phonon excitation wave number should follow the anharmonic behaviour (due to usual thermal lattice contraction) which is described by the following expression [44]:

$$\omega_{anh}(T) = \omega_0 - C \left(1 + \frac{2}{e^{\frac{\hbar\omega_0}{K_B T}} - 1} \right).$$

Where ω_0 and C are the adjustable parameters, T is the temperature, \hbar is reduced Planck’s constant and K_B is the Boltzmann’s constant. According to this function, the phonon frequency of a particular mode should exhibit gradual hardening with decreasing temperature and reach a plateau at sufficiently low temperatures. From figures 3(c) and (d), such phonon mode hardening down to the temperature $T_N \sim 270$ K can be

observed for both of the stretching and anti-stretching modes. Thus, it clearly suggests that anharmonicity is playing a dominant role in the temperature dependence of PCFO’s phonon modes. Interestingly, it is discernible from figures 3(c) and (d) that both the stretching and anti-stretching modes, i.e. ω_2 and ω_1 deviate from the anharmonic behaviour below magnetic ordering temperature T_N . However, for the stretching mode ω_2 , the theoretical curve attains the plateau region after going down to sufficiently low temperature < 150 K above which it continues the hardening while the experimental curve shows a dramatic slope change and exhibits anomalous softening below T_N (figure 3(c)). On the other hand, as evident from figure 3(d) the anti-stretching mode shows relatively larger deviation from anharmonic behaviour by showing more pronounced anomalous softening below T_N which is typically observed due to the spin–phonon coupling in other systems [6, 16, 40–43, 45–47]. Thus, these observations of anomalous softening of phonon modes (near T_N) involving vibrations of magnetic Fe ions indicate towards effective modulation in the lattice vibrations due to the magnetic ordering, thus leading to the spin–phonon coupling. However, in most of the perovskite compounds exhibiting spin–phonon coupling, such anomalous phonon softening was observed only in the stretching mode. On the contrary, the above results suggest that for PCFO atleast two phonon modes are exhibiting the spin–phonon coupling and thus it eventually places this system amongst the rare materials.

It is pertinent to mention here that magnetostriction effect can also affect the phonon frequency (by altering the unit cell volume and lattice constants) leading to the anomaly in its temperature variation [42, 43, 46–48]. Thus, it is crucial to confirm whether it is the spin–phonon coupling or the magnetostriction which one is causing the observed phonon anomaly. As a matter of fact, the full width at half maximum (FWHM) or line width of the relevant phonon modes remain unaffected by the subtle changes occurred in the volume/lattice parameters caused by magnetostriction effect. On the contrary, FWHM is related to the process of the phonon delay (i.e. lifetime) and thus can be affected by the spin–phonon coupling showing anomaly across magnetic transition [47]. Hence, we have investigated the thermal variation of the FWHM of the two modes (ω_2 and ω_1) as shown in figures 4(a) and (b). Interestingly, for both of the modes, their FWHM showed an anomalous broadening below $T_N \sim 270$ K and thus showed clear deviation from the expected anharmonic behaviour (i.e. monotonous increase in phonon lifetime or decrease in FWHM with decreasing temperature due to anharmonic perturbations) [47, 48]. In this case, the observed temperature dependence of phonon line-widths cannot be explained by anharmonic behaviour alone. Thus, the observed anomalous FWHM broadening can be realized by the decrease in the phonon lifetime beyond T_N which is related to activation of some additional phonon decay modes due to entanglement of phonons with underlying long range magnetically ordered spins. Generally the phonon lifetimes are changed mainly due to two reasons (1) spin–phonon coupling and (2) electron–phonon coupling [20, 47, 48]. However, the present XPS study and previous other experimental and theoretical studies

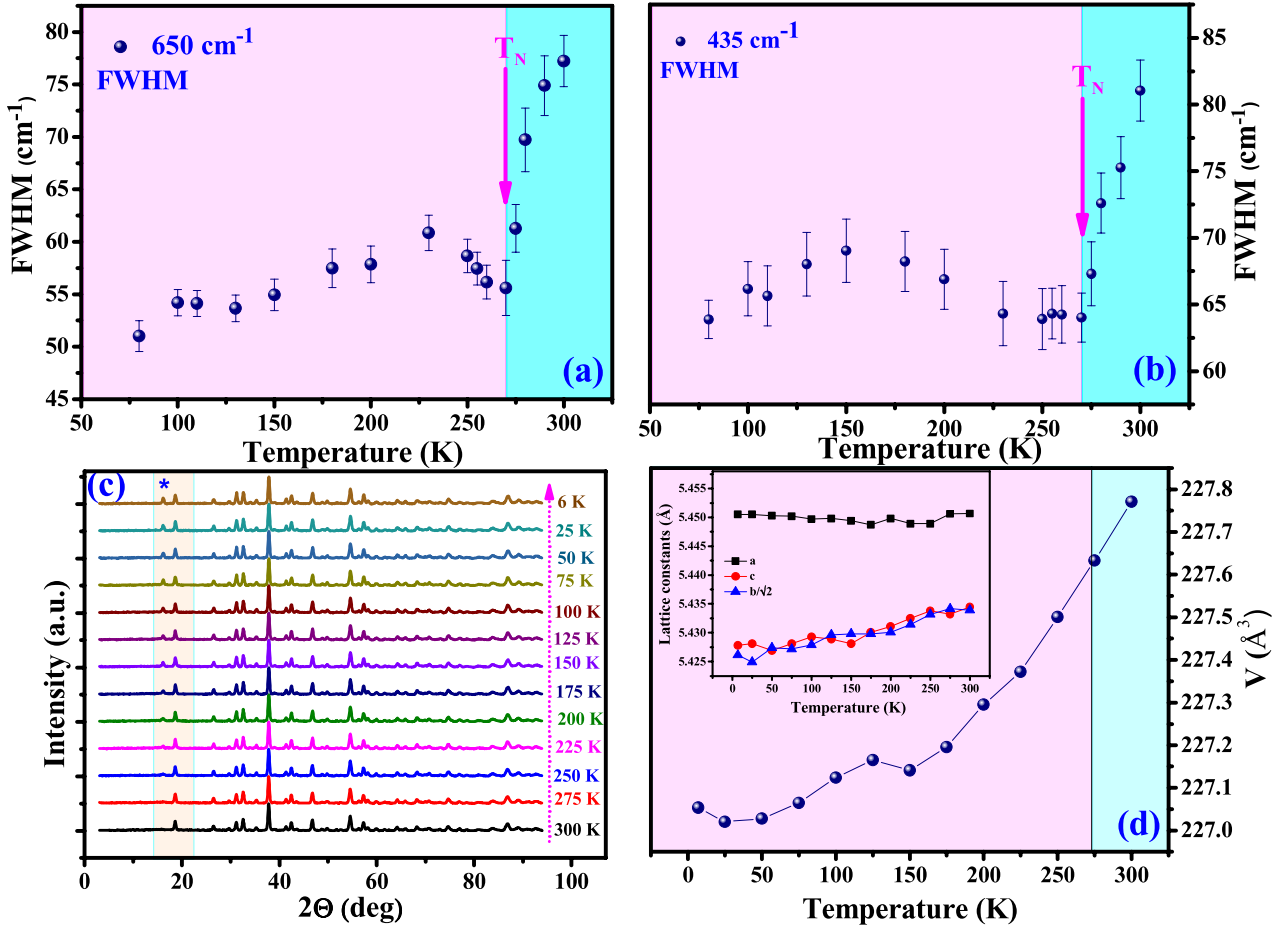


Figure 4. (a) and (b) Variation of FWHM with temperature for stretching and anti-stretching modes respectively. (c) Neutron diffraction at different temperatures. (d) Temperature variation of cell volume. Inset: thermal variation of lattice volume and lattice constants (a , $b/\sqrt{2}$ and c).

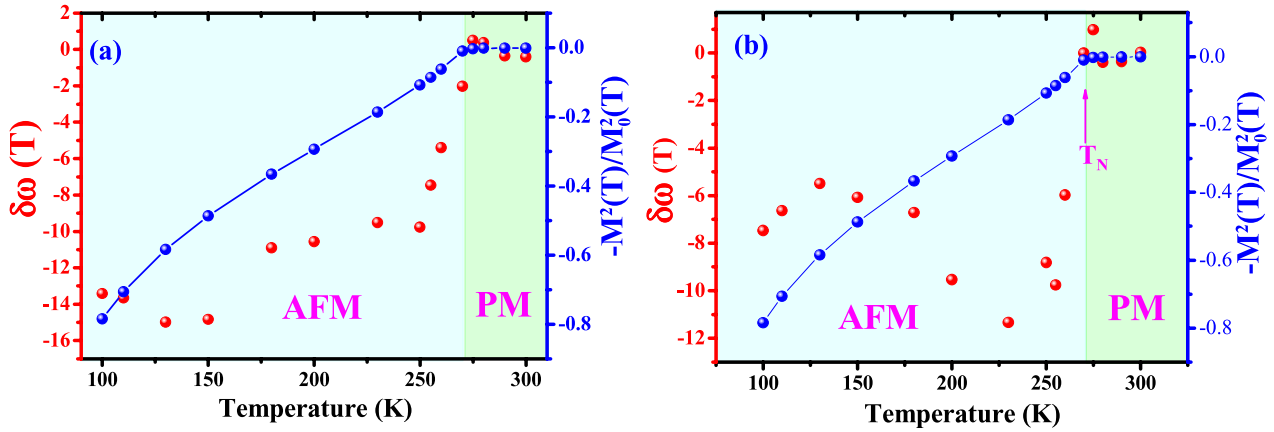


Figure 5. (a) and (b) Temperature variation of $\delta\omega(T)$ and $(M(T)/M_0)^2$ for the stretching and anti-stretching modes respectively.

performed on this system showed it to be an insulator which readily discards the possibility of electron–phonon coupling [25]. Thus, the observation of FWHM anomaly can univocally be ascribed to the spin–phonon coupling in PCFO.

However, to further ascertain the absence of the role of magnetostriction effect in the observed phonon anomaly, we have investigated the temperature variation of the unit cell volume and the lattice parameters (figure 4(d)). The lattice parameters

were obtained by refining the temperature dependent neutron diffraction (ND) data by Rietveld method (figure 4(c)). It can be noted that a magnetic reflection (011) (marked by *) starts appearing at $\sim 16^\circ$ below T_N which is suggesting the onset of long-range ordering in PCFO. The magnetostriction effect is typically manifested in the form of a remarkable anomaly in the volume and/or lattice parameter data across T_N , which provides a shred of direct evidence for this effect [47–49].

However, as evident from the figure 4(d), no such remarkable anomaly can be observed in the volume and lattice parameters curves. Hence, it directly rules out the possibility of magnetostriction effect causing the observed phonon anomaly across T_N . Therefore, all these above facts unambiguously establish the presence of the strong interplay among the microscopic degrees of freedom viz., spin and phonon in this system.

Moreover, according to the mean field approximation when the long-range magnetic ordering sets in a structure, it induces a renormalization of the phonon frequency [18, 19, 43, 45, 46]. The phonon renormalization is found to be proportional to spin-spin correlation function ($\langle S_i \cdot S_j \rangle$), where S_i and S_j are denoting the nearest neighbour spins situated at i^{th} and j^{th} sites. The change in the phonon frequency due to this renormalization follows the same trend as the normalized magnetization leading the following formula:

$$\delta\omega(T) = \omega(T) - \omega_{anh}(T) = \left(\frac{M^2(T)}{M_0^2} \right).$$

Where $M(T)$ represents the average magnetization at temperature T and M_0 is the saturation magnetization. The difference between the observed and theoretical anharmonic fitted data is denoted by $\delta\omega(T)$. Hence, to further investigate the spin-phonon coupling, we have plotted the temperature variation of $\delta\omega(T)$ and $(M(T)/M_0)^2$ for both the phonon modes (figures 5(a) and (b)). As evident from the figures, $\delta\omega(T)$ and $(M(T)/M_0)^2$ follow a similar trend showing a downturn nearly at the same temperature ($T_N \sim 270$ K). This gives further confirmation that there is interplay between the lattice dynamics and the magnetic excitation via strong spin-phonon coupling in the system. However, for both the modes, $\delta\omega(T)$ and $(M(T)/M_0)^2$ do not overlap with each other. This can be presumably attributed to the existence of multiple magnetic phases in the system viz., AFM, FM, and spin glass phases which contributes towards different exchange interactions (both with values and signs) which in turn contribute differently in phonon renormalization [25, 42, 43, 46]. Similar deviations from mean field theory were observed in few other systems viz., Y_2CoMnO_6 , La_2CoMnO_6 , $Sr_{0.6}Ba_{0.4}MnO_3$, etc where complex FM/AFM and/or spin glass states co-exist, thus adding more complexity in the spin-phonon coupling process [42, 43, 46]. However, we hope that the present work may provoke theoretical studies to understand the spin ordering driven altered phonon behaviours in such site-disordered double perovskites. Further study on its single crystal or epitaxial thin film may be helpful to understand more about the intriguing underlying physics in it.

Conclusions

To summarize, we have investigated the electronic structure of PCFO by analyzing the XPS and XAS spectra at 300 K. Both the data analysis supported each other and unanimously confirmed the nominal oxidation states of B-site cations (i.e. Co, and Fe) to be +3 which in turn predicts towards a B-site disordered structure of PCFO. The XPS analysis yielded the trivalent valence states for the Pr ions. The XPS valence band spectra analysis showed the absence of electronic states at

the Fermi level, thus suggesting an insulating nature of the system. Moreover, the XPS valence band spectra have been compared with the theoretically (DFT) obtained cross-section weighted partial density of states followed by Lorentzian (lifetime) and Gaussian (instrumental) broadening. The Raman spectra analysis yielded a random distribution of B-site ions (Co/Fe) which is primarily triggered by the same charge states of the relevant ions. Moreover, the anomalous behaviour observed in the relative intensities of the stretching and anti-stretching Raman modes across T_N indicated the interplay of the spins and phonons in PCFO. Interestingly, both the Raman modes showed anomalous softening below T_N and deviated from anharmonic behaviour, thus confirming the existence of spin-phonon coupling for at least two modes. Besides, the temperature variation of the line widths of these two modes also showed remarkable anomaly below T_N which gave further confirmation of the strong coupling between spin and phononic degrees of freedom. Again, no anomaly in the lattice volume or lattice constants (a, b and c) across T_N could be observed in their temperature variation as obtained from neutron diffraction data analysis. This unambiguously confirmed the absence of magnetostriction effect in the observed phonon anomaly, thus, in turn, established the existence of the spin-phonon coupling in the system. Observation of such spin-phonon coupling for at least two phonon modes is very scarce for such compounds which eventually place it amongst the rare materials.

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