Electronic structure of PrCoO$_3$ and its temperature evolution

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We investigate the detailed electronic structure of PrCoO$_3$ and its temperature evolution using state-of-the-art photoemission spectroscopy and *ab initio* band structure calculations. We observe that in addition to the correlation effect, spin-orbit interaction plays an important role in determining the electronic properties of this system. Pr 4f states are found to be strongly hybridized with the O 2p and Co 3d valence electronic states, and thus influences the electronic properties significantly. The calculated results corresponding to the intermediate spin state of Co provide a good description of the experimental spectra at 300 K. The decrease in temperature from 300 K leads to a gradual enhancement of the low spin state contributions in the electronic structure. The temperature evolution of the band gap is found to be consistent with the transport data.

I. INTRODUCTION

Cobaltates with general formula ACoO$_3$ (A $\equiv$ rare-earth ions) forms an interesting class of compounds in the perovskite family.[1] The primary concerns in these systems is the understanding of the temperature induced spin state transition. Extensive effort has been put forward both theoretically and experimentally to understand this effect. The ground state of these compounds are believed to be nonmagnetic (spin $S = 0$) insulator having Co^{3+} ion in low spin (LS) configuration with fully filled Co t_{2g} orbitals. Increase in temperature leads to non-magnetic insulator to paramagnetic metal transitions.[2,3,4,5,6] It was suggested that such transitions occurs due to thermally driven spin state transition of Co^{3+} ions.[7,8,9] The major controversy in these studies involves the identification of the spin state in the intermediate temperatures range. Some studies[9,10,11,12,13,14,15,16,17,18] suggest that the spin state of Co is an intermediate spin (IS $\Rightarrow t_{2g\uparrow}^3 e_{g\uparrow}^1 t_{2g\downarrow}^2$, S = 1) state, while the others suggest a mixed low spin and high spin (HS $\Rightarrow t_{2g\uparrow}^3 e_{g\uparrow}^2 t_{2g\downarrow}^1$, S = 2) state.[7,8,19,20,21,22,23] Despite numerous investigations on this issue, the controversy in the spin state transition is still unresolved.

Most of the studies mentioned above have focussed on the spin state transitions in LaCoO$_3$, where the crystal field splitting is close to the exchange interaction strength. If we replace La by Pr, the smaller ionic radius of Pr compared to La provides a chemical pressure on the system. It is observed that the crystal structure of PrCoO$_3$ is different from that of LaCoO$_3$. The powder diffraction work has shown that the crystal structure of LaCoO$_3$ and PrCoO$_3$ are rhombohedral and orthorhombic, respectively.[6,12] The average Co-O bond length of PrCoO$_3$ is less than that of LaCoO$_3$ and hence the crystal field splitting is expected to be enhanced in PrCoO$_3$. The Co-O-Co bond angle is smaller in PrCoO$_3$ compared to that in LaCoO$_3$. In addition, 4f electrons corresponding to Pr atoms and the hybridization of the 4f states with the valence electronic states will play an important

role in determining the magnetic properties in this system.

The transport and optical conductivity measurements exhibit a larger band gap and higher insulator to metal transition temperature in PrCoO$_3$ compared to that in LaCoO$_3$.[4] It was suggested that the decrease in valence band width due to the change in Co-O-Co bond angle leads to such effect. The temperature dependent infrared spectroscopy data of PrCoO$_3$ have shown the LS to IS state transition around 220 K.[16] The susceptibility data of PrCoO$_3$ obtained after subtracting the contributions from Pr^{3+} ions have shown increased population of the IS state around 200 K.[17] Thus, PrCoO$_3$ is an ideal system to throw some light in understanding the interplay between crystal field splitting and exchange coupling strength in the spin state transition in cobaltates.

In the present work, we investigate the temperature evolution of spin state of Co ion in PrCoO$_3$ using state-of-the-art photoemission spectroscopy and *ab initio* band structure calculations. The experimental valence band spectra exhibit signature of gradual increase in band gap with the decrease in temperature. The comparison of the experimental and calculated results for the valence band indicates that the Co ion presumably possesses an IS state configuration in the temperature range, 150-300 K. This is also manifested in the shallow core level spectra. Spin orbit coupling (SOC) plays an important role in determining the electronic structure in this system.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

PrCoO$_3$ was prepared in the polycrystalline form by combustion method.[24] Nitrates of Pr and Co were taken in appropriate amount and mixed in double distilled water. In this mixture, 2 moles of glycine per 1 mole of metal cation was added and stirred until all compounds dissolved in the water. The resulting solution was heated slowly at temperature around 200 ^{0}C till all the water

evaporated. The precursor thus formed catches fire on its own making the powder of the compound. The hard pallets of this powder were formed and heated at 1200 ^{0}C for one day. The sample was characterized by x-ray powder diffraction and resistivity measurements. The powder diffraction data did not show any impurity peak; all the peaks were well fitted with orthorhombic phase (space group Pbnm) using Rietveld refinement technique. The lattice parameters obtained from the fitting match well with those reported in the literature. Resistivity data are also consistent with the available data in the literature.[4,6]

The photoemission spectra were recorded using a spectrometer equipped with monochromatic sources such as x-ray source, Al $K\alpha$ (1486.6 eV), ultraviolet sources, He II (40.8 eV) and He I (21.2 eV). The electron detection was carried out by a Gammadata Scienta analyzer, SES2002. The energy resolution for the x-ray photoemission (XP) was set to 0.3 eV for the valence band and 0.6 eV for the core level spectra. The energy resolution for the He II and He I spectra were fixed to 4.2 meV and 1.4 meV, respectively. The base pressure during the measurements was about 4×10^{-11} Torr. We have used a He-cryostat, LT-3M from Advanced Research Systems for the measurements at different temperatures.

The sample was cleaned *in situ* by scraping the sample surface using a diamond file. The cleanliness of the sample was ascertained by tracking the sharpness of O $1s$ peak and absence of C $1s$ peak. The O $1s$ spectra recorded at 150 K and 300 K are shown in Fig. 1. The contribution of impurity peak around 531 eV binding energy is negligible ($< 3\%$) indicating the good quality of the sample. The Fermi level was aligned by recording the valence band spectrum of an Ag foil mounted on the same sample holder.

The GGA (generalized gradient approximation) and GGA+U (U = the electron correlation strength) calculations were carried out using LMTART 6.61.[25] For calculating charge density, full-potential linearized Muffin-Tin orbital method working in plane wave representation was employed. In the calculation, we have used the Muffin-Tin radii of 3.43, 2.019, and 1.688 a.u. for Pr, Co and O, respectively. The charge density and effective potential were expanded in spherical harmonics up to $l = 6$ inside the sphere and in a Fourier series in the interstitial region. The initial basis set included $6s$, $5p$, $5d$, and $4f$ valence, and $5s$ semicore orbitals of Pr; $4s$, $4p$, and $3d$ valence, and $3p$ semicore orbitals of Co, and $2s$ and $2p$ valence orbitals of O. The exchange correlation functional of the density functional theory was taken after H.S. Vosko *et al.*[26] and GGA was implemented using J.P. Perdew *et al.* prescription.[27] The effect of spin-orbit coupling (SOC) was also considered in the calculations.

In the GGA+U calculations the Hubbard U and exchange J are considered as parameters. We have taken $U = 3.5$ eV for Co $3d$ and Pr $4f$ electrons and $J = 1.0$ eV for Co $3d$ electrons. We have not considered the value of J for Pr $4f$ electrons exclusively in the calculations. It is estimated under GGA formulation. The values of U

and J for $3d$ electrons are consistent with our previous studies.[28,29] These calculations were performed by taking LS, IS and HS configurations, which correspond to ($t_{2g\uparrow}^3 t_{2g\downarrow}^3$), ($t_{2g\uparrow}^3 t_{2g\downarrow}^2 e_{g\uparrow}^1$) and ($t_{2g\uparrow}^3 t_{2g\downarrow}^1 e_{g\uparrow}^2$) electronic configurations, respectively, as initial input. Self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10^{-4} Ryd/cell. Final orbital occupancies for Pr $4f$, Co t_{2g} and e_g states were obtained from self-consistent GGA+U calculations for different initial state configurations. (8, 8, 6) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate the density of states (DOS).

III.   RESULTS AND DISCUSSIONS

Co t_{2g}, Co e_g and O $2p$ partial density of states (PDOS) obtained from GGA calculations are plotted in Fig. 2(a) and PDOS of Pr $4f$ in Fig. 2(b). It is evident from the figures that there are finite PDOS of Co e_g, O $2p$ and Pr $4f$ at the Fermi level indicating the metallic ground state which is contrary to the experimentally observed insulating ground state. The PDOS below the Fermi level can be divided into three regions: (i) region A up to -1.6 eV from the Fermi level, (ii) region B from -1.6 eV to -3.4 eV and (iii) region C below -3.4 eV. Region A has dominating Co $3d$ character along with small O $2p$ contributions having similar energy distribution of the PDOS. This feature is attributed to the antibonding states. The Co $3d$ states having t_{2g} symmetry appear between -1.6 eV to -0.2 eV and the contribution of Co $3d$ states having e_g symmetry appear between -0.5 to 2.5 eV. Region B is essentially contributed by non-bonding O $2p$ states. The bonding states having t_{2g} and e_g symmetry contribute in region C with dominant contribution from O $2p$ electronic states. The contribution of Pr $4f$ PDOS appears in the narrow region from -0.1 eV to 0.4 eV indicating the highly localized nature of Pr $4f$ electrons.

In order to investigate the role of SOC in the electronic structure in the limit of generalized gradient approximations, we have calculated the density of states including SOC. The calculated PDOS of Co t_{2g}, Co e_g and O $2p$ states are shown in Fig. 2(c) and that of Pr $4f$ states in Fig. 2(d). It is clear from the figure that inclusion of SOC has negligible influence on the Co $3d$ and O $2p$ PDOS. However, SOC drastically modifies the Pr $4f$ PDOS as evident from Fig. 2(d). It splits into two well separated regions. Region below 0.25 eV is identified to be Pr $4f_{5/2}$ states and region above 0.25 eV appears due to Pr $4f_{7/2}$ contributions. The spin-orbit splitting of Pr $4f$ states is found to be about 0.4 eV.

It is clear from Fig. 2 that the DOS at the Fermi level, ϵ_F is finite in both the cases (with SOC and without SOC); an indication of a metallic ground state. Thus, the consideration of electron correlation is necessary to capture the insulating ground state observed experimen-

tally.

The inclusion of on-site Coulomb correlation on Co $3d$ electrons ($U_{dd} = 3.5$ eV) under GGA+U formulation modifies the positions and distributions of Co $3d$ and O $2p$ PDOS as evident in Fig. 3(a). The most significant effect of U_{dd} is observed in the antibonding Co t_{2g} states (the feature A in the figure), which shifts to lower energy by about 0.8 eV. The contribution of the O 2p states enhances significantly in this energy range. As expected U_{dd} does not affect Pr $4f$ bands. Interestingly, Co e_g states have finite contribution at the Fermi level, which is not expected as the inclusion of U_{dd} of 3.5 eV was sufficient to create a hard gap of about 0.22 eV in LaCoO$_3$.[28] This indicates that Pr $4f$ states strongly hybridize with the O $2p$ and Co e_g orbitals in the vicinity of the Fermi level. This is also manifested by the shape of the energy distribution of the DOS in this energy region. Still, there is finite DOS at ϵ_F characterizing the system to be metallic.

In order to capture the correct ground state of PrCoO$_3$, we have included the on-site Coulomb correlation among Pr $4f$ electrons (U_{ff}). Since, the f electrons are more localized than the d electrons, the electron correlation strength among f electrons is expected to be larger than that for d electrons. In our calculations, we have considered U_{ff} to be similar to U_{dd} ($= 3.5$ eV) so that it corresponds to the lower limit in U_{ff}. In Fig. 3(c), we show the Co t_{2g}, Co e_g and O $2p$ PDOS. Pr $4f$ PDOS obtained are shown in Fig. 3(d). Pr $4f$ PDOS exhibit a large splitting leading to the formation of lower and upper Hubbard bands representing the localized density of states. The energy gap between these bands is as large as 2.2 eV. Interestingly, such splitting introduces significant modification in the Co $3d$ and O $2p$ DOS. The $4f$ symmetry adapted Co $3d$ and O $2p$ states also appear in the same energy range as that of the $4f$ bands and a band gap of 0.27 eV appears between the t_{2g} and e_g states characterizing the system to be an insulator.

In addition, the inclusion of U_{ff} introduces a large shift of the features A, B and C towards the Fermi level along with a significant change in the energy separation among themselves. While the feature A is predominantly contributed by Co $3d$ PDOS in Fig. 3(a), the contribution from O $2p$ PDOS to the feature A enhances significantly making almost equal to that from Co $3d$ state. It is thus evident that Pr $4f$ states play an important role in determining the electronic states in the vicinity of ϵ_F and hence the electronic properties of this system.

We now study the effect of different spin configurations of Co^{3+} ion on the valence band calculated using GGA+U method. The Pr $4f$, Co $3d$ and O $2p$ PDOS corresponding to Co^{3+} ion in LS, IS and HS configurations are plotted in Figs. 4(a), 4(b) and 4(c), respectively. It is evident from the figure that the insulating gap of about 0.27 eV observed for LS configuration is not present in the other cases. In addition, there are several changes in the valence band corresponding to the IS and HS state compared to that for the LS state. The low energy spread of the valence band increases from LS to IS by about 1 eV and it further increases by about 0.3 eV in the HS state. The Co $3d$ character of the energy bands at lower energies gradually enhances with the increase in spin state. The Co $3d$ character of the energy bands close to ϵ_F observed in LS state reduces significantly in the IS state. In the HS state, the energy band with dominant Co $3d$ character appear below -5 eV.

In Fig. 5, we show the background subtracted experimental valence band spectra of PrCoO$_3$ recorded at room temperature using monochromatic Al Kα, He II and He I. All the spectra show zero intensity at the Fermi level indicating the insulating behavior of the compound. All the spectra exhibit three distinct peaks at about 1.1, 3.2 and 4.9 eV marked by A, B and C, respectively. The Al Kα spectrum is dominated by the intensity of peak A. This trend is reversed in the He II and He I data. Due to the matrix element effect, the photoemission cross section corresponding to various electronic states changes significantly with the change in photon energy. The relative cross section for O $2p$ states with respect to that of the Co $3d$ and Pr $4f$ states is significantly higher in ultraviolet photon energies. The x-ray energies correspond to the reverse case. Thus, large intensity of the features B and C in the He I and He II spectra compared to the intensity of the feature A indicates that the features B and C has dominant O $2p$ character and the feature A is essentially contributed by the Co $3d$ and Pr $4f$ states. In order to investigate the energy positions of the Pr $4f$ and Co $3d$ contributions, we compare the Al $K\alpha$ spectrum of PrCoO$_3$ with that of LaCoO$_3$. Clearly, the intensity around 1 eV has dominant Co $3d$ character. The large intensity difference observed around 1.7 eV as marked by D in the figure correspond to the intensities from Pr $4f$ states. This is consistent with the previous studies.[29,30]

A comparison of the results in Figs. 4 and 5 indicates that the experimental results in Fig. 5 correspond closely to the results in Fig. 4(b) indicating large IS state contributions at room temperature. In order to bring out the comparison more clearly, we show the spin-integrated DOS corresponding to IS state in Fig. 5. Evidently, the character of various features and their energy positions observed in the calculated DOS are very close to the experimental results. The experimental O $2p$ non-bonding band appears at slightly higher binding energy compared to that observed in the calculated results. Such small shift in energy position of the O $2p$ non-bonding states is often observed due to the neglect of electron correlation effect among O $2p$ electrons.[31] It is to note here that the observation of Co $3d$ band at about 6 eV binding energy in the HS state has no resemblance with the experimental spectra. This indicates that the contribution from HS state at room temperature is essentially absent.

It is important to note here that although features in the DOS corresponding to IS state provide a remarkable representation of the experimental spectra, the insulating gap observed in the experimental spectra as well as in the bulk measurements could not be captured in our

calculations for these parameters. One needs to enhance the values to U unrealistically high to achieve such insulating phase. In that case, the features in the DOS will be significantly different. It is well known that orbital ordering plays an important role in determining the electronic structure of these systems. To get an insulating state, one should consider the orbital ordering in the calculations.[9] However, such considerations does not have significant influence in the energy position of the features.

We now turn to the temperature evolution of the electronic structure. In Fig. 6, we show the valence band spectra collected at different temperatures. The XP spectra shown in Fig. 6(a) exhibit almost identical lineshape of the spectra at 300 K and 150 K. The band edge appears to shift slightly towards higher binding energies. The He II spectra shown in Fig. 6(b), however, exhibit significant change with temperatures. The decrease in temperature leads to gradual increase in intensity of the feature around 5 eV characterized as the bonding features. Subsequently, the intensity of the features around 1 eV decreases. Since, the photoemission cross section corresponding to O $2p$ states is significantly enhanced in the He II photon energies, the change in Fig 6(b) suggests gradual enhancement of the O $2p$ character of the bonding feature with the decrease in temperature. We have expanded the near ϵ_F region of the He II spectra in Fig. 6(c) to clearly investigate the spectral changes. It is clear that the intensity at about 1 eV reduces to a lower value at 250 K compared to the intensity at 300 K. However, further reduction in temperature does not have significant influence in the intensity of the feature.

From the *ab initio* results (see Fig. 4), we have observed that the increase in spin state leads to an enhancement of the Co $3d$ character at higher binding energies and the O $2p$ contributions shift towards ϵ_F. Thus, the increase in O $2p$ character at higher binding energies with the decrease in temperature indicates that the contribution from LS state enhances gradually with the decrease in temperature. These results thus provide a direct experimental evidence of dominant IS contribution at 300 K and an evolution towards LS state with the decrease in temperature. We could not measure the spectra at lower temperatures due to the charging effect.

In order to investigate the shift of the valence band edge leading to an enhancement of the band gap with the decrease in temperatures, we have extracted the Co $3d$ and Pr $4f$ part by subtracting the O $2p$ contributions appearing at higher binding energies. The subtraction procedure is shown in Fig. 6, where the lines in the figure represent the O $2p$ spectra obtained by using a combination of Lorentzians convoluted by a Gaussian. The extracted features are shown in Figs. 7(a) and (b) for XP and He II spectra, respectively. Although this feature is contributed by Pr $4f$ and Co $3d$ states, the large change in photon energy (from 40.8 eV to 1486.6 eV) thereby different change in the photoemission cross section does not have significant influence in the lineshape of the fea-

ture. This suggests a strong overlap between the $4f$ and $3d$ contributions in this energy range.

We have expanded the band edge part of the high-resolution He II spectra in Fig. 7(c). Interestingly, the band edge gradually shifts towards higher binding energies with the decrease in temperature. The shift is most significant between 300 K and 275 K. In the temperature range of 275 K to 200 K, the change is almost negligible and further decrease in temperature again leads to a shift of the band edge towards higher binding energies. Such change can be correlated to the transport data too. In Fig. 7(d) we show the activation gap calculated from the resistivity data. Interestingly, the temperature induced change of the band gap corresponds well to the shift of the band edge in Fig. 7(c).

In Fig. 8, we show the calculated majority and minority O $2s$ and Pr $5p$ PDOS corresponding to LS, IS and HS states. These PDOS can be divided into four regions as marked in the figure. In the LS state, the region 1 spreading over -15.1 to -16.3 eV has dominating Pr $5p$ character and can be attributed to the spin-orbit split Pr $5p_{3/2}$ states. The region 4 (between -18.8 and -19.3 eV) has predominantly Pr $5p$ character corresponding to spin-orbit split Pr $5p_{1/2}$ state. In region 2 (from -16.4 to -17.1 eV), the contribution from O $2s$ states is most evident and region 3 (from -17.4 to -18.0 eV) has highly mixed O $2s$ and Pr $5p$ characters. It is evident from the figures that the overall shape and spread of O $2s$ and Pr $5p$ bands remain almost the same for all the spin state configurations. However, the energy position of these bands are very much sensitive to the spin state of the Co ion. The whole pattern is shifted to lower energy side by about about 1.0 and 1.1 eV in the IS and HS states, respectively.

The calculated O $2s$ and Pr $5p$ PDOS for the IS state are compared with the experimental spectra in Fig. 9. There are two distinct features in the experimental spectra centered around 16.8 and 20.6 eV. The intensity ratio of the two features are different from 1:2 expected for Pr $5p$ signals due to the overlap of the O $2s$ signal appearing in this energy range. In order to identify the character of the features, we overlap the Mg $K\alpha$ spectrum over the Al $K\alpha$ spectrum. This change in photon energy leads to a larger enhancement of the photoemission cross section of the O $2s$ states compared to that for Pr $5p$ states.[32] A normalization by the Pr $5p_{3/2}$ peak intensity exhibits an enhancement in the energy region of 17 - 20 eV. This clearly indicates that the presence of O $2s$ feature in this energy region.

The calculated DOS corresponding to the IS state is shown in Fig. 9(b). Evidently, the calculated DOS provide a remarkable representation of the experimental spectra in terms of energy position and relative intensities. It is clear that the energy positions obtained for IS and HS configurations are very similar to to the experimental results and the energies for LS configuration is very different.

Finally, we discuss the electronic occupancies of differ-

ent orbitals and corresponding magnetic moments obtained from self-consistent calculations by considering initial spin state of Co ion in LS, IS and HS configurations. The electronic occupancies of Pr $4f$, Co t_{2g} and Co e_g for majority and minority spin channels corresponding to LS, IS and HS states are given in Table I. The occupancies of Pr $4f_\uparrow$ and Pr $4f_\downarrow$ are closer to 2.2 and 0.2, respectively, and insensitive to the spin state of Co ion. However, the occupancies of $t_{2g\uparrow}$, $t_{2g\downarrow}$, $e_{g\uparrow}$ and $e_{g\downarrow}$ are very much sensitive to initial spin state configurations as expected. The total occupancy of Co $3d$ orbitals is significantly higher (~ 6.69) than 6 expected for Co^{3+} and gradually decreases with the increase in spin state as also observed in the case of $LaCoO_3$ compounds in earlier studies.[28,33] Interestingly, $e_{g\downarrow}$ orbitals are also partially occupied; 0.56, 0.44 and 0.42 electrons in the results corresponding to LS, IS and HS states, respectively. This is not *a priori* expected for Co^{3+} electronic configuration. Moreover, one can also see a remarkable increase in the total occupancies of Pr $4f$ (by $\sim$0.4). This increment in the occupancies is a clear indication of the strong hybridization between Pr $4f$ with the valence electrons having O $2p$ and Co $3d$ characters facilitating large charge transfer. This is also manifested in Fig. 3; the shape of the Co $3d$ and O $2p$ PDOS in the energy range of Pr $4f$ bands are very similar to Pr $4f$ PDOS.

Spin and orbital part of the magnetic moment of Pr $4f$, Co $3d$ and O $2p$ for different spin state is given in Table II. Spin part of the magnetic moment for Pr $4f$ state is almost insensitive to the spin state of Co ion and it is closer to 2 μ_B. This indicates that Pr^{3+} ion is in spin triplet state. Spin part of the magnetic moments for Co $3d$ state when Co ion is in LS, IS and HS states are 0.03, 1.79 and 2.96 μ_B, respectively. Surprisingly, the orbital part of the magnetic moment for Pr $4f$ comes out to be negative and strongly depends on the spin state of the Co ion. It's magnitude increases with the increase in spin state. The negative sign indicates that the orbital and spin moments are antiparallely coupled. The orbital moment of the Co $3d$ electrons is almost zero for LS and IS state and for HS state it is 0.21 μ_B. Interestingly, one can also see the contribution of spin part of magnetic moment from O $2p$ electrons when Co ion is in HS state.

Using the values of magnetic moments given in Table II, one can calculate the effective magnetic moment of $PrCoO_3$. This quantity can be directly compared with susceptibility data. The calculated values obtained for LS, IS and HS states are about 2.0, 3.1 and 4.3 μ_B, respectively. The value of the effective magnetic moments thus obtained for the IS state is closer to the experimental value of about 3.6 μ_B obtained by fitting magnetic susceptibility data between 100-150 K by using Curie-Weiss law.[6]

IV. CONCLUSIONS

In summary, we have investigated the detailed electronic structure of $PrCoO_3$ and its temperature evolutions using various forms of *ab initio* calculations and high resolution photoemission spectroscopy. We observe that GGA+U calculations provide a good description of the ground state properties. Partial density of states obtained for various configurations and parameters exhibit signature of strong hybridization of Pr $4f$ states with Co $3d$ and O $2p$ valence electrons. In addition to the electron correlations, spin-orbit coupling plays an important role in determining the electronic structure of this compound.

The calculated Pr $4f$, Pr $5p$, Co $3d$, O $2s$ and O $2p$ partial density of states corresponding to intermediate spin (IS) state of Co ion provide a good representation of the experimental spectra at 300 K. The contribution from high spin state configurations appears to be negligible. Pr $5p$ and O $2s$ core level spectra could be captured reasonably well within this formalism. The decrease in temperature from 300 K leads to an enhancement of the LS contributions in the electronic structure. The band gap gradually enhances with the decrease in temperature as observed in the transport data.

The calculated effective magnetic moment for IS state is also consistent with the magnetic susceptibility data. The calculated spin moment of Pr $4f$ electrons indicates that the Pr^{3+} ion is in spin triplet state and the spin-orbit coupling is antiparallel. The orbital part of the magnetic moment of Pr ion is highly sensitive to the spin state of the Co ion. Its magnitude increases gradually with the increase in spin state.

V. ACKNOWLEDGEMENTS

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VI. FIGURE CAPTIONS:

Fig. 1: (color online) O $1s$ core level spectra recorded at 300 K (solid circles) and 150 K (hollow circles). The shaded region shows the impurity contributions.

Fig. 2: (color online) (a) O $2p$ (dashed line) and Co $3d$ partial density of states having t_{2g} (thin solid line) and e_g (thick solid line) symmetries and (b) Pr $4f$ partial density of states obtained from GGA calculation. (c) O $2p$ (dashed line) and Co $3d$ partial density of states having t_{2g} (thin solid line) and e_g (thick solid line) symmetries and (d) Pr $4f$ partial density of states obtained from GGA calculation including spin-orbit coupling (SOC).

Fig. 3: (color online) (a) O $2p$ (dashed line) and Co $3d$ partial density of states having t_{2g} (thin solid line) and e_g (thick solid line) symmetries and (b) Pr $4f$ partial density of states obtained from GGA+U calculation when on-site Coulomb correlation between Co $3d$ electrons is considered. (c) O $2p$ (dashed line) and Co $3d$ partial density of states having t_{2g} (thin solid line) and e_g (thick solid line) symmetries and (d) Pr $4f$ partial density of states obtained from GGA calculation when on-site Coulomb correlation between Co $3d$ and Pr $4f$ electrons is considered. In all the calculations spin-orbit coupling (SOC) is included.

Fig. 4: (color online) Calculated Pr $4f$ (thin solid line), Co $3d$ (thick solid line) and O $2p$ (dashed line) partial density of states corresponding to (a) low spin (LS), (b) intermediate spin (IS) and (c) high spin (HS) configurations using GGA+U method including spin-orbit coupling.

Fig. 5: (color online) Experimental valence band spectra collected at room temperature using Al $K\alpha$, He II and He I radiations. The lines denote the calculated Pr $4f$ (thin solid line), Co $3d$ (thick solid line) and O $2p$ (dashed line) partial density of states corresponding to intermediate spin configuration of Co ion obtained from GGA+U calculation including spin-orbit coupling. Room temperature experimental valence band spectrum of LaCoO$_3$ recorded using Al $K\alpha$ radiation is also shown by hollow circles.

Fig. 6: (color online) (a) Valence band spectra collected at 300 K (hollow circles) and 150 K (plus signs) using Al $K\alpha$ radiation. (b) Valence band spectra collected at 300 K (hollow circles), 250 K (solid circles), 200 K (solid triangles) and 150 K (plus signs) using He II radiation. (c) Spectra collected at 300 K (hollow circles), 250 K (solid circles), 200 K (solid triangles) and 150 K (plus signs) in the narrow region of the Fermi level using He II radiation. Solid lines in panels (a) and (b) indicate the contribution from O $2p$ states.

Fig. 7: (color online) Co $3d$ and Pr $4f$ contributions extracted (a) from the XP spectra at 300 K (solid triangles) and 150 K (plus signs), and (b) from the He II spectra at 300 K (solid triangles), 225 K (hollow circles) and 150 K (plus signs). Temperature evolution of the spectra in the vicinity of Fermi level is shown in panel (c) and band gap obtained from resistivity data is shown

in panel (d).

Fig, 8: (color online) Pr $5p$ (solid line) and O $2s$ (dashed line) PDOS calculated using (a) low spin (LS), (b) intermediate spin (IS) and (c) high spin (HS) configurations of Co ion.

Fig. 9: (color online) (a) Background subtracted La $5p$ and O $2s$ core level spectra collected at 300 K using Al $K\alpha$ (hollow circles) and Mg $K\alpha$ (solid lines). (b) Calculated Pr $5p$ (solid lines) and O $2s$ (dashed lines) PDOS corresponding to intermediate spin (IS) state configuration.

TABLE I: Electronic occupancies of Pr $4f$, Co t_{2g} and Co e_g orbitals obtained from GGA+U calculations for low spin (LS), intermediate spin (IS) and high spin (HS) configurations of Co ion in PrCoO$_3$.

	Pr $4f \uparrow$	Pr $4f \downarrow$	Pr $4f$	$t_{2g\uparrow}$	$e_{g\uparrow}$	$t_{2g\downarrow}$	$e_{g\downarrow}$	Co $3d$
LS	2.18	0.21	2.39	2.77	0.59	2.77	0.56	6.69
IS	2.16	0.22	2.38	2.8	1.4	1.98	0.44	6.62
HS	2.17	0.22	2.39	2.83	1.89	1.36	0.42	6.5

TABLE II: Spin and orbital part of magnetic moments of Pr $4f$, Co $3d$ and O $2p$ orbitals when Co ion is in low spin (LS), intermediate spin (IS) and high spin (HS) configurations.

	Pr $4f$ (μ_B)		Co $3d$ (μ_B)		O $2p$ (μ_B)		μ_{eff} (μ_B)
	Spin	Orbital	Spin	Orbital	Spin	Orbital	
LS	1.97	-0.47	0.03	~ 0	0.02	~ 0	2.0
IS	1.96	-0.74	1.79	0.03	0.02	0.005	3.1
HS	1.99	-0.95	2.96	0.21	0.13	0.005	4.3

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