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Electronic states of PrCoO₃: x-ray photoemission spectroscopy and LDA + *U* density of states studies

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Abstract

Electronic states of PrCoO₃ are studied using x-ray photoemission spectroscopy. The Pr 3d_{5/2} core level and valence band (VB) were recorded using an Mg K α source. The core level spectrum shows that the 3d_{5/2} level is split into two components of multiplicity four and two, respectively, due to coupling of the spin states of the hole in 3d_{5/2} with the Pr 4f hole spin state. The observed splitting is 4.5 eV. The VB spectrum is interpreted using density of states (DOS) calculations under LDA and LDA + *U*. It is noted that LDA is not sufficient to explain the observed VB spectrum. Inclusion of on-site Coulomb correlation for Co 3d electrons in LDA + *U* calculations gives DOS which is useful in qualitative explanation of the ground state. However, it is necessary to include interactions between Pr 4f electrons to get better agreement with the experimental VB spectrum. It is seen that the VB consists of Pr 4f, Co 3d and O 2p states. Pr 4f, Co 3d and O 2p bands are highly mixed, indicating strong hybridization of these three states. The band near the Fermi level has about equal contributions from Pr 4f and O 2p states with somewhat smaller contribution from Co 3d states. Thus in the Zaanen, Sawatzky and Allen scheme PrCoO₃ can be considered as a charge transfer insulator. The charge transfer energy Δ can be obtained using LDA DOS calculations and the Coulomb-exchange energy U' from LDA + *U*. The explicit values for PrCoO₃ are $\Delta = 3.9$ eV and $U' = 5.5$ eV; the crystal field splitting and 3d bandwidth of Co ions are also found to be 2.8 and 1.8 eV, respectively.

1. Introduction

Perovskite type transition metal oxides have been of much interest for more than 50 years. Recently, research activities have been intensified in this class of materials due to the emergence of exotic properties like charge disproportionation, charge ordering (CO), orbital ordering

(OO), phase separation, colossal magneto-resistance (CMR) etc [1]. The interplay between the on-site and inter-site Coulomb interaction, the charge transfer energy, the hybridization strength between the cation 3d and oxygen 2p states and the crystal field splitting for the $d^n p^m$ configuration of the MO_6 ($M = 3d$ transition metal ion) octahedron control the ground state electronic structure and magnetic and transport properties of these perovskites.

Cobaltates $ACoO_3$, where A is the rare earth element, form an interesting class of compounds in the perovskite family. These compounds show insulator to metal transition with increase in temperature [2]. It is believed that such transition occurs due to the thermally driven spin state transition of Co^{3+} ions [3]. Goodenough originally proposed that, instead of an intermediate spin (IS) $t_{2g}^5 e_g^1$ state that could undergo a disproportionation reaction $2t_{2g}^5 e_g^1 \leftrightarrow t_{2g}^5 e_g^0 + t_{2g}^5 e_g^2$, the system would find it energetically more favourable to stabilize high-spin (HS) $t_{2g}^4 e_g^2$ states where the nearest neighbours can be in the low-spin (LS) $t_{2g}^6 e_g^0$ state; such an ordered configuration could achieve the extra covalent bonding in an LS CoO_6 site without costing the energy required to create Co^{4+} and Co^{2+} ions. In 1995, Potze *et al* revived the interest in these compounds by giving a three-spin-state (LS–IS–HS) model for $LaCoO_3$. In this mechanism Co^{3+} ions are thermally activated to the IS state from the LS state at 100 K, and then from the IS state to a mixed state of IS and HS around 500 K.

Electronic structures of these compounds depend on the effective d–d Coulomb and exchange energy (U') required for $d_i^n d_j^n \leftrightarrow d_i^{n-1} d_j^{n+1}$ (where i and j are the labels for transition metal site) and the charge transfer energy (Δ) required for $d_i^n \rightarrow d_i^{n-1} \underline{L}$, where \underline{L} denotes a hole in the anion valence band. Zaanen *et al* [4] proposed a model for describing bandgaps (E_g) and electronic structures of transition metal (TM) compounds. They divided these compounds into four categories; two of them are relevant in the context of cobaltates, (1) Mott–Hubbard (MH) and (2) charge-transfer (CT) type, depending on the values of U' and Δ . In the case of MH type $U' < \Delta$ and E_g is proportional to U' , whereas for CT type compounds $U' > \Delta$ and E_g is proportional to Δ . In addition to these two parameters electronic structures of such compounds depend on hybridization of the TM 3d and ligand 2p states. Generally Δ is equal to the difference between the centre of gravity (CG) of d and p bands when the correlation between d electrons (i.e. U') is not considered [1]. In this case systems show metallic behaviour because of finite d symmetric density of states at the Fermi level and p bands lie below d bands. On invoking U' , a bandgap is created at the Fermi level and the system shows insulating behaviour. In the case of MH type compounds, electrons near the Fermi level are of d character, whereas for the CT type compounds they are of p character.

It is seen that in many TM compounds the LMM Auger spectrum shows sharp atomic-like features. Sawatzky [5] showed that d–d correlation can give rise to such effects and the sharp line appears on the lower kinetic energy (KE) side of the broad band arising from the self-convolution of the 3d band involved. The energy separation between the peaks of the sharp line and the broad band is a measure of the Coulomb correlation energy U' . Experimentally such interpretation has been used for $LaFeO_3$, $LaCoO_3$ and $LaNiO_3$ [6]; however, such an interpretation has also been questioned in $LaCoO_3$ [7].

We report here a study of electronic states of $PrCoO_3$ by room temperature x-ray photoemission spectroscopy (XPS) and electronic structure calculations using the LDA + U method [8]. Although considerable work is seen in the literature on electronic states of $LaCoO_3$, hardly any work exists on $PrCoO_3$. In contrast to rhombohedral $LaCoO_3$, $PrCoO_3$ is orthorhombic. Its ground state is a paramagnetic insulator with low spin state [9]. Two main differences can be readily seen in the $LaCoO_3$ and $PrCoO_3$ compounds: (a) 4f states of the La^{3+} ion are unoccupied and those of Pr^{3+} contain two electrons; (b) the ionic size of Pr^{3+} is smaller than the ionic size of La^{3+} . Differences in the ionic size result in changed lattice

distortion and directly affect the hybridization and thus the bandwidth. This also affects the crystal-field splitting energy and spin state transition, since the latter occurs due to competition between crystal-field energy and Hund's coupling energy. Due to the presence of two electrons in 4f states of the Pr³⁺ ion one expects the contribution of these states in the valence band. As mentioned above, the inclusion of on-site Coulomb and exchange interactions completely changes the energy positions of d and p bands; therefore, it would be interesting to see their effects, especially on the occupied 4f band. We also look at the possibility of finding the values of parameters Δ and U' using LDA and LDA + U density of states (DOS), respectively. This will help in understanding whether the compound under study is MH or CT type as per the scheme of Zaanen, Sawatzky and Allen (ZSA) [4].

The experimental core level spectrum shows that the Pr 3d_{5/2} level is split into two components of multiplicity four and two, respectively, due to coupling of the spin states of the hole in 3d_{5/2} with that of Pr 4f holes. The observed splitting is 4.5 eV. The valence band (VB) spectrum of PrCoO₃ consists of O 2p, Co 3d and Pr 4f states as revealed by calculated occupied DOS. Within the LDA formulation, the DOS of occupied states near the Fermi level is a mixture of Pr 4f and Co 3d states. On invoking LDA + U , the energy position as well as DOS of all the bands are affected in such a way that the occupied O 2p band is shifted near the Fermi level and Co 3d and Pr 4f bands move away from it, so that the band near the Fermi level is more of O 2p and Pr 4f character than Co 3d character. The calculated values of U' and Δ are 5.5 and 3.9 eV, respectively, indicating that PrCoO₃ is a CT type compound. The crystal field splitting and 3d bandwidth of Co ions are found to be 2.8 and 1.8 eV, respectively.

2. Experimental details

Single-phase polycrystalline powder samples of PrCoO₃ and Pr_{0.8}Ca_{0.2}CoO₃ were prepared by the combustion method [10]. They were characterized by powder x-ray diffraction (XRD) and resistivity techniques. Lattice parameters obtained from Rietveld analysis match well with the literature. Resistivity measurements revealed that both the samples are insulating. The XPS measurements were carried out using a photoelectron spectrometer equipped with an OMICRON electron analyser (model EA125). All the core levels, Auger and valence band spectra reported in the present work were carried out using Mg K α radiation at 50 eV pass energy of the spectrometer. The measured resolution was about 0.85 eV. The sample was mounted in the form of a compressed hard pellet and it was scraped uniformly by a diamond file before carrying out the measurements. The final spectrum was taken only when the feature coming from carbon contamination of the surface merged in the spectrum background. The Fermi level (E_f) was aligned by recording the VB spectrum of *in situ* cleaned gold foil. In order to check for any deviation in E_f , VB spectra of gold were recorded immediately after taking the photoemission spectrum of each compound under present study. The vacuum of the chamber during the experiment was 5×10^{-10} Torr.

3. Computational details

Spin unpolarized electronic structure calculations were carried out using LMTART 6.52 [11]. To calculate the charge density, the full-potential LMTO method working in the plane wave representation was used. In the calculation we have used the muffin-tin radii of 3.521, 2.03 and 1.728 au for Pr, Co and O sites, respectively, corresponding to lattice parameters of PrCoO₃. The charge density and effective potential are 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

Table 1. The best values of on-site Coulomb interaction, U , and exchange interaction, J , for Co 3d and Pr 4f electrons corresponding to the experimental valence band spectrum of PrCoO₃.

Method of calculation	On-site Coulomb-exchange interaction for	U (eV)	J (eV)
LDA	—	0.0	0.0
LDA + U	Co 3d electrons	3.5	1
	Pr 4f electrons	3.5	0.698

density functional theory was taken after Vosko, Wilk and Nussair and the generalized-gradient approximation scheme of Perdew *et al* [12] was also invoked. (6, 6, 6) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate the DOS. Self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10^{-4} Ryd/cell.

LDA + U gives a better explanation for electronic properties of the systems containing transition metal or rare-earth metal ions or both with partially filled d (and/or f) orbitals, whereas LDA is useful for the systems consisting of delocalized s and p electrons [8]. We used both LDA and LDA + U methods to calculate the DOS of PrCoO₃. In the LDA the interaction potential depends on the average local electronic density and hence the occupied and unoccupied orbitals are degenerate. Due to this LDA fails to create gap at the Fermi level and the calculated DOS shows metallic behaviour. This discrepancy is resolved in the LDA + U method where interaction potential depends on the orbital degrees of freedom and hence the eigenvalues of occupied and unoccupied orbitals are different. Thus the method is capable of creating a gap at the Fermi level and giving the correct ground state of the system. In the LDA + U method three input parameters are required for 3d electrons. They are Slater integrals F^0 , F^2 and F^4 . These integrals are directly related to on-site Coulomb interaction (U) and exchange interaction (J) by relations $U = F^0$, $J = (F^2 + F^4)/14$ and $F^4/F^2 \sim 0.625$ [13]. We have tried several values of U (1.5–8.5 eV in steps of 1.0 eV) and J (0.3–1.2 eV in steps of 0.1 eV). The calculated DOS with $U = 3.5$ and $J = 1.0$ eV were the most representative of the experimental VB spectrum. Moreover, these values of U and J gave the ground state with lowest energy. This value of J is close to the earlier reported value for CoO [14]. Four input parameters are also required when the on-site Coulomb and exchange interactions between 4f electrons are considered in the calculations. They are Slater integrals F^0 , F^2 , F^4 and F^6 (the same symbol F is used for simplicity as in the 3d case; this should cause no confusion). These integrals are directly related to on-site Coulomb interaction (U) and exchange interaction (J) by relations $U = F^0$, $J = (286F^2 + 195F^4 + 250F^6)/6435$ [8]. For rare-earth elements $F^4/F^2 = 0.624$ and $F^6/F^2 = 0.448$ [15]. Judd *et al* [15] have also given the value of $F^2 = 8.647$ eV for the Pr³⁺ ion. We have taken this value of F^2 in our calculations and varied F^0 from 1.5 to 9.5 eV in steps of 0.5 eV. The values of U and J for Co 3d and Pr 4f electrons obtained from the above relations that give the DOS which is the best representative of the experimental VB spectrum are given in table 1. The DOS calculated using these values is used for discussion in the next section. It is interesting to note that the value of $U = 3.5$ eV, giving the DOS which is the best representative of the experimental VB spectrum, is approximately equal to the separation of two Co L₃M_{4,5}M_{4,5} Auger peaks (figure 1). It will be interesting to see whether this observation is unique for PrCoO₃ or is a common feature for all such compounds.

4. Results and discussions

Figure 2 shows the satellite subtracted and fitted core level spectrum of Pr 3d_{5/2} states. It contains two peaks, one at 928.5 eV and another at 933.0 eV. The binding energy (BE) of Pr

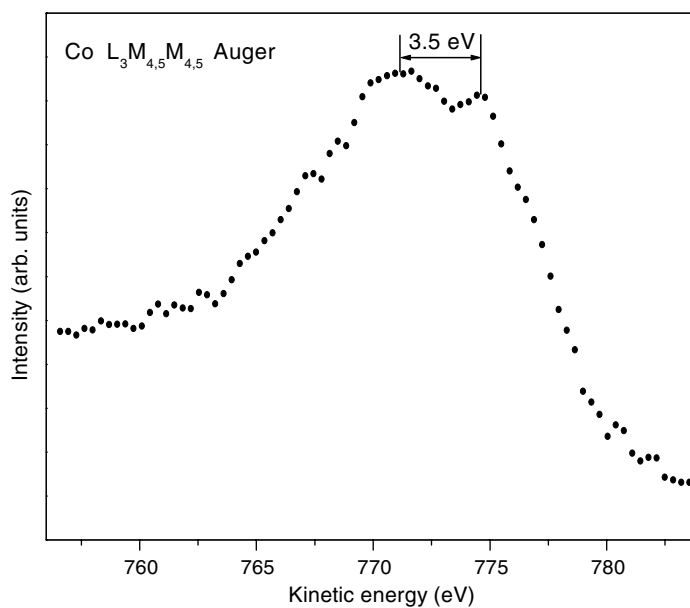


Figure 1. Co L₃ M_{4,5} M_{4,5} Auger spectrum of PrCoO₃.

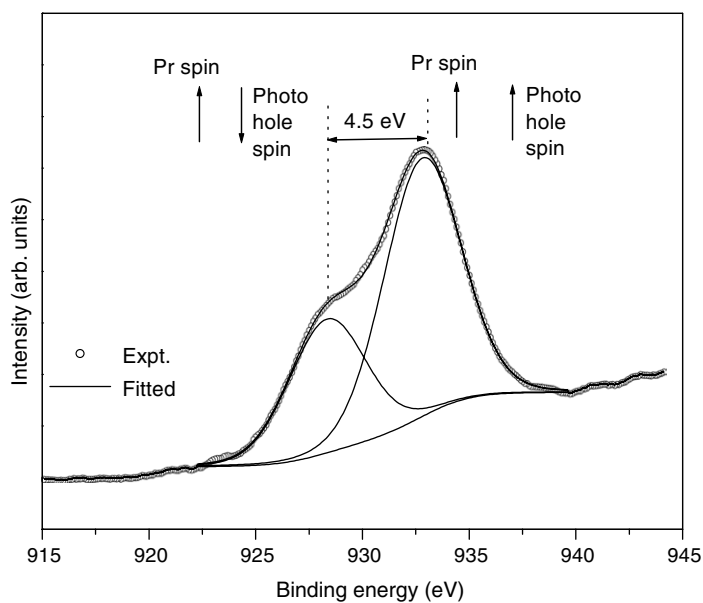


Figure 2. Pr 3d_{5/2} x-ray photoemission spectrum. Two peaks arise from spin coupled exchange interaction with 4f holes. Open circles represent the experimental spectrum and solid lines correspond to the fitted curves including the background.

3d_{5/2} and Co 2s states for neutral Pr and Co atoms are 928.8 and 925.1 eV, respectively. These values are expected to increase for Pr³⁺ and Co³⁺ ions. The theoretical ratio of cross sections of Pr 3d_{5/2} to Co 2s is about 7.8 for Mg K α radiation [16]. The integrated intensity under the experimental peak at 933.0 eV is 1.93 times that under the peak at 928.5 eV. If one of the

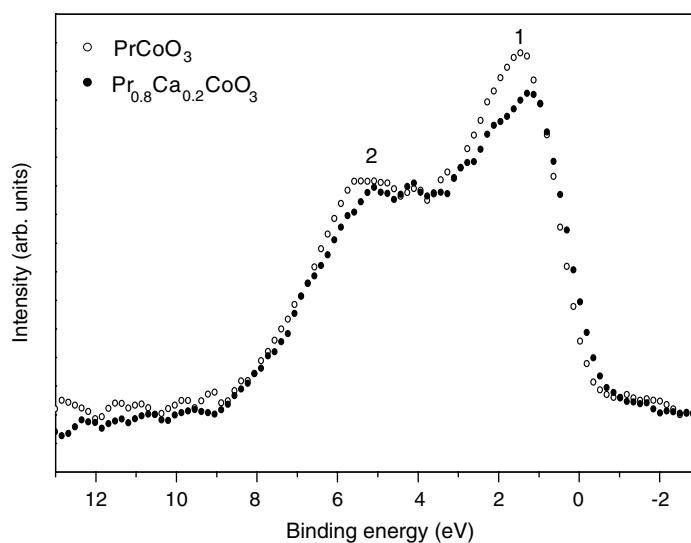


Figure 3. Background subtracted valence band spectra of PrCoO_3 (open circles) and $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ (closed circles).

peaks is considered as arising from Co 2s and another from Pr $3d_{5/2}$, the observed intensities are in contradiction with the known cross sections for these peaks. We thus interpret both the peaks as arising from Pr $3d_{5/2}$. There might be some Co 2s contribution in the experimental data; however, it is not resolvable. The two peaks can be understood by considering exchange splitting of the Pr $3d_{5/2}$ level. In the photoelectron emission process one hole is created in the Pr $3d_{5/2}$ state. The spin state of this hole couples with the spin state of Pr 4f holes and results in exchange splitting of the Pr $3d_{5/2}$ state. The multiplicity of the doublet thus created is four and two and hence the ratio of the integrated intensity of the two peaks should be 2:1, which is close to the observed value. The energy separation of the doublet formed by exchange splitting is the energy difference between these two peaks, which is 4.5 eV. We have also observed two similar peaks in the PrFeO_3 compound [10].

In figure 3 the background subtracted VB spectrum of PrCoO_3 is shown by open circles. At the Fermi level, the curve exhibits a very low intensity, i.e. a shape corresponding to the tail of decreasing photoemission signal. Such a small intensity gives an impression that the sample is metallic at room temperature. But our resistivity data show insulating behaviour. It is well established that a small intensity at the Fermi level may be seen even in the insulating samples due to finite resolution of the spectrometer. Such a situation has been noted by other workers as well [6, 17]. Two peaks, labelled as 1 and 2, are clearly visible in the VB spectrum, a sharper one at 1.6 eV and a broader one at 5.2 eV. To identify the contribution of different bands to these peaks we have calculated the partial DOS. Figure 4 shows the DOS of PrCoO_3 including the partial DOS of Pr 4f, Co 3d and O 2p calculated under the local density approximation (LDA). It is evident from the figure that the occupied DOS can be divided into three distinct bands labelled by 1', 1 and 2. Band 1' mainly consists of Co 3d and Pr 4f states. Band 1 has a contribution mainly from O 2p states and band 2 has mixed O 2p and Co 3d character. These three bands are well separated and the separation between them is greater than the experimental resolution. Thus the experimental VB spectrum with only two peaks cannot be accounted for by using these DOS. Moreover, there is finite DOS at the Fermi level due to contribution from Pr 4f and Co 3d states, indicating that the PrCoO_3 should be conducting, which is contrary to

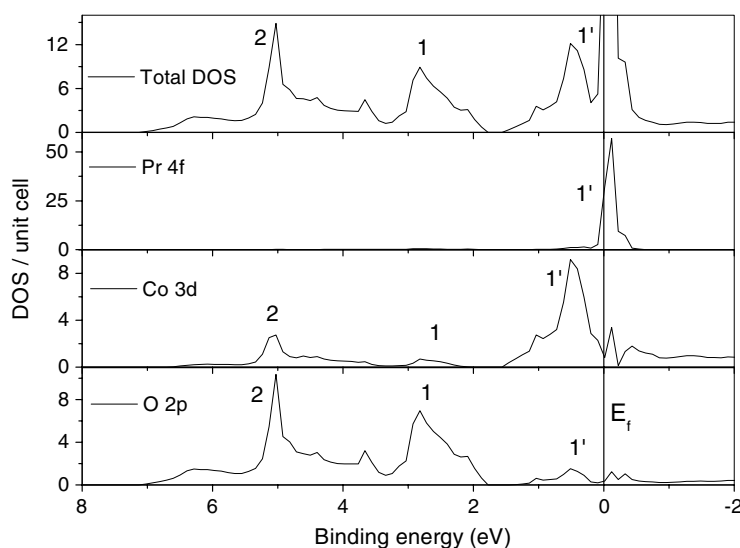


Figure 4. DOS of PrCoO₃ calculated using the LDA method (different Y-scales are used for different partial DOS for the sake of clarity).

the experimentally observed insulating behaviour. Such failure of LDA in explaining transport properties of transition metal oxides from Fe onwards has been seen in the literature. Hence we used the LDA + U method to calculate the DOS.

Figure 5 shows the calculated DOS of PrCoO₃ using the LDA + U method ignoring Coulomb and exchange interactions between Pr 4f electrons but including them for Co 3d electrons. The upper part of the figure shows the total DOS of the system. It shows that all bands are affected in such a way that bands of metal ions (i.e. Co³⁺ and Pr³⁺) shift to higher BE and that of ligand ion (i.e. O²⁻) to lower BE. The total occupied DOS consists of Pr 4f, Co 3d and O 2p bands. It can be divided into three bands indicated by 1', 1 and 2 in the figure. Band 1' lies just near the Fermi level, band 1 between 1.5 and 3.5 eV and, band 2 between 3.6 and 6.6 eV. The bandwidths of bands 1 and 2 are about 2.0 and 3.0 eV, respectively, whereas band 1' is very sharp. The separation between bands 1' and 1 is about 1.1 eV, which is more than the experimental resolution. From the figure it is evident that bands 1 and 2 have highly mixed character of Co 3d and O 2p electronic states, indicating strong hybridization between them. This fact is also indicated by the total occupancy of the 3d orbitals. Calculations give this to be 6.8, which is 0.8 larger than the nominal occupancy, 6, of the 3d orbitals in Co³⁺. For LaCoO₃ the total occupancy of 3d orbitals found by Korotin *et al* [3] is 7.2, a value greater than our value of 6.8 in PrCoO₃. This may be due to the fact that PrCoO₃ is more distorted than LaCoO₃, thereby decreasing the overlap of O 2p and Co 3d orbitals. If we look at the top of the VB (excluding the contribution from Pr 4f states) we find that it is a mixture of dominant O 2p orbitals with Co t_{2g} orbitals. Such behaviour of the top of the VB would indicate that PrCoO₃ is a charge transfer type compound under the ZSA scheme [4]. The top of the VB of CuO, which is a well known CT type compound, also shows similar nature [8].

A simple way to understand the behaviour of electronic states in PrCoO₃ and similar compounds is shown schematically in figure 6. This figure is a modified form of the one given by Imada *et al* [1]. The left side of this figure gives calculated DOS under LDA and the right side shows the expected change when LDA + U is considered. When on-site Coulomb and exchange interaction (U') is not considered, i.e. under LDA, the top of the valence band has

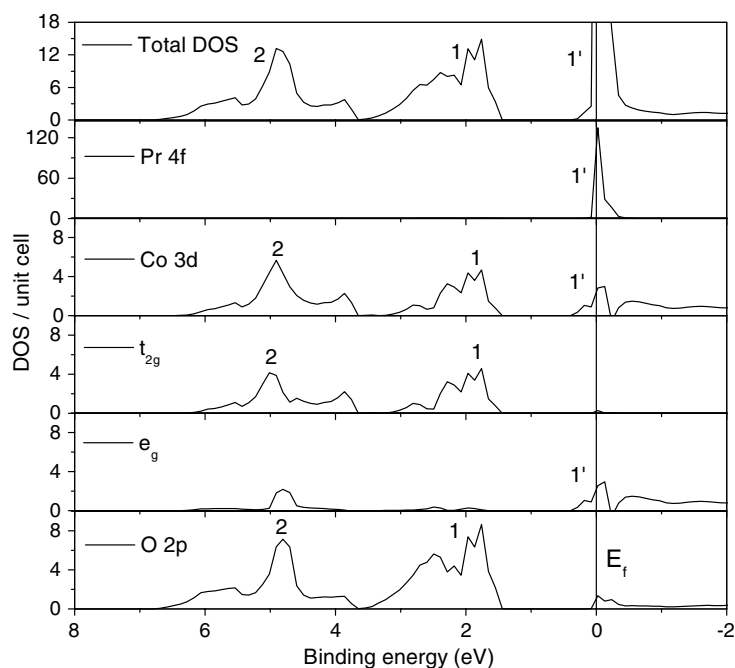


Figure 5. DOS of PrCoO_3 calculated using the LDA + U method with on-site Coulomb and exchange interaction between Co 3d electrons included (different Y -scales are used for different partial DOS for the sake of clarity).

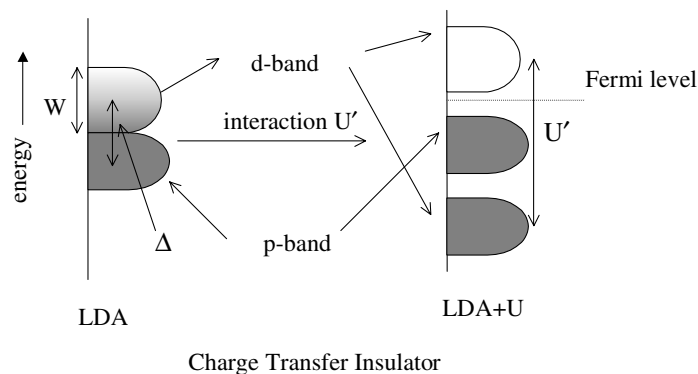


Figure 6. Schematic diagram of DOS for CT insulator; left corresponding to LDA and right corresponding to LDA + U .

only d character and the p band lies just below the d band. The separation between their CGs is the charge transfer energy Δ . On including U' , the p band shifts up closer to the Fermi level and the d band shifts down away from the Fermi level in such a way that the occupied d band lies below the p band. The energy difference of CG between the occupied and unoccupied d bands is then equal to U' . As can be seen from the comparison of figures 4 and 5, on inclusion of the U' band 1 of Co 3d states shifts to higher BE by 1.5 eV while the CG of band 2 remains almost unchanged. However, the DOS of band 2 grows at the cost of the DOS of band 1. Both bands of O 2p states show opposite behaviour to Co 3d bands. Band 1 of O 2p states shifts

to lower BE by 0.4 eV with increased DOS, whereas the position of band 2 remains almost unchanged but its DOS decreases. On considering on-site Coulomb and exchange interaction of 3d electrons, readjustment of the BE positions and DOS of O 2p and Co 3d bands occurs in such a way that the top of the VB has dominating 2p character, which is characteristic of the CT type system. It is thus seen that LDA and LDA + U can be used to extract the values of parameters Δ and U' , respectively. For PrCoO₃, Δ is found to be about 3.9 eV. This value is close to the value obtained by Chainani *et al* [6] for LaCoO₃. The value of U' for PrCoO₃ is about 5.5 eV. This value is closer to the value obtained by Saitoh *et al* [17] by analysing the Co 2p core level XPS spectrum of LaCoO₃. The values of U' and Δ thus obtained are compatible for a CT type insulator as $U' > \Delta$. Hence LDA and LDA + U methods can together be used to categorize the materials based on the ZSA scheme. It is interesting to note that the value of U' is not a simple sum of Coulomb and exchange contributions; instead, in the present compound it is $U + 2J$. This has also been observed in other systems; e.g., in Mn alloy it is $U + 4J$ [18].

Thus we see that inclusion of on-site Coulomb and exchange interactions between only Co 3d electrons gives a considerable understanding of the system. However, the experimental VB spectrum with only two peaks cannot be accounted for by using these DOS. Moreover, there is significant DOS at the Fermi level due to contribution from Pr 4f. As PrCoO₃ is insulating, there should be a gap at the Fermi level. Thus, only on-site Coulomb and exchange interaction between Co 3d electrons is not sufficient to give the correct ground state for PrCoO₃. This deviation of the calculated DOS from the observed behaviour is mainly due to non-inclusion of the on-site Coulomb and exchange interaction between Pr 4f electrons. Pr 4f electrons are more localized than Co 3d electrons and the on-site Coulomb and exchange interaction is expected to be more than that for Co 3d electrons. Thus it may be anticipated that the Pr 4f band (i.e. band 1') will merge with band 1 on including on-site interaction, thereby creating a gap at the Fermi level.

To check this explicitly, we calculated the DOS including on-site Coulomb and exchange interactions for both Co 3d and Pr 4f electrons. Figure 7 shows the calculated DOS including the partial DOS of PrCoO₃. Total occupied DOS is shown in the upper part of the figure. It consists of Pr 4f, Co 3d, and O 2p states. Closer inspection of the total DOS near the Fermi level shows a clear jump just above the Fermi level. The DOS just below the Fermi level is about 25 times lower than that just above it. The occupied DOS can be divided into two bands indicated by 1 and 2 in figure 7. Band 1 lies between 1.2 and 3.4 eV and, band 2 between 3.7 and 6.5 eV. As can be seen from the comparison of figures 5 and 7, on inclusion of interaction between 4f electrons, band 1 shifts near to the Fermi level by 0.3 eV, making it broader, whereas the position and width of band 2 remains almost unchanged. The peak position and bandwidth of band 1 is 1.6 and 2.2 eV, respectively. This peak position is almost the same as the position of peak 1 of the VB spectrum (figure 3). Thus the calculated DOS clearly represents the experimental VB spectrum.

The calculated partial DOS indicates that Pr 4f states contribute only in peak 1 of the VB spectrum whereas Co 3d and O 2p states contribute to both the peaks. The region near the Fermi level has the largest contribution from Pr 4f states and the least from the Co 3d states. Peak 1 has highly mixed character of Pr 4f, O 2p and Co 3d states and peak 2 has highly mixed character of only O 2p and Co 3d states. The mixing of these states is an indication of their strong hybridization. This fact is indicated by the total occupancies of 3d and 4f orbitals. Calculations give the total occupancy of 4f orbitals to be 2.4, which is 0.4 larger than the nominal occupancy of these orbitals in Pr³⁺. The total occupancy of 3d orbitals does not change on inclusion of interaction between 4f electrons. Such values of total occupancies of the Pr 4f and Co 3d orbitals may indicate the transfer of charge from O sites to Pr and Co sites. A simple way to check the contribution of Pr 4f in peak 1 experimentally is to change the relative concentration

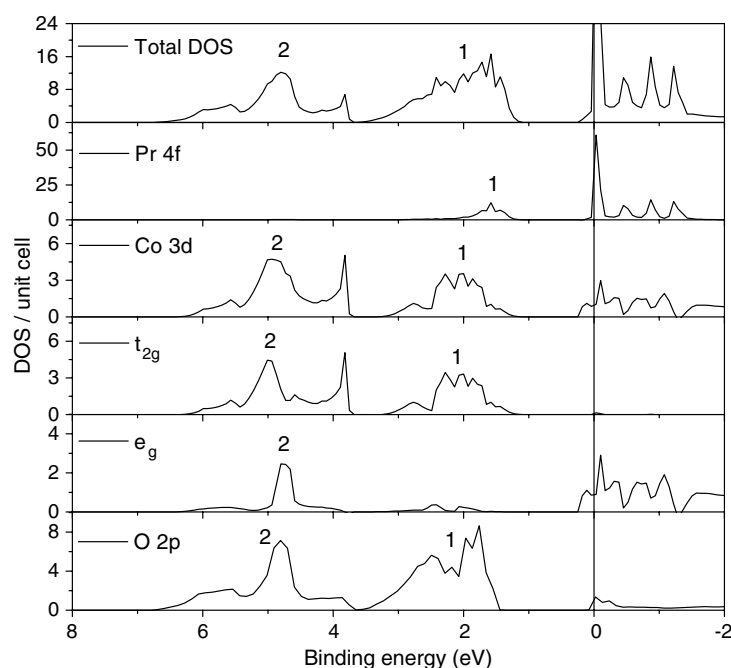


Figure 7. DOS of PrCoO_3 calculated using the LDA + U method with on-site Coulomb and exchange interaction between Co 3d and Pr 4f electrons included (different Y -scales are used for different partial DOSs for the sake of clarity).

of Pr by doping. We replaced 20% Pr by Ca and recorded the VB spectrum. Closed circles in figure 3 indicate the VB spectrum of $\text{Pr}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$. It also consists of two peaks, 1 and 2 around 1.6 and 5.2 eV, respectively. The intensity of peak 1 decreases with respect to peak 2, indicating the contribution of Pr 4f states in peak 1.

On inclusion of on-site Coulomb and exchange interaction between Pr 4f electrons the energy difference of the CG of occupied and unoccupied 3d bands remains almost unchanged, giving the same value of U' as obtained earlier, indicating that PrCoO_3 is indeed a CT insulator. Besides U' and Δ , the crystal-field-splitting energy and bandwidth W of the transition metal 3d band are also important physical parameters for cobaltates. The crystal-field-splitting energy governs the temperature dependent spin state transitions. It is the energy difference between the CG of t_{2g} and e_g orbitals, which is 2.8 eV for PrCoO_3 . This value, though larger than that of LaCoO_3 [19], is compatible with the higher spin state transition temperature of PrCoO_3 in comparison to LaCoO_3 . W is the bandwidth of the 3d band of transition metal when on-site Coulomb and exchange interaction is absent. It is the measure of delocalization of electrons. The competition between W and U' decides the physical properties of the system. For PrCoO_3 , $W \sim 1.8$ eV was obtained from LDA DOS calculations.

5. Conclusions

Electronic states of PrCoO_3 have been studied using XPS core level, valence band (VB); LDA and LDA + U DOS calculations. The Pr $3d_{5/2}$ core level showed the spin coupled exchange splitting of 4.5 eV. It is found to be necessary to include on-site Coulomb and exchange interactions between Pr 4f electrons in addition to those between Co 3d electrons to get better

agreement with the experimental VB spectrum. VB consisted of highly mixed Pr 4f, Co 3d and O 2p states. Bands near the Fermi level have dominating O 2p and Pr 4f character rather than Co 3d character. The values of charge transfer energy $\Delta = 3.9$ eV and Coulomb and exchange energy $U' = 5.5$ eV were found, indicating that PrCoO₃ is a CT insulator in conformity with the Zaanen, Sawatzky and Allen scheme. The crystal-field-splitting energy was found to be 2.8 eV and the bandwidth of the Co 3d band was obtained to be 1.8 eV.

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