Electronic structure of Pr$_2$MnNiO$_6$ from x-ray photoemission, absorption and density functional theory

Padmanabhan Balasubramanian$^{1,2}$, Shalik Ram Joshi$^2$, Ruchika Yadav$^1$, Frank M F de Groot$^4$, Amit Kumar Singh$^{5,6}$, Avijeet Ray$^1$, Mukul Gupta$^7$, Ankita Singh$^1$, Satyendra Maurya$^5$, Suja Elizabeth$^3$, Shikha Varma$^2$, Tulika Maitra$^1$ and Vivek Malik$^1$

$^1$ Department of Physics, Indian Institute of technology, Roorkee-247667, Uttarakhand, India
$^2$ Institute of Physics, Bhubaneshwar-750012, India
$^3$ Department of Physics, Indian Institute of Science, C.V. Raman Avenue, Bangalore-560012, India
$^4$ Inorganic Chemistry & Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, Utrecht 3584 CG, Netherlands
$^5$ Institute Instrumentation Centre, Indian Institute of technology, Roorkee-247667, Uttarakhand, India
$^6$ Department of Physics, Marwari College, Darbhanga 846004, Bihar, India
$^7$ UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 017, India

E-mail: bpaddy123@gmail.com

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Abstract

The electronic structure of double perovskite Pr$_2$MnNiO$_6$ was studied using core x-ray photoelectron spectroscopy and x-ray absorption spectroscopy. The 2$p$ x-ray absorption spectra show that Mn and Ni are in 4+ and 2+ states respectively. Based on charge transfer multiplet analysis of the 2$p$ XPS spectra of both ions, we find charge transfer energies $\Delta$ of 3.5 and 2.5 eV for Ni and Mn respectively. The ground state of Ni$^{2+}$ and Mn$^{4+}$ ions reveal a higher $d$ electron count of 8.21 and 3.38 respectively as compared to the ionic values. The partial density of states clearly show a charge transfer character of the system for $U - J \geq 2$ eV. The O 1$s$ edge absorption spectra reveal a band gap of 0.9 eV, which is close to the value estimated from analysis of Ni and Mn 2$p$ photoemission and absorption spectra. The combined analysis of nature of spectroscopic data and first principles calculations reveal that the material is a $p - d$ type charge transfer insulator with an intermediate covalent character according to the Zannen–Sawatzky–Allen phase diagram.

Keywords: double perovskites, ferromagnetism, x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, density of states

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

1. Introduction

Transition metal compounds have always been of great interest since they show diverse physical properties like metal-insulator transition, high-temperature superconductivity, multiferroicity and various interesting phenomena like charge/orbital ordering and complex magnetic structures [1–12]. They include oxides like NiO, MnO or more complex materials like KNiF$_3$, rare-earth manganites, cuprates and nickelates [3, 9, 13–16]. In most cases, the parent compound is usually insulating and becomes metallic under influence of doping or pressure [2, 17]. In a unified scenario, insulating behaviour of the various oxides (or sulphides, dihalides) can be described by the Zannen–Sawatzky–Allen(ZSA) phase...
diagram, which classifies the materials into Mott–Hubbard and charge-transfer insulators [18]. The electronic behaviour is governed mainly by three parameters: \( d \rightarrow c \) Coulomb repulsion \( U_{dd} \) in the transition metal ion, ligand-to-metal charge transfer energy \( \Delta \) and metal-ligand hybridization strength \( V_{pd} \) [18]. In the compounds based on early series of the transition metals (Ti, V and Cr), \( U_{dd} \leq \Delta \) and the bandgap, \( E_g \propto U_{dd} \). These compounds are known as Mott–Hubbard insulators. The late transition metal based compounds (e.g.: hole doped cuprates, NiCl\(_2\), NiBr\(_2\)), show greater ligand-metal charge transfer effect and for which \( U_{dd} > \Delta \) [19, 20]. Their band gap \( E_g \propto \Delta \), due to which these materials are known as charge transfer insulators. In a charge transfer insulator, the ground state involves a strong fluctuation between \( d^0 \) and \( d^{\pm 1}L \) states where \( L \) is the ligand hole. In compounds involving Mn and Fe, the scenario is much more complicated and the band gap shows intermediate character between the Mott–Hubbard and charge transfer insulators. In addition to \( U_{dd} \), \( V_{pd} \) and \( \Delta \), the 3d bandwidth \( W \) and anion bandwidth \( w \) play an important role in determining whether the given compound is a metal or insulator.

X-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) studies at the \( 2p \) core levels of transition metal ions are probes of the electronic structure, Mn and Ni ions are randomly arranged, since they occupy the same Wyckoff position 2\( f \). However charge disproportionation results in formation of Mn\(^{3+}\) and Ni\(^{2+}\) ions in accordance to the following reaction, Ni\(^{3+}\) + Mn\(^{2+}\) ⇌ Ni\(^{2+}\) + Mn\(^{3+}\) [26, 27]. This favours a rocksalt like arrangement of Mn and Ni in La\(_2\)MnNiO\(_6\). Our studies are based on Pr\(_2\)MnNiO\(_6\), which is a less explored member of the R\(_2\)MnNiO\(_6\) series. Its ‘parent compounds’, PrMnO\(_3\) and PrNiO\(_3\) are A-type and G-type antiferromagnetic insulators respectively, while Pr\(_2\)MnNiO\(_6\) is a ferromagnetic insulator [28]. The Mn\(^{3+}\)–Ni\(^{2+}\) super-exchange interactions are ferromagnetic in nature, yield a transition temperature, as high as 280 K in the case of La\(_2\)MnNiO\(_6\) [29]. With decreasing cationic radii due to increasing \( R \), the decrease in (Mn–O–Ni) bond angle affects the exchange interaction and decreases the magnetic transition temperature in a systematic manner. Even in perfectly ordered monoclinic structure, there occurs small percentage of randomness in distribution of Mn and Ni which are known as anti-site disorders. This result in Mn\(^{3+}\)–Mn\(^{4+}\) and Ni\(^{2+}\)–Ni\(^{3+}\) super-exchange interactions which are anti-ferromagnetic in nature. In the extreme limit of anti-site disorders and random occupations, there occurs formation of Mn\(^{3+}\) and Ni\(^{3+}\) regions, which can result in Mn\(^{3+}\)–Ni\(^{3+}\) ferromagnetic-super-exchange interactions. This results in second transition at lower temperature, sometimes leading to a glassy state at low temperatures [26, 30]. Using XPS, one can probe the valence state of Mn with greater precision, since the 3s splitting is proportional to the local spin of the Mn ion [31]. Moreover the large saturation moment at 5 K clearly suggest that this compound can be prepared with minimal presence of anti-site disorders as compared to the much studied La\(_2\)MnNiO\(_6\) and Nd\(_2\)MnNiO\(_6\) compounds.

However, the homovalent substitution of Mn and Ni as in LaMn\(_{1-x}\)Ni\(_x\)O\(_3\) leads to totally different electronic properties, especially for \( x = 0.5 \). The half doped compound, LaMn\(_{0.5}\)Ni\(_{0.5}\)O\(_3\) also crystallizes as La\(_2\)MnNiO\(_6\) depending on synthesis technique [26]. The former is orthorhombic (Pbnm), while the latter belongs to the class of double perovskite compounds with monoclinic symmetry. In the orthorhombic structure, Mn and Ni ions are randomly arranged, since they occupy the same Wyckoff position 2\( b \). However charge disproportionation results in formation of Mn\(^{3+}\) and Ni\(^{2+}\) ions in accordance to the following reaction, Ni\(^{3+}\) + Mn\(^{2+}\) ⇌ Ni\(^{2+}\) + Mn\(^{3+}\) [26, 27]. This favours a rocksalt like arrangement of Mn and Ni in La\(_2\)MnNiO\(_6\). Our studies are based on Pr\(_2\)MnNiO\(_6\), which is a less explored member of the R\(_2\)MnNiO\(_6\) series. Its ‘parent compounds’, PrMnO\(_3\) and PrNiO\(_3\) are A-type and G-type antiferromagnetic insulators respectively, while Pr\(_2\)MnNiO\(_6\) is a ferromagnetic insulator [28]. The Mn\(^{3+}\)–Ni\(^{2+}\) super-exchange interactions are ferromagnetic in nature, yield a transition temperature, as high as 280 K in the case of La\(_2\)MnNiO\(_6\) [29]. With decreasing cationic radii due to increasing \( R \), the decrease in (Mn–O–Ni) bond angle affects the exchange interaction and decreases the magnetic transition temperature in a systematic manner. Even in perfectly ordered monoclinic structure, there occurs small percentage of randomness in distribution of Mn and Ni which are known as anti-site disorders. This result in Mn\(^{3+}\)–Mn\(^{4+}\) and Ni\(^{2+}\)–Ni\(^{3+}\) super-exchange interactions which are anti-ferromagnetic in nature. In the extreme limit of anti-site disorders and random occupations, there occurs formation of Mn\(^{3+}\) and Ni\(^{3+}\) regions, which can result in Mn\(^{3+}\)–Ni\(^{3+}\) ferromagnetic-super-exchange interactions. This results in second transition at lower temperature, sometimes leading to a glassy state at low temperatures [26, 30]. Using 3s XPS, one can probe the valence state of Mn with greater precision, since the 3s splitting is proportional to the local spin of the Mn ion [31]. Moreover the large saturation moment at 5 K clearly suggest that this compound can be prepared with minimal presence of anti-site disorders as compared to the much studied La\(_2\)MnNiO\(_6\) and Nd\(_2\)MnNiO\(_6\) compounds.
2. Methodology

2.1. Experimental

The polycrystalline samples of Pr\textsubscript{2}NiMnO\textsubscript{6} were synthesized by conventional solid-state reaction using stoichiometric proportions of highly pure (99.99\%) precursors Pr\textsubscript{6}O\textsubscript{11}, NiO and MnO\textsubscript{2} by repeated sintering. Samples were synthesized at different temperatures in the temperature range (1000–1200) °C. The sintered powder, was mixed with small amounts of polyvinyl alcohol (PVA), was pressed into pellets using high pressure setup. The pellets were again sintered at 1250 °C in air.

Resistivity studies were carried out in temperature range of 4 to 300 K using four probe method. Magnetic properties were measured using a superconducting quantum interference device (SQUID) in the temperature range 10–300 K. AC susceptibility measurements were carried out in a commercial CYROBIND set-up in the temperature range 4.2–280 K.

The x-ray photoelectron spectroscopy (XPS) studies were carried out on a VG Mikrotek x-ray photoelectron spectroscopy system (Al K\textsubscript{α} source). This system operates under UHV at base pressure of 1 × 10\textsuperscript{-11} mbar. The load lock chamber is maintained at a base pressure of 1 × 10\textsuperscript{-8} mbar. The load lock chamber is equipped with 3 keV Ar ion gun to etch the sample surface. Before scans the sample surface was etched for two minutes. The take-off angle has been set to 0° w.r.t. surface normal. For our sample, survey scan from 0–1200 eV was acquired by operating the analyzer with pass energy of 200 eV. High resolution scans with 26 eV pass energy are obtained for quantitative analysis of XPS spectrum. The resolution of the system is 0.9 eV. Shirley background correction has been used to subtract the background from XPS spectrum. For analysis and peak fitting of XPS spectrum, VGX900 software has been used. The binding energies were calibrated based on C 1s spectra with binding energy of 284.6 eV. The spectra was collected at the Mn and Ni 2p edges and Mn 3s edge. The x-ray absorption spectroscopy (XAS) measurements were carried out at BL-01 beamline in INDUS-2 synchrotron centre, India at room temperature. The base pressure of sample chamber was at 10\textsuperscript{-8} mbar. The absorption spectra was obtained at O 1s edge, Mn and Ni 2p edges using the total electron yield method. Energy calibration was done using a standard graphite sample [32].

2.2. Computational studies

Computational studies were performed using the projector augmented wavefunction (PAW) method within the ambit of the density functional theory. The Vienna \textit{ab initio} simulation package (VASP) was used for this purpose [33]. The calculations were performed within the generalized gradient approximation (GGA) formalism. Both GGA and GGA + U formalism were used to see the effect of Coulomb correlations [34]. The Pr 5d, Mn 3d/4s, Ni 3d/4s, O 2s O 2p states were treated as valence orbitals while the Pr 4f state was treated as core orbital. The plane wave basis was used with a cutoff of 500 eV. Initially the crystal structure was relaxed until the forces on the atoms were less than 0.05 eV Å\textsuperscript{-1}. The structural optimisation was carried out assuming a ferromagnetic ordering between the Mn and Ni atoms in accordance with experiments. The selfconsistent electronic calculations were performed till the energy difference between successive cycles were less than 10\textsuperscript{-5} eV. The partial spin polarized density of states were obtained by performing integrations using a 7 × 7 × 5 Monkhorst pack.

3. Results and discussion

Figure 1(a) shows the Rietveld refinement of XRD pattern of powdered sample of Pr\textsubscript{2}MnNiO\textsubscript{6}. The pattern shows a single phase with absence of impurity peaks. The x-ray powder diffracion data of Pr\textsubscript{2}MnNiO\textsubscript{6} was refined to monoclinic space group P2\textsubscript{1}/n. The structural parameters obtained from our refinement are a = 5.4672 Å, b = 5.5362 Å and c = 7.7336 Å with β = 89.88°. The average Mn–O and Ni–O bondlengths are 1.93 and 2.04 Å respectively. The parameters are in agreement with the reported values [29]. The bondlengths of the three distinct Mn–O and Ni–O bonds in the octahedra are almost equal indicating absence of any structural distortions. The bond valence sums of 3.83 and 2.2 for Mn and Ni atoms suggests that their valencies are close to formal valencies of +4 and +2 respectively.
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Figure 1(b) shows plot of resistivity ($\rho$) versus temperature ($T$) of Pr$_2$MnNiO$_6$, which shows an insulating behaviour. The plot is shown only till 160 K, since the value of resistance exceeds the instrument range below this temperature. The inset of figure 1(b) shows a plot of ln($\sigma$) versus 1/T which shows a linear behaviour in a wide temperature range. From the slope we obtain an activation energy of 0.3 eV by fitting the conductivity to Arrhenius equation. The smaller value of activation energy is in agreement with the predicted band gap as obtained from GGA-based calculations as we would discuss below.

Figure 2 shows magnetization plots of Pr$_2$MnNiO$_6$ for ZFC and FC cooling. The paramagnetic–ferromagnetic transition occurs at 210 K which arises due to O$_2^-$ mediated Mn$^{4+}$–Ni$^{2+}$ super-exchange interactions. Absence of second transition in our system indicates a very low concentration of anti-site disorders. The magnetic moment of Pr$_2$MnNiO$_6$ at 15 K and 5 T is around 4.8 $\mu_B$ which is close to the expected value of 5 $\mu_B$ due to perfectly ordered system. However the slightly reduced value and absence of complete saturation in magnetization suggest presence of small amount of anti-site disorders, in addition to role of Pr$^{3+}$ spins. Ac susceptibility studies(not shown) rule out presence of a glassy phase at low temperatures.

3.1. X-ray photoemission and x-ray absorption spectroscopy studies

3.1.1. O 1s XPS. In figure 3(a), we show the O 1s XPS spectrum. The O 1s spectrum shows a major peak at 530 eV. The O 1s spectrum can be considered as a convolution of two or more peaks with shoulder-like features at 531 eV and 532 eV. The broad nature of the spectrum indicates that in addition to the bulk contribution, there arises contribution from the surface [35].

3.1.2. Mn 3s XPS. The role of anti-site disorders in affecting the total magnetic moment can also be obtained from Mn 3s spectrum. The 3s spectrum arises due to transition from the initial $|3s^2, 3d^3\rangle$ to final $|3s^1, 3d^3\rangle$ states. The Mn 3s spectrum shown in figure 3(b) exhibits a characteristic doublet due to the exchange splitting. The difference between interaction of 3s electron with the parallel and anti-parallel spins of the 3d$^3$ shell gives rise to the exchange splitting. This scenario is valid only in the case of early transition metal ions. In the case of Ni 3s XPS, the effect of charge transfer reduces the observed exchange splitting.

The magnitude of splitting is proportional the Slater exchange integral $G^2(3s, 3d)$ which is given by Van-Vleck theorem as [36],

$$\Delta E_{\text{ex}} = \left(\frac{2S + 1}{2l + 1}\right) G^2(3s, 3d),$$

where $l = 2$. The magnitude of $\Delta E_{\text{ex}}$ increases with decreasing valency [31]. Our experimental spectrum reveals an exchange splitting of 4.6 eV, which was obtained by fitting the data to sum of two Gaussian functions. Assuming that $G^2(3s, 3d)/ (2l + 1) = 1.1$ eV, the observed splitting corresponds to a net spin, $S = 1.6$ [37] based on the above equation. For an Mn$^{4+}$ system like CaMnO$_3$, the value of $\Delta E_{\text{ex}}$ observed is 4.5 eV [31], which corresponds $S = 3/2$. 
Thus in our material, though very close to the expected value of $S = 3/2$, the value of spin is greater than that expected in a complete Mn$^{3+}$ system. The higher value of $S$, indicates presence of Mn$^{3+}$ ions which arises due to anti-site disorders and mixed occupancy of the Ni(Mn) sites. However the signature of Mn$^{3+}$ is not so evident from our Mn 2p XPS and XAS studies.

3.13. Simulation of Ni and Mn 2p XPS and XAS spectra. In this section, we briefly discuss the theoretical simulation of the 2p XPS and XAS spectra. The simulations were done in the configuration interaction cluster model, using charge transfer multiplet program CTM4XAS [38] for individual Ni$^{2+}$ and Mn$^{4+}$ ions, both surrounded by oxygen ligand in octahedral (O\(_6\)) symmetry. The ground state electron configuration of Ni$^{2+}$ is $d^8$, which in O\(_6\) symmetry can be written as $^3A_2g(t^2_g)^2$. We consider two charge transfer configurations, $d^\beta L^2$ and $d^{\beta+1}L^2$, where $L$ corresponds to a ligand hole in the $O$ 2p state. The Mn$^{4+}$ ion has $d^3$ configuration in ground state, which can be written as $^4A_2g(t^2_g)$ in O\(_6\) symmetry. The calculation of Mn 2p spectra involving two charge transfer configurations is computationally difficult. Hence we consider only the $d^3L$ configuration. Also, the effects of $d^3L^2$ configuration is not so prominent in the Mn 2p XPS spectra. The ground state wavefunctions for Ni$^{2+}$ and Mn$^{4+}$ ions can be written as,

\[
\Psi_{Ni}^g = \alpha_0 |d^8\rangle + \beta_0 |d^\beta L^2\rangle + \gamma_0 |d^{\beta+1}L^2\rangle.
\]

(2)

\[
\Psi_{Mn}^g = \alpha_0 |d^3\rangle + \beta_0 |d^\beta L^2\rangle.
\]

(3)

The ligand-metal charge transfer energy is defined as, $\Delta = E(d^\beta+1L^2) - E(d^\beta) = 2\Delta + U_{dd}$, where $U_{dd} = E(d^{\beta+1}) - E(d^\beta) - 2E(d^\beta)$ is the $d-d$ Coulomb interaction [39]. The hybridization between the metal 3d and O 2p are defined by the off-diagonal matrix elements, $T = \langle d^\beta L | H | d^{\beta+1}L^2 \rangle$. The anisotropy in $T$ due to splitting between the $t_{2g}$ and $e_g$ states in Ni$^{2+}$ and Mn$^{4+}$ are denoted as $V_{e_g}$ and $V_{t_{2g}}$ respectively. The hybridizations strengths are related to Slater–Koster transfer integrals $V_{pder}$ and $V_{pdsr}$, through the expressions $V_{e_g} = -\sqrt{3}V_{pder}$ and $V_{t_{2g}} = -2V_{pdsr}$, while the Slater–Koster transfer integrals themselves are fixed by $V_{pdsr}/V_{pder} = -2.2$ [40]. The final state involves effect of 2p core hole which reduce final state energies by a constant term. This term, $U_{dc}$, corresponds to the attractive potential between the 2p core hole and the 3d electron. For 2p XPS the final states are,

\[
\Psi_{Ni}^{f} = \alpha_1 |d^8\rangle + \beta_1 |d^\beta L^2\rangle + \gamma_1 |d^{\beta+1}L^2\rangle.
\]

(4)

\[
\Psi_{Mn}^{f} = \alpha_1 |d^3\rangle + \beta_1 |d^\beta L^2\rangle.
\]

(5)

In the case of 2p XAS, the final states which are of the type $2p^33d^{\beta+1}$ are given by,

\[
\Psi_{Ni}^{f} = \alpha_1 |d^8\rangle + \beta_1 |d^{\beta+1}L^2\rangle.
\]

(6)

In the above equations $\zeta$ denotes the core-hole wavefunction. The calculations were performed for the entire multiplet spectrum [39]. The $3d - 3d$ and $2p - 3d$ Slater integrals were reduced to 80% of the Hartree–Fock values. The effect of bare crystal field splitting between the $t_{2g}$ and $e_g$ states were also included in the calculation by varying the separation 10$D_Q$ between 0 to 2.5 eV. The intensity of XPS and XAS spectra are calculated using sudden approximation [20, 39]. For matching the calculated and experimental spectra, $\Delta$, $V$ and $U_{dd}$ were systematically varied. The ratio $U_{dd}/U_{dc}$ was varied between 0.8 and 0.9 for optimum matching between the two spectra. The defination of $\Delta$ and $U_{dd}$ are based on the centre of gravity of multiplet of each charge transfer configuration. However, their actual values are defined based on the difference between the lowest multiplet energy of each configuration. These values are appropriately labelled as $\Delta_{eff}$ and $U_{eff}$. Both the parameters, play a major role in determining the ground state electronic properties of the system.

3.1.4. Ni 2p XPS spectra. In figure 4, we show the Ni 2p XPS spectrum of Pr$_2$NiMnO$_6$ along with simulated spectra. The XPS spectrum shows a single satellite peak of 2p$_{3/2}$ and 2p$_{1/2}$ regions with the main peaks located at 855 and 875 eV, respectively. Both the 2p regions show two additional satellite features. The second satellite of the 2p$_{3/2}$ is less prominent and has a lower intensity as compared to the satellite peaks of 2p$_{1/2}$. The second satellite of 2p$_{1/2}$ peak shows greater broadening effect. The Ni$^{2+}$ ion in Pr$_2$NiMnO$_6$ is surrounded by oxygen octahedra, similar to that in NiO. However the XPS spectra of NiO shows only a single satellite peak at each edge. This is seen in the spectra of bulk as well as thin films of NiO [20, 21, 41]. However, the second satellite feature is prominently seen in nickel dihalides, NiCl$_2$ and NiBr$_2$ while NiF$_2$ shows only a single satellite peak [20, 42]. Among the Ni dihalides, NiF$_2$ has the largest value of $\Delta$ due to the high electronegativity of fluorine, while $\Delta$ is smallest in the case of NiI$_2$. The prominent appearance of the second
satellite in our system clearly indicates a lower charge transfer energy and a greater covalency in our material as compared to the largely ionic characters of NiO and NiF₂.

The simulated Ni 2p XPS spectrum for an NiO₆ cluster is also shown in figure 4. The spectrum is optimised for \( \Delta = 3.5 \) eV and hybridization ratio \( V_\text{p}\)/\( V_\text{pu} = 2.1 \) to match with the experimental spectrum. The values of \( U_{\text{dd}} \) and \( U_{\text{dc}} \) are 7.5 and 9.0 eV respectively. The higher value of \( U_{\text{dd}} \) is in agreement with the greater charge transfer character of the late transition metal compounds. From the relative values of \( \Delta, U_{\text{dd}} \) and \( U_{\text{dc}} \), the ground states and final states of the Ni 2p XPS spectrum can be classified in four regimes as follows [20]. In our material since, \( \Delta > 0 \), the ground state has the following energy level sequence, \( E(\ell^\pi) < E(\ell^d L) < E(\ell^{10} L^2) \). As the three parameters satisfy the following inequalities, \( 2\Delta + U_{\text{dd}} < U_{\text{dc}} \) and \( U_{\text{dc}} - U_{\text{dd}} < \Delta < U_{\text{dc}} - U_{\text{dd}}/2 \), in the final state, the level energy level sequence becomes \( E(\ell^d L) < E(\ell^{10} L^2) < E(\ell^\pi) \). Thus in figure 4, the main peak has a majority \( \ell^d L \) character while the first and second satellite peaks have majority \( \ell^{10} L^2 \) and \( \ell^d \) characters respectively. The position and intensity of the satellites are dependent on the ratio, \( \Delta/V \). The weights of the \( \ell^d, \ell^d L \) and \( \ell^{10} L^2 \) components in the ground state are 0.78701, 0.20697 and 0.00603 respectively, which yields the average electron number \( \langle n_d \rangle = 8.21 \) in the ground state.

Using the relation mentioned by Fujimori et al [43], we have determined \( \Delta_{\text{eff}} \) and \( U_{\text{eff}} \), which are mentioned in table 1. We find that \( \Delta_{\text{eff}} > \Delta \) and \( U_{\text{eff}} < U \) as seen in the late transition metal ions. Thus analysis of Ni 2p XPS spectra suggests that the Ni–O bond in Pr₂MnNiO₆ has a greater covalency, especially when compared with Ni–O bonds in NiO.

3.15. Ni 2p XAS spectra. The Ni 2p x-ray absorption spectrum shown in figure 5, is split due to spin–orbit coupling into \( 2p_{3/2} \) and \( 2p_{1/2} \) peaks. The spectra displays characteristic feature of an Ni²⁺⁺ system [44]. Compared to the XPS spectra, the satellite intensities are weaker in XAS. The XAS spectrum contains distinct features marked a to f as shown in figure 5. The separation between the main peak a and the shoulder peaks b and c, along with shape of the peaks are affected by \( \Delta \) and V. The XAS spectrum qualitatively resembles the spectra of NiBr₂ and NiCl₂ similar to the XPS spectrum [44]. In figure 5, we also show the simulated Ni²⁺⁺ XAS spectra, which was obtained for \( \Delta = 3.5 \) eV and \( V = 2.1 \). Unlike the simulation of XPS spectra, we have assumed only a single charge transfer configuration \( d^3 L \) in the ground state since the 3d states becomes filled for \( d^{10} L^2 \) configuration. The simulated spectra was broadened by convoluting the line spectra with a Lorentzian function (0.3 eV) and Gaussian function (0.4 eV). However our experimental spectrum also shows an additional broadening, especially for features b and c compared to that observed in the Ni dihalides.

3.16. Mn 2p XPS spectra. In figure 6, we show the Mn 2p XPS spectrum of Pr₂NiMnO₆. The spectrum shows \( 2p_{3/2} \) and \( 2p_{1/2} \) spin–orbit doublet peaks located at 642 and 654 eV, respectively. In addition we observe the satellite peak of \( 2p_{1/2} \), at a binding energy of 666 eV. The satellite peak of \( 2p_{3/2} \) is not visible since it overlaps with the \( 2p_{1/2} \) peak. The position of the satellite peak relative to the main peak is sensitive to the d-electron count [45]. In figure 6 we also show the calculated Mn 2p spectrum for an MnO₆ cluster. The calculated spectra was convoluted with energy dependent Lorentzian function and energy independent Gaussian function. The Mn spectra is broader compared to Ni due to greater multiplet effects in the Mn⁴⁺ ion. The experimental spectra is well reproduced for \( \Delta = 2.5 \) eV and \( V = 2.1 \) along with \( U_{\text{dd}} = 6.5 \) and \( U_{\text{dc}} = 8.5 \) eV. Based on the values of the above four parameters, the main peak can be attributed to majority \( \ell^d L \) character, while the satellite peak can be attributed to majority \( \ell^d \) character. Moreover, the position and relative intensity of the satellite peak conforms to our simulation results, thereby indicating that the system can be described by a single Mn⁴⁺ configuration. A possible contribution of Mn⁵⁺ ions is not so clearly seen in the spectra. This is unlike the case of doped rare earth manganite systems where the satellite feature of the Mn 2p spectrum can be expressed as a linear combination of Mn in 3+ and 4+ valence states [45]. The weights of the \( \ell^d, \ell^d L \) configurations in the ground state are 0.625 and 0.375 respectively, resulting in \( d \)-electron count, \( \langle n_d \rangle = 3.38 \). The higher value of \( n_d \) than the ionic value of 3, indicates the greater charge transfer character and hybridization in the Mn–O bonds. The relatively smaller value of the charge transfer energy is comparable to the values obtained in isosstructural

| Table 1. Best fit parameters obtained from Ni and Mn 2p XPS and XAS spectra for Pr₂NiMnO₆. |
|----------------|--------|--------|
| Component      | Ni     | Mn     |
| Δ              | 3.5    | 2.5    |
| Δ_{eff}        | 4.5    | 1.5    |
| \( U_{\text{dd}} \) | 7.5    | 6.5    |
| \( U_{\text{dc}} \) | 5.5    | 6.0    |
| \( n_d \)     | 8.21   | 3.38   |
| \( V_{\text{p}}/V_{\text{pu}} \) | 2.1    | 2.0    |
| \( V_{\text{pbf}} \) | 1.21   | 1.2    |

Figure 5. Ni 2p absorption spectra of Pr₂NiMnO₆ along with simulated spectra.
Mn$^{4+}$ manganites, CaMnO$_3$ and SrMnO$_3$ [25, 46]. Thus the Mn–O bonds possess a greater covalency character as compared to Ni–O bonds in Pr$_2$MnNiO$_6$.

3.1.7 Mn 2p XAS spectra. The Mn 2p absorption spectra of Pr$_2$MnNiO$_6$ is shown in figure 7. The spectra comprises of two main features corresponding to 2$p_{3/2}$ and 2$p_{1/2}$. Unlike the XPS spectra, the absorption spectra does not show any satellite features. The spectral features are similar to that observed in CaMnO$_3$ and also La$_2$MnNiO$_6$, without any distinct sign of features associated with Mn$^{3+}$ ion [47]. The Mn 2p XAS spectra is also theoretically simulated for $d^3$ and $d^4L$ configurations in the ground state. The Mn 2p absorption spectra is highly sensitive to the crystal field splitting $10D_q$, unlike the XPS spectra. The feature at 650 eV becomes prominent with increase in the bare crystal field term $10D_q$. The experimental spectra is successfully reproduced for $10D_q = 2.5$ eV. This value is similar to that used for simulation in the case of La$_{0.9}$Ca$_{0.1}$MnO$_3$, which is predominantly an Mn$^{4+}$ system [47].

3.2. O 1s XAS spectra and density of states

Figure 8(a) shows the normalized O 1s XAS edge spectrum of Pr$_2$MnNiO$_6$ collected in the total electron yield mode. The first prominent peak (536–539 eV) of the spectrum arises due to the transition from O 1s to unoccupied O 2p states that are hybridized with 3d states of Mn and Ni above the Fermi energy($E_F$). For determination of $E_F$, we present spectrum of LaNiO$_3$, which is metallic compound, as well as LaMnO$_3$, which has a known band gap. The position of $E_F$ was fixed at the rising edge of LaNiO$_3$(10% of peak intensity) as shown in figure 8(a). The rise in spectra of LaMnO$_3$ occurs around 1.1 eV above $E_F$, which can thereby be considered as its bandgap. This value is close to the bandgap of 1.2 eV obtained from optical conductivity measurements [48]. In a similar manner, the bandgap of Pr$_2$MnNiO$_6$ is found to be
near states show sufficient mixing between the Mn and Ni states to a continuum. The peak intensity of Pr\(_2\)MnNiO\(_6\) is almost due to crystal field. Below \(E_F\), the Ni \(e_g\) states dominate the spin-up channel with a peak occurring around \(+1.5\) eV. The Mn \(t_{2g}\) states from the spin-down channel are nearer to \(E_F(+0.5\) eV), with a strong overlap with the Ni \(e_g\) states.

From our first principles calculations, the the Mn moments show a value of 2.8\(\mu_B\) which is close to its ionic value +3. However the Ni moments show a lesser value of 1.4\(\mu_B\) compared to its ionic value of 2.0 \(\mu_B\). The Ni states show a greater delocalization as compared to the Mn states, which reduces its magnetic moment.

Even for \(U-J=0\) eV, Pr\(_2\)MnNiO\(_6\) shows a band gap of 0.5\(eV\) which is close to the value obtained in La\(_3\)MnNiO\(_6\) [51]. This is unlike the case of RMnO\(_3\) which yield a ferromagnetic metallic ground state in the absence of correlations from first principles calculations. However the band gap is much smaller than CaMnO\(_3\) or NiO which are Mn\(^{4+}\) and Ni\(^{3+}\) systems due to the overlap between Ni and Mn 3d states. The effect of Coulomb correlations is more complex due to the inequivalent nature of the two transition metal ions. To probe its effect, the calculations were also performed for \(U-J=2, 5\) and 8\(eV\). With increase in \(U-J\), the spectral weight of O 2p states increase below \(E_F\), while the spectral weights of Ni and Mn 3d states, become negligible. Also for \(U-J=2\)\(eV\), the calculations show a higher band gap of 1.2\(eV\), which does not change even for \(U-J=8\)\(eV\). This is unlike the RMnO\(_3\), in which show a greater increase in band gap with increase in \(U\) in a systematic manner. The Coulomb correlations in Pr\(_2\)MnNiO\(_6\) hardly have any affect on the Mn \(e_g\) states above \(E_F\). On the other hand, the Mn \(t_{2g}\) and \(e_g\) states along with Ni\(_{eg}\) states move to higher energy above \(E_F\).

Since the 0\(s\) pre-edge is a direct representation of the unoccupied DOS we make a correspondence between the two. An optimal matching of the peak positions is seen for \(U-J=4\)\(eV\), which is shown in figure 8(b). Based on the DOS, the O 1\(s\) pre-edge region can be divided into two parts. The first part comprises of the highly overlapping Mn \(e_g\) and Ni \(e_g\) states. The high intensity of the central peak (538\(eV\)) in the spectrum can be attributed entirely to the Mn \(t_{2g}\) states followed by Mn \(e_g\) states around 539\(eV\).

### 3.3. Role of charge transfer, covalency in band gap

Unlike in NiO, the the Ni\(^{3+}\) in Pr\(_2\)MnNiO\(_6\) has smaller charge transfer energy due to which the \(d^3L\) state has significant occupancy in the ground state, thus showing a greater covalency in the Ni–O bond. Similarly, the \(d^8\) states are strongly hybridized to the \(d^3L\) states in the Mn\(^{4+}\) ion. The band gap of the material is determined by interplay of \(U_{dd}\), \(\Delta\) and \(V\), the later two reflecting the degree of covalency between the Ni–O and Mn–O bonds. An estimate of the hybridization strength is obtained from the Slater–Koster method, according to which \(V_{pd\sigma}\sim\beta_0\sim1/d_{\text{NiO}}^{1/2}\), where \(d_{\text{NiO}}\) corresponds to the average Ni–O bond distance.

**Figure 9.** Spin polarized local density of states per formula unit of Pr\(_2\)MnNiO\(_6\) for Mn and Ni 3d states and O 2p states for (a) \(U_{\text{eff}}=0\) eV, (b) 2\(eV\) and (c) 5\(eV\), where \(U_{\text{eff}}=U-J\). The zero is the Fermi energy \(E_F\).
and Mn–O bond lengths. The average Ni–O and Mn–O bond lengths in Pr$_2$MnNiO$_6$ which are 2.04 and 1.9 Å respectively, yield $V_{pd}$r = 1.13 eV for Ni–O bonds and a greater value of 1.8 eV for the Mn–O bonds. However the analysis of 2p XPS spectra yield nearly equal values, ie $V_{pd}$r = 1.21 eV for both the ions. In case of Ni$^{2+}$–O bond, $V_{pd}$r is comparable to its bare Slater–Koster integral, and also to the value obtained for NiO compound from analysis of its XPS spectra [40]. However the Mn$^{4+}$–O bond in Pr$_2$MnNiO$_6$ shows considerable reduction in $V_{pd}$r, when compared to values obtained for isovalent SrMnO$_3$ and CaMnO$_3$. For the Mn$^{4+}$–O bond in both these compounds, $V_{pd}$r is in the range between 1.5 and 1.6 eV, as obtained from XPS and XAS spectra [25, 45].

Thus CaMnO$_3$ and SrMnO$_3$ with a much smaller $\Delta_{eff}$ show a strongly hybridized ground state due to which they are considered as charge transfer insulators, though with a much larger bandgap. In the case of parent manganite LaMnO$_3$ even though a larger value of 2.2 eV is obtained for $V_{pd}$r, but due to relatively higher value of $\Delta_{eff}$ the RMnO$_3$ compounds have a mixed character, ie they lie between that of a Mott–Hubbard and charge transfer insulator in the ZSA phase diagram [52].

In the case of RNiO$_3$, the scenario is entirely different. Based on the average Ni–O bondlength of 1.94 Å, bare hybridization strength of 0.9 eV is obtained in the case of PrNiO$_3$. However the cluster calculation yields a ground state with large value of $\beta^2 \sim 0.55$ and $V_{pd}$r = 1.5 eV, which is much more than the bare Slater–Koster transfer integrals. The large covalency due to a small charge transfer energy ($\Delta \sim 1$ eV) and Ni–O–Ni hopping integrals are more sensitive to structural variation in nickelates [16]. Increase in Ni–O bond length and reduction in Ni–O–Ni bond angles from La to Nd drastically affect the hopping integrals and the $e_g$ bandwidths [53, 54]. Thus with varying R from La to Nd, this results in a transition from metallic to insulating state with a very small band gap in PrNiO$_3$ and NdNiO$_3$. Due to this, PrNiO$_3$ and NdNiO$_3$ are considered as ‘covalent insulators’ which are intermediate between charge transfer insulator and $p - d$ metal in the ZSA phase diagram [54].

However in the case of R$_2$MnNiO$_4$, the changes in Mn(Ni)–O bond lengths and Mn–O–Ni bond angles do not affect the Mn–O–Ni hopping integrals and the band width of the $e_g$ orbitals, even though there occurs changes in superexchange strength, which reduces the magnetic transition temperatures. This is also seen indirectly from high pressure studies on La$_2$MnNiO$_6$ which retains its ferromagnetic character even under 30 GPa pressure, with a small variation in $T_C$ and reduction in magnetic moments [55]. Thus in the R$_2$MnNiO$_6$ based double perovskites, the charge transfer from oxygen to Mn$^{4+}$ and Ni$^{2+}$ ions have a more robust character due to which the bandgap remains largely unaffected.

Within the ZSA formalism, the bandgap of various charge transfer insulators can be expressed as, $E_g = \Delta + \delta - W/2$; where $W$ corresponds to the ligand bandwidth, and $\delta = 2\delta^d - \delta^{e-1} - \delta^{n+1}$, corresponds to lowering of energy of $3d^8$ configuration due to hybridization [18].

In a simplified approximation of the above expression, the band gap $E_g$ is given by $\Delta_{eff} - W$, where $W = (W_d + W_p)/2$, is the average of the transition metal and ligand bandwidths [43]. From the single impurity Anderson model, we can assume that $W_p = 4$ eV and $W_d = 0.5$ eV (for Ni and Mn 3d bandwidths). Thus if we consider $\Delta_{eff}$ of Ni$^{2+}$ ion alone in Pr$_2$MnNiO$_6$ we would obtain a band gap of 2.25 eV, which though smaller than NiO by half still is much greater than the experimental bandgap of 0.9 eV. Due to the highly reduced $\Delta_{eff}$ of Mn$^{4+}$ ion, we can consider a net charge transfer energy of the system which is average of Mn and Ni. Thus for a net average charge transfer energy, $\Delta_{eff} = 3$ eV, we obtain a band gap of 0.75 eV, which is much closer to the experimentally obtained values, thereby suggesting a net Ni$^{2+}$–O–Mn$^{4+}$ charge transfer effect. The effect of charge transfer nature is also seen from the DOS in figure 9. At $U = 0$ eV, since the highest spectral weight is of 3$d$, the gap is of $d - d$ type. With increase in $U$, there is a large shift in spectral weight from 3$d$ to O 2$p$ states. Thus from first principles along with XPS studies we can establish that the double perovskite Pr$_2$MnNiO$_6$ is an intermediate covalent compound according to the ZSA phase diagram, with ‘$p - d$’ type bandgap.

3.4. Conclusions

To summarize, the electronic structure of double perovskite compound Pr$_2$MnNiO$_6$ is studied using 2p x-ray photoemission, x-ray absorption and O 1$s$ absorption spectroscopies. The Ni 2p XPS spectra shows a three peak structure indicating a greater charge transfer effect between the Ni$^{2+}$ and O$^{2-}$ ions. Using the charge transfer multiplet theory it is found that Ni$^{2+}$ ion has a charge transfer energy of 3.5 eV which is lower than that of isovalent compound NiO. The ground state of Ni$^{2+}$ ion can be written as 78% $d^8$, 21% $d^6L$ and 0.6% $d^{10}L^2$. Similarly, analysis of Mn 2p XPS spectra reveal that Mn$^{4+}$ has a charge transfer energy of 2.5 eV, which is close to that of isovalent compounds, CaMnO$_3$ and SrMnO$_3$. The ground state of Mn$^{4+}$ ion which has a highly mixed character, can be written as 62% $d^9$ and 38% $d^7L$. The Ni$^{2+}$ and Mn$^{4+}$ ions reveal a higher d electron count of 8.21 and 3.38 respectively. Based on our charge transfer analysis, we estimate a band gap of 0.75 eV which is close to the experimentally obtained value of 0.9 eV, from the O 1$s$ edge spectra. The density of states reveal a band gap of 1.2 eV for $U - J > 2$ eV, and remains constant even for $U - J = 8$ eV. Also, from the density of states, it can be inferred that the band gap is mainly of $p - d$ type. Since for Mn$^{4+}$ and Ni$^{2+}$ ions, $U > \Delta$ and $U_{eff} > \Delta_{eff}$ conditions are satisfied, Pr$_2$MnNiO$_6$ can be considered as a charge transfer insulator, with an intermediate covalent character.

**ORCID iDs**

Padmanabhan Balasubramanian  
https://orcid.org/0000-0003-4811-8246

Vivek Malik  
https://orcid.org/0000-0001-8792-2419
