

Contrasting behavior of homovalent-substituted and hole doped-systems: O *K*-edge spectra from $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Mn, Fe, and Co}$) and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

D.D. Sarma*

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

O. Rader and T. Kachel

*Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung G.m.b.H. (BESSY), Lentzeallee 100,
1000 Berlin 33, Germany*

A. Chainani and M. Mathew

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

K. Holldack and W. Gudat

*Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung G.m.b.H. (BESSY), Lentzeallee 100,
1000 Berlin 33, Germany*

W. Eberhardt

Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich 1, Germany

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We report x-ray absorption spectra at the oxygen *K* edge for $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Mn, Fe and Co}$) for values of x spanning the entire composition range which exhibit metal-insulator transitions at critical values of x . This study clearly shows that the metal-insulator transition in the homovalent substituted series is achieved by transferring hole states from near E_F to an energy position above E_F due to the potential of the substituent. This is in strong contrast to hole doping, e.g., as in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ where states are formed within the band gap of the underlying electronic structure. The sensitivity of the O *K*-edge spectra to substitution confirms the large oxygen *2p* admixture to states at the Fermi level due to a substantial hopping interaction strength between the transition-metal *3d* and oxygen *2p* derived states in these perovskite oxides. The present results suggest that the electronic structures of these perovskite oxides are dominated by local interactions.

INTRODUCTION

The metal-insulator transition in transition-metal oxides has been one of the most challenging, unresolved questions in solid-state physics.¹ In recent times there has been renewed interest in this area both theoretically and experimentally, following the discovery of high- T_c cuprate superconductors,² which helped to focus on many unanswered questions. In this class of compounds, the insulator-metal transition is brought about by doping charge carriers (electrons or holes) in a parent insulating oxide by substituting one component in the oxide with another component having a different formal oxidation state. This class of compounds has been extensively studied by various techniques in general, and by high-energy spectroscopies in particular, over the last few years.³ These studies have clearly demonstrated that such chemically *heterovalent substitution* of La^{3+} with Sr^{2+} leads to the formation of hole states with substantial O *2p* character near E_F , causing the insulator-metal transition. In particular, x-ray-absorption spectroscopy (XAS) and electron energy loss spectroscopy at the oxygen *K* edge, probing the unoccupied density of states, have shown the systematic growth of doped hole states on heterova-

lent substitutions in the nickelates and cuprates.³ From these studies it is now well established that the lowest energy charge excitation in the parent insulating oxides of the late transition metals is of the charge-transfer type. However, there is another class of compounds exhibiting substitutionally driven metal-insulator (MI) transitions due to *homovalent substitutions* without involving any electron or hole doping. While there is a considerable amount of results available on the electronic structure of hole doped systems, there is hardly any study of the electronic structure of compounds undergoing MI transitions driven by such homovalent substitutions. In view of this, it was thought to be desirable that a comparative study of the two different classes of compounds be carried out in order to understand the nature of these two kinds of MI transitions, using high-energy spectroscopies. For our purpose, the MI transitions known⁴⁻⁶ in the LaMO_3 series ($M = 3d$ transition metals) of compounds appear to be the most suitable for carrying out such a systematic study. The entire series with $M = \text{Ti-Ni}$ in the 3+ oxidation state form in the three-dimensional perovskite structure with very similar lattice parameters. In these oxides, it is known that LaNiO_3 is a metal, while LaMO_3 ($M = \text{Mn, Fe, and Co}$) are semiconducting. More interestingly,

$\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ exhibit⁴ MI transitions as a function of the homovalent substitution of Ni^{3+} with M^{3+} at about $x = 0.1, 0.2,$ and 0.65 for $M = \text{Mn}, \text{Fe},$ and Co , respectively. On the other hand, semiconducting LaMnO_3 can be driven to a metallic state by the heterovalent substitution of La^{3+} by Sr^{2+} , thereby effectively doping holes into the system.^{5,6}

We have investigated the electronic structure of these two systems across the metal-insulator transitions using soft x-ray-absorption spectroscopy at the oxygen K edge. There is a recent report of the O K -edge x-ray-absorption spectra of the heterovalent substituted $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (Ref. 7); our results for this system are very similar to those presented in Ref. 7. However, the main results in the present work are on the three series of homovalent substituted compounds $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$, for which there has been no microscopic investigation of the electronic structure. Our results, besides providing information on the electronic structure, clearly demonstrate the distinctly different behavior of the underlying electronic structure in these two different classes of MI transitions.

EXPERIMENT

The compounds $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.0, 0.05, 0.1,$ and 0.2), $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3, 0.5, 0.7,$ and 1.0) and $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.2, 0.5, 0.6, 0.7, 0.8$ and 1.0) were prepared by dissolving required proportions of dried $\text{La}_2\text{O}_3, \text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}, \text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}, \text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O},$ and $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in concentrated nitric acid. The mixture was decomposed at about 400°C and subsequently heated at 800°C with frequent regrinding. The compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.0, 0.1, 0.2, 0.3,$ and 0.4) were prepared in an identical manner using dried $\text{La}_2\text{O}_3, \text{MnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O},$ and SrCO_3 in the required proportions. The phase purity of each compound was verified using x-ray diffraction. Potentiometric titrations were carried out to determine the oxygen content of the compounds. In the first series, the compositions were found to be $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_{2.91 \pm 0.01}$ for all values of x studied here. For the series $\text{LaNi}_{1-x}\text{Co}_x\text{O}_{3-\delta}$, δ was found to vary smoothly from 0.1 to 0.0 with changing x ; in particular, there was no perceptible change in δ across the compositions showing the MI transition. On the other hand, in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, δ was found to be $0.1, 0.09, 0.07, 0.03$ and 0.0 for $x = 0.0, 0.1, 0.2, 0.3,$ and $x \geq 0.5$, respectively. MI transitions in all the systems were ascertained by resistivity measurements. The soft x-ray-absorption spectra at the oxygen K edge were recorded on sintered pellets in the bulk sensitive fluorescence yield mode at the HE-PGM2 beamline of BESSY, Berlin. The overall resolution at the O K edge was about 0.4 eV. The Fermi edge in each series was determined by inspection of the leading low-energy edge in the spectrum of the most conducting metallic sample. The samples were scraped *in situ* with an alumina file in order to remove the top few contaminated layers. The base pressure in the spectrometer chamber was better than 5×10^{-10} mbar.

RESULTS AND DISCUSSION

In Fig. 1(a) we show the oxygen K -edge spectra recorded in the fluorescence yield mode for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with different values of x . These spectra are similar to those from the same compounds recorded in the total electron yield mode.⁷ For $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ we find the most intense peak at about 7.8 eV above E_F , attributed to oxygen p states covalently mixed with the La $5d$ and Sr $4d$ states, similar to the case of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (Ref. 8). In Fig. 1(a), we also find a peak at about 2.4 eV above E_F in the LaMnO_3 spectrum; this peak shows an

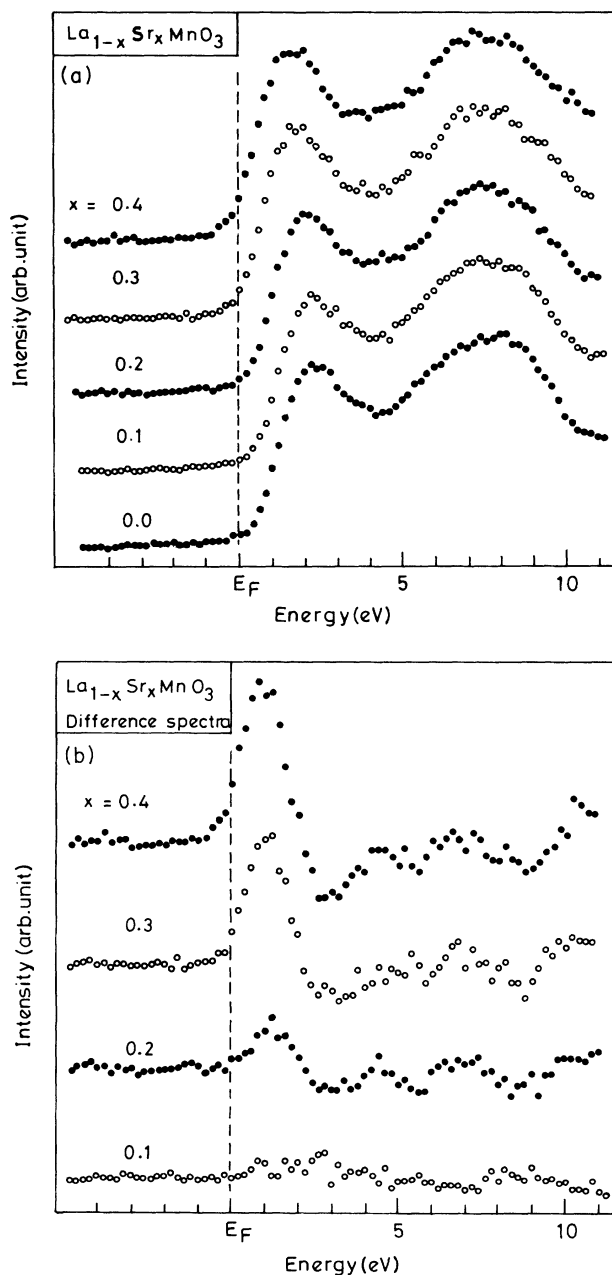


FIG. 1. (a) The O K -edge XAS of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $x = 0.0, 0.1, 0.2, 0.3,$ and 0.4 . (b) The difference spectra of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $x = 0.1, 0.2, 0.3,$ and 0.4 showing the formation of new hole states.

important tailing towards E_F . This peak at 2.4 eV is attributed to the spectral signature of the upper Hubbard band derived from the mixing of the Mn 3d states with oxygen 2p states; this covalent mixing must be substantial in order to explain the large intensity of this feature in the O K -edge XA spectrum. This is consistent with the interpretation⁹ of the ground state of LaMnO_3 being an admixture of 50% d^4 , 41% $d^5\bar{L}^1$, and 9% $d^6\bar{L}^2$ characters, where \bar{L} represents a ligand hole state. When the band gap is estimated by the midpoint of the rising edge of the upper Hubbard band, we obtain a band gap larger than 1 eV. This value is considerably larger than the resistivity band gap^{5,6} of about 0.25 eV. Such discrepancies between the high-energy spectroscopies and resistivity measurements are not uncommon; this primarily arises from the presence of impurity states that are normally too weak to be detected in the spectroscopic measurements but effectively reduce the transport band gap. Specifically, the composition of the as-prepared sample has been found⁹ to be close to $\text{LaMnO}_{3.13}$, indicating the presence of extensive hole states due to excess oxygen. This is certainly a cause for the tailing of the spectral feature at 2.4 eV towards E_F in LaMnO_3 . In this situation, the Fermi level will be pinned by these doped hole states. Thus the band gap will be determined by the onset of the occupied valence band states. The gap between E_F and the onset of the occupied bands has been found to be about 0.3 eV in LaMnO_3 (Ref. 9) in good agreement with resistivity data.

The changes in the spectral features on introducing Sr are most easily seen in the difference spectra [Fig. 1(b)] obtained by subtracting out the spectrum of LaMnO_3 from those of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with $x > 0.0$. While there is no significant change in the spectral features for $x = 0.1$, we see a systematic emergence of the doped hole states for $x \geq 0.2$ near E_F [Fig. 1(b)]. Thus, we find that the most significant change in the spectral features on substituting Sr^{2+} in place of La^{3+} is to introduce hole states with substantial oxygen p character, while leaving the underlying electronic structure relatively unaffected. This is in agreement with most other reports on the spectral changes obtained on doping holes by heterovalent substitutions in transition-metal oxides^{3,8} and is due to the substantial mixed-valent character of the ground state of LaMnO_3 .

The first series of homovalent substitution compounds that we discuss here is $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$. It is interesting to note that this series can be thought of as LaMnO_3 with Ni^{3+} doping at Mn^{3+} sites, instead of Sr^{2+} doping at La^{3+} sites as in the heterovalent substituted series, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. Thus, these two differing ways of driving insulator-metal transitions is based on the same parent insulating end member. We show the O K -edge spectra for $x = 0.0, 0.05, 0.1$, and 0.2 in $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ [Fig. 2(a)]. The spectrum of LaNiO_3 exhibits a broad peak at about 8.0 eV above E_F due to the O p -La $5d$ hybridized states in good correspondence with the similar peak in Fig. 1(a) for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. The spectral feature at about 1.2 eV above E_F corresponding to transitions into the empty band states in this case, however, is much closer to E_F compared to that in LaMnO_3 , with

substantial intensity at E_F in accordance with the metallic ground state of this compound. Noting the low-spin $t_{2g}^6e_g^1$ configuration of Ni^{3+} in LaNiO_3 , it is evident that this spectral feature with a peak at 1.2-eV is primarily due to $e_{g\uparrow}$ and $e_{g\downarrow}$ antibonding bands. The considerable intensity of this 1.2 eV feature is also an indication of extensive covalent mixing between Ni 3d and O 2p states. This is once again consistent with the analysis of Ni 2p core-level spectrum in LaNiO_3 (Ref. 10) indicating a ground state having 37.6% d^7 , 50.1% $d^8\bar{L}^1$, and 11.8%

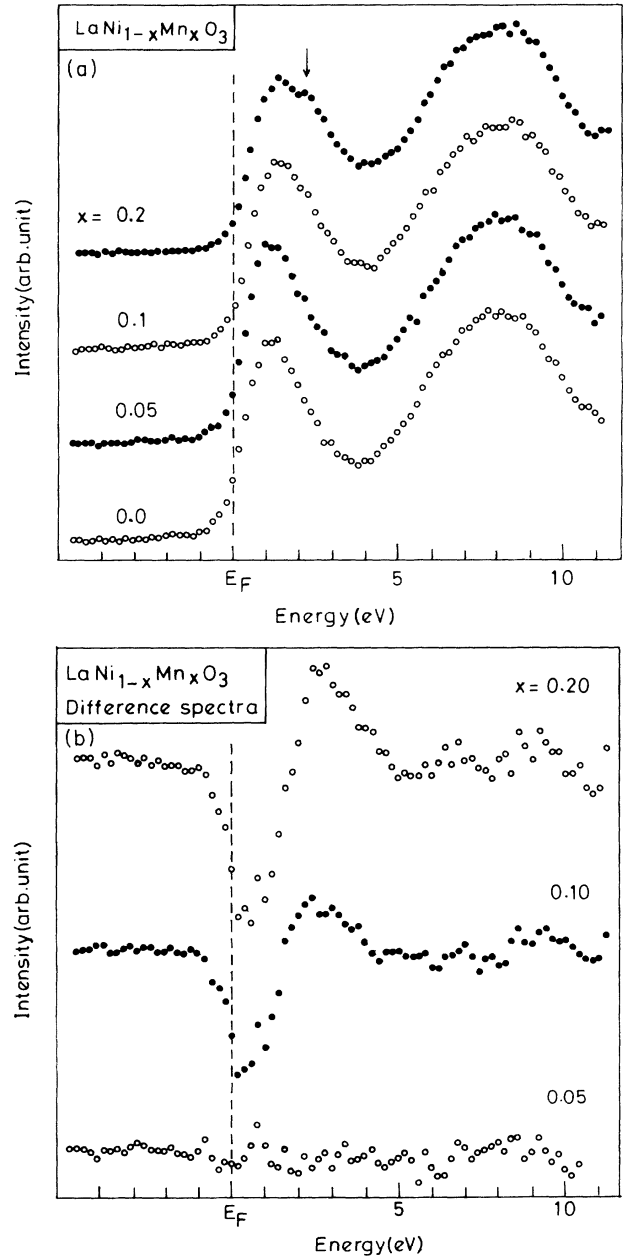


FIG. 2. (a) The O K -edge XAS of $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$, $x = 0.0, 0.05, 0.1$, and 0.2 . The arrow indicates the position of the prepeak in the LaMnO_3 spectrum. (b) The difference spectra of $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ obtained by subtracting the LaNiO_3 spectrum.

$d^9\bar{L}^2$ contributions.

On substituting Ni^{3+} with Mn^{3+} , we find a systematic decrease in the spectral intensity at and near E_F and the emergence of a new spectral feature at about 2.2 eV above E_F with increasing x . These changes are best illustrated in the difference spectra [Fig. 2(b)] between $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ with $x > 0.0$ and LaNiO_3 , in an analogous way to that of Fig. 1(b). While the sample with $x = 0.05$ shows very little change in the spectral features, the difference spectra corresponding to $x = 0.1$ and 0.2 clearly exhibit the removal of empty states from E_F by the presence of a negative dip and the emergence of new empty states by a positive peak in Fig. 2(b). Both the dip and the peak are more pronounced for the $x = 0.2$ compared to the $x = 0.1$ sample. The peak position in the difference spectra appear at about 2.5 eV above E_F . Comparing this peak energy with that corresponding to the upper Hubbard band in LaMnO_3 appearing at 2.4 eV above E_F (see Fig. 1), it is apparent that there is good agreement between the two values. Moreover, it is to be noted that the integrated areas under the peak and the dip in the difference spectra of Fig. 2(b) are approximately equal in each case. Thus it appears that the substitution of Mn^{3+} for Ni^{3+} leads to a redistribution of the empty states in sharp contrast to the case of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ discussed earlier, where *new* hole states were introduced on substitution. The energy positions of the difference spectral features suggest that the potential at the Mn^{3+} sites effectively removes states from close to E_F , to a new energy position considerably above E_F and in agreement with that found in LaMnO_3 . Thus the potential mismatch between the Mn^{3+} and Ni^{3+} sites results in the redistribution of spectral weights across the Fermi level and is responsible for the metal-insulator transition in $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$.

The above interpretation is substantiated further by the changes in the spectral features in the O K -edge XAS of the two other homovalent substituted series $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ and $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$. Figure 3(a) clearly shows a systematic decrease in the spectral intensity at and near E_F with the concomitant emergence of a two peak structure at about 2.2-eV and 3.8 eV above E_F for the series $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$. These two spectral features correspond very well with the characteristic two peak structure in LaFeO_3 [Fig. 3(a)]. The high-spin $3d^5$ ($t_{2g}^3 e_g^2$) configuration of Fe^{3+} in LaFeO_3 suggests that the unoccupied Fe $3d$ spectral density will have primarily $t_{2g\downarrow}$ and $e_{g\downarrow}$ characters.^{7,11} Thus, we attribute the 2.2-eV feature to transitions into the Fe $t_{2g\downarrow}$ and the 3.8-eV feature to $e_{g\downarrow}$ bands, the energy difference between the two being governed by the bare crystal-field splitting and hybridization shifts. These results are in very good agreement with results obtained from bremsstrahlung isochromat spectroscopy.¹¹ It has also been shown there that the ground state of LaFeO_3 has 47.5% d^5 , 43.3% $d^6\bar{L}^1$, and 8.7% $d^7\bar{L}^2$ characters. The difference spectra for the series $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $x = 0.2, 0.3, 0.5,$ and 0.7 across the metal-insulator transition are shown in Fig. 3(b). These spectra, once again, illustrate the progressive removal of empty states from close to E_F to an energy region dictated by the electronic structure of LaFeO_3 ,

with increasing Fe^{3+} substitution for Ni^{3+} . The same trend is also exhibited by Co^{3+} substitution for Ni^{3+} in the series $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ as shown in Fig. 4. In Fig. 4(a) we plot the O K -edge XA spectra of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ for $x = 0.2, 0.5, 0.6, 0.7, 0.8,$ and 1.0. On increasing the Co content x , the spectra show a broadening on the higher-energy side of the prepeak observed in LaNiO_3 [Fig. 2(a)]. In the spectrum for the $x = 1.0$ composition,

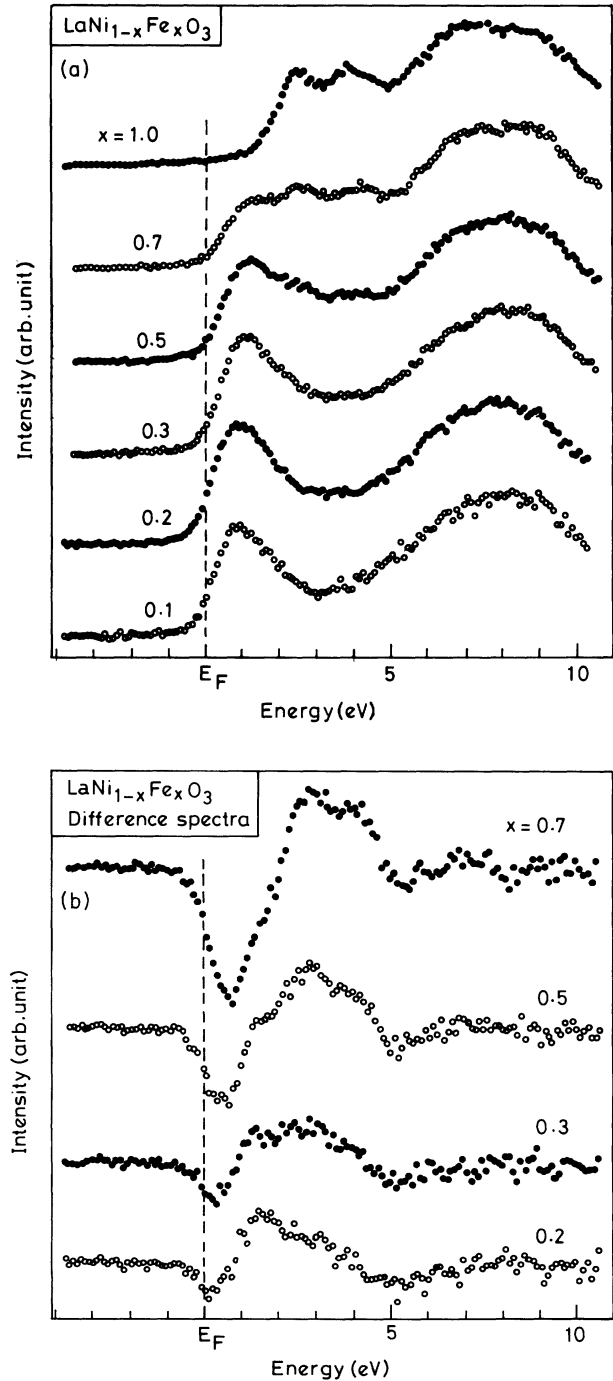


FIG. 3. (a) The O K -edge XAS of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$, $x = 0.1, 0.2, 0.3, 0.5, 0.7,$ and 1.0. (b) The difference spectra of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$.

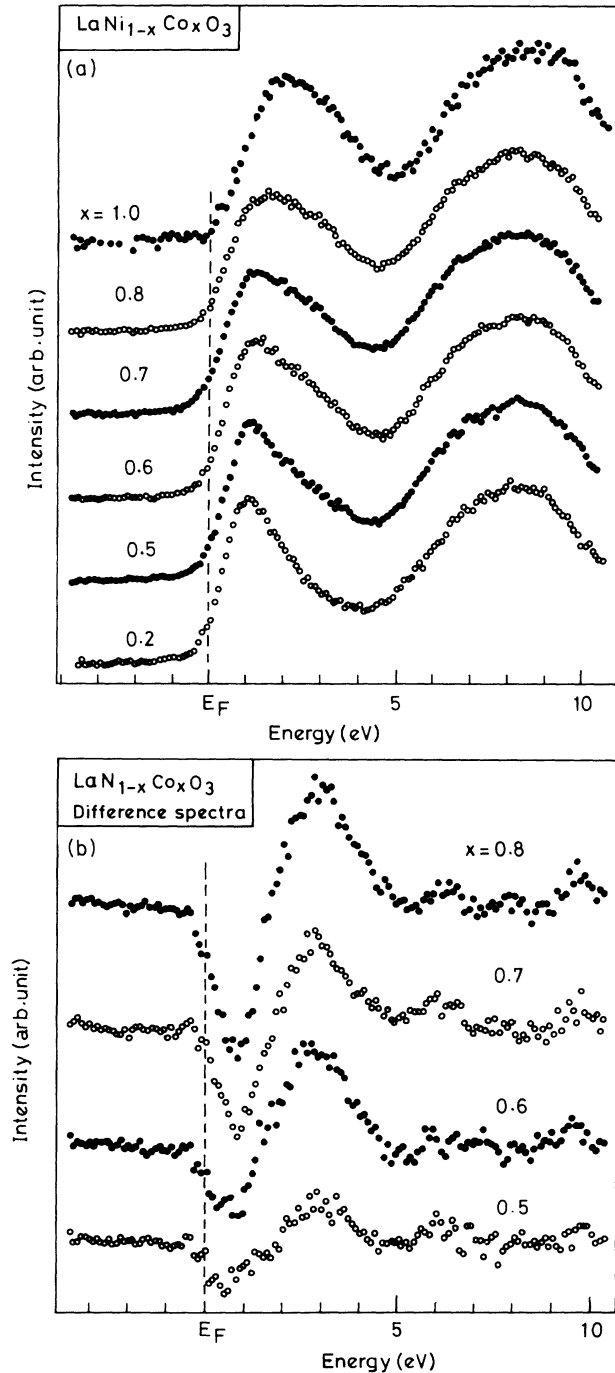


FIG. 4. (a) The O K -edge XAS of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$, $x = 0.2, 0.5, 0.6, 0.7, 0.8,$ and 1.0 . (b) The difference spectra of $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$.

i.e., LaCoO_3 , we see a broad prepeak associated with the Co $3d - \text{O } 2p$ hybridized states centered at about 2.8 eV above E_F . These correspond to excitations into the e_g derived empty states of low-spin LaCoO_3 which has been analyzed to have a predominantly charge-transfer character (38.5% d^6 , 45.4% $d^7\bar{L}^1$, and 14.5% $d^8\bar{L}^2$) as shown

earlier.¹² To see the effects of the homovalent substitutions near E_F more clearly, we show the difference spectra in Fig. 4(b) for $x = 0.5, 0.6, 0.7,$ and 0.8 , across the metal-semiconductor transition at $x = 0.65$. The difference spectra show a systematic growth of empty states centered at about 2.8 eV above E_F , with an accompanying decrease in intensity at and near E_F , for increasing Co content. This behavior is very analogous to that observed in $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ and $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$, giving rise to a dip and peak of nearly equal area in the difference curves [Figs. 2(b), 3(b), and 4(b)].

Thus, we find that the spectral changes on substitution of Ni by Fe or Co are similar to the case of $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$, establishing the general validity of the above description, wherein the potential mismatch between the substituents and Ni is suggested to induce a transfer of spectral weight driving the metal-insulator transition in these systems. The spectra in Figs. 2, 3, and 4 clearly show that the spectral features related to the NiO_6 octahedra do not exhibit any perceivable change with substitution, suggesting that it is dominated by local interactions and there is no substantial change in the ground-state character. This is in agreement with Ni $2p$ core level spectra that do not show any pronounced change in any of these compounds.¹⁰ It would be interesting to study the valence band photoemission spectra of these compounds to investigate the existence of similar changes in the spectral features of the occupied density of states.

In conclusion, we have reported the bulk sensitive fluorescence yield spectra as a function of photon energy across the oxygen K edge in three homovalent substituted series, $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0.0, 0.05, 0.1,$ and 0.2), $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0.1, 0.2, 0.3, 0.5, 0.7,$ and 1.0), and $\text{LaNi}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.2, 0.5, 0.6, 0.7, 0.8,$ and 1.0), and the heterovalent substituted system $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. While the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ series clearly shows the expected introduction of *new* hole states with increasing x leading to the insulator-metal transition, the homovalent substituted series $\text{LaNi}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Mn, Fe, and Co}$) exhibit a contrasting behavior of redistribution of spectral weights. This redistribution is essentially in terms of removal of states from near E_F to considerably above E_F and is governed by the potential mismatch between the substituent metal ion, M^{3+} ($M = \text{Mn, Fe, and Co}$) and Ni^{3+} in these compounds, leading to the MI transitions.

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* Electronic address: sarma@sscu.iisc.ernet.in

- ¹ N.F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1974); P.P. Edwards and C.N.R. Rao, *The Metallic and Nonmetallic States of Matter* (Taylor & Francis, London, 1985).
- ² J.G. Bednorz and K.A. Müller, *Z. Phys. B* **64**, 189 (1986).
- ³ Z.-X. Shen *et al.*, *Phys. Rev. B* **36**, 8414 (1987); A. Fujimori *et al.*, *ibid.* **35**, 8814 (1987); D.D. Sarma, *ibid.* **37**, 7948 (1988); D.D. Sarma and A. Taraphder, *ibid.* **39**, 11 570 (1989); D.D. Sarma and S.G. Ovchinnikov, *ibid.* **42**, 6817 (1990); H. Romberg *et al.*, *ibid.* **42**, 8768 (1990); J. Fink *et al.*, *Phys. Rev. B* **42**, 4823 (1990); P. Kuiper *et al.*, *Phys. Rev. Lett.* **62**, 221 (1989); C.T. Chen *et al.*, *ibid.* **66**, 104 (1991).
- ⁴ N.Y. Vasanthacharya, P. Ganguly, J.B. Goodenough, and C.N.R. Rao, *J. Phys. C* **17**, 2745 (1984); P. Ganguly, N.Y. Vasanthacharya, and C.N.R. Rao, *J. Solid State Chem.* **54**, 400 (1984).
- ⁵ G.H. Jonker and J.H. van Santen, *Physica* **XVI**, 337 (1950); **XVI**, 599 (1950).
- ⁶ A. Chainani, M. Mathew, D.D. Sarma, I. Das, and E.V. Sampathkumaran, *Physica B* **186–188**, 995 (1993).
- ⁷ M. Abbate, F.M.F. de Groot, J.C. Fuggle, A. Fujimori, O. Strelbel, F. Lopez, M. Domke, G. Kaindl, G.A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, and S. Uchida, *Phys. Rev. B* **46**, 4511 (1992).
- ⁸ D.D. Sarma, A. Chainani, R. Cimino, P. Sen, C. Carbone, M. Mathew, and W. Gudat, *Europhys. Lett.* **19**, 513 (1992).
- ⁹ A. Chainani, M. Mathew, and D.D. Sarma, *Phys. Rev. B* **47**, 15 397 (1993).
- ¹⁰ D. D. Sarma and A. Chainani, *J. Solid State Chem.* (to be published).
- ¹¹ A. Chainani, M. Mathew, and D.D. Sarma, *Phys. Rev. B* **48**, 14 818 (1993).
- ¹² A. Chainani, M. Mathew, and D.D. Sarma, *Phys. Rev. B* **46**, 9976 (1992).