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Transition metal oxide perovskites by photoelectron and x-ray absorption spectroscopy*

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Abstract. X-ray and ultraviolet photoelectron spectroscopy as well as x-ray absorption spectroscopy have been employed to investigate transition metal oxide perovskites of the general formula ABO_3 (A=La or rare-earth ion, B=trivalent transition metal ion). Systematics in the core levels and in the valence bands in the series of $LaBO_3$ compounds have been discussed. Lanthanum chemical shifts in the x-ray absorption spectra in this series show interesting trends. Photoelectron spectra of the solid solutions, $LaNi_{1-x}Co_xO_3$, $LaNi_{1-x}Fe_xO_3$ and $LaFe_{1-x}Co_xO_3$ show that the rigid band model is applicable to these systems. It is shown that x-ray photoelectron spectroscopy can be employed to identify multiple oxidation states of transition metal ions in oxide perovskites.

Keywords. Photoelectron spectroscopy; ESCA; x-ray (K, L_{III}) absorption spectra; transition metal oxides; perovskites.

1. Introduction

Transition metal oxide perovskites of the general formula ABO_3 where B is a trivalent transition metal cation and A is La, Y or rare earth (Ln), exhibit novel electronic and magnetic properties depending on the electronic configuration of the transition metal ion (Goodenough and Longo 1970; Rao and Subbarao 1970). Thus, while $LaTiO_3$ and $LaNiO_3$ are metallic and Pauliparamagnetic, $LaMnO_3$ and $LaFeO_3$ are antiferromagnetic insulators. The nature of *d*-electrons in these oxides has been shown to depend upon the spin configuration S of the transition metal ion (Goodenough 1974; Rao 1974), the low spin state favouring itinerant electron behaviour as in $LaTiO_3$ and $LaNiO_3$ ($S=\frac{1}{2}$); localised electron behaviour is found when the transition metal ion is in the high spin state as in the case of $LaMnO_3$ and $LaFeO_3$ with S of 2·0 and 2·5 respectively. We considered it instructive to investigate the perovskite oxides of transition metals of the formula $LaBO_3$ by photoelectron spectroscopy (PES) in order to examine the nature of changes in the valence bands and core levels in this related series of interesting solids. Another aspect of interest was to study changes in the core levels of the transition metal ions, if any, with change in the rare earth cation in two typical $LnBO_3$ series of compounds. We have also studied several $LnBO_3$ compounds by x-ray absorption spectroscopy to see if the chemical shifts reflect changes in the properties of these oxides.

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In addition to examining individual perovskite oxides, we have investigated the PES of their solid solutions, $LaNi_{1-x}Co_xO_3$, $LaNi_{1-x}Fe_xO_3$ and $LaCo_{1-x}Fe_xO_3$. $LaNi_{1-x}Co_xO_3$ remains metallic upto $x=0{\cdot}5$ and becomes a semiconductor at higher values of x; $LaNi_{1-x}Fe_xO_3$ is metallic upto $x=0{\cdot}2$ (Rao *et al* 1975). The system $LaCo_{1-x}Fe_xO_3$ is a semiconductor or an insulator throughout the composition range. Since the electronic properties of the component perovskite oxides forming the solid solutions are quite different, we expected to see interesting features in the PES of the solid solutions, particularly in the valence bands. A study of the valence bands of the oxide solid solutions would permit us to find out whether the rigid band model or the coherent potential approximation (Watson and Perlman 1975) would be applicable in a system where the conduction is by *d*-electrons rather than by *s*-electrons as in the usual transition metal alloys. We have also measured the x-ray absorption chemical shifts of the transition metal ions in the oxide solid solutions.

Substitution of bivalent cations for Ln in $LnBO_3$ perovskites gives rise to interesting magnetic and electronic properties (see for example, Rao *et al* 1977; Goodenough 1963). In a system like $Ln_{1-x}Sr_xCoO_3$, it is difficult to identify the oxidation states of the transition metal ion because of the fast hopping of electrons between the two states (Bhide *et al* 1975). We have studied the PES of some of these systems to investigate how this technique can be effectively employed to identify multiple oxidation states of transition metals.

2. Experimental

$LaVO_3$ was prepared by the hydrogen reduction of $LaVO_4$. $LaCrO_3$ and $LaMnO_3$ were prepared by the thermal decomposition of the corresponding mixture of nitrates. $LnFeO_3$ and $LnCoO_3$ (Ln=La or rare earth) were prepared by the thermal decomposition of the corresponding ferricyanide and cobalticyanide. $LaNiO_3$, $LaNi_{1-x}Co_xO_3$, $LaNi_{1-x}Fe_xO_3$ and $LaCo_{1-x}Fe_xO_3$ were prepared by mixing the corresponding chloride solutions in the required proportion, co-precipitating as carbonates and decomposing in air followed by heating in oxygen atmosphere at 1100K. $Nd_{1-x}Sr_xCoO_3$ and $La_{1-x}Ca_xMnO_3$ were prepared by the decomposition of the mixture of oxalates. $SrFeO_{3-\delta}$ and $SrCoO_{3-\delta}$ were prepared by the decomposition of carbonates of strontium and iron or cobalt. All the starting materials used in the study had purity better than 99·9%.

Photoelectron spectra were recorded employing an ESCA 3 Mark II spectrometer of VG Scientific Limited, UK. The accompanying sample preparation chamber was fitted with an argon ion gun and a quadrupole mass spectrometer. X-ray photoelectron spectra (XPES) were recorded using AlK_α (1486·6 eV) radiation. Ultraviolet photoelectron spectra (UVPES) were recorded with HeII (40·8 eV) radiation. Fermi level of gold was used as the reference for binding energies. The uncertainty in energies in the valence band is about 0·1 eV whereas in the case of the core levels it is about 0·5 eV.

X-ray absorption spectra were photographed employing a bent crystal spectrograph. Whereas spectra of Co, Ni and Fe were taken with MoK radiation, those of La were taken with CuK radiation. The uncertainty in chemical shifts of Co, Ni and Fe is $\pm 0{\cdot}5$ eV and it is $\pm 0{\cdot}4$ eV in the case of La.

3. Results and discussion

3.1. *Oxide perovskites*

Valence bands of a few typical transition metal oxide perovskites of the formula $LaBO_3$ are shown in figure 1. The photoelectronic excited states of transition metal ions in this region depend on the $3d^{n-1}$ final states left behind and the possible final states depend on the original $3d^n$ configuration (Bagus *et al* 1977). In the case of $LaVO_3(d^2)$ and $LaCrO_3(d^3)$, there will be a single final state while in $LaMnO_3(d^4)$ and $LaFeO_3(d^5)$ there are two possible final states. Accordingly, we see a single *d*-band in $LaVO_3$ and $LaCrO_3$, and two bands in $LaMnO_3$ and $LaFeO_3$. These band positions along with their final state assignments are shown in table 1. In $LaCoO_3(d^6)$

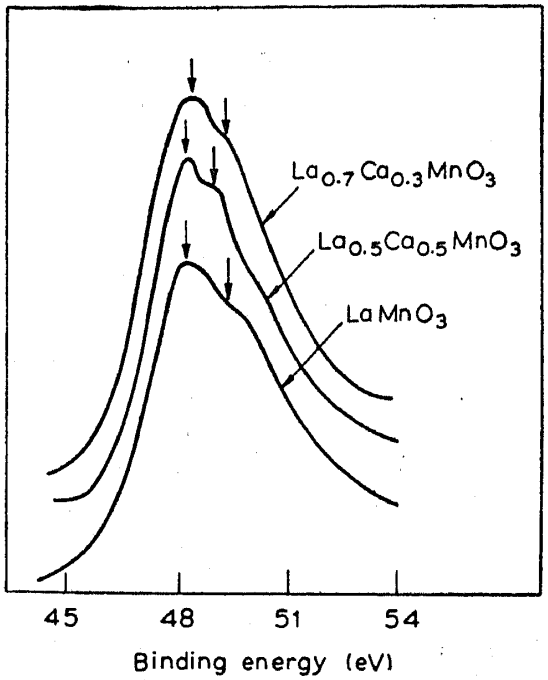

Figure 1. XPES valence bands of $LaNiO_3$, $LaFeO_3$ and $LaVO_3$. Arrows show positions of bands arising from removal of *d* electrons. The *d* band intensity increases with the number of *d* electrons in the series as expected.

Table 1. XPES valence bands of $LaBO_3$ compounds[a]

B	Final states in *d* band	Metal-oxygen π	Metal-oxygen σ	$\Delta E_{\sigma-\pi}$
V	1·0 ($^2T_2$)	5·1	6·9	1·8
Cr	2·4 ($^3T_1$)	4·7	6·8	2·1
Mn	1·0 ($^4A_2$), 3·5 ($^4T_2$, $^4T_1$)	5·5	7·0	1·5
Fe	2·0 (^5E), 4·0 ($^5T_2$)	5·6	7·0	1·4
Ni	1·0 ($^3T_2$, $^3T_1$), 2·8 ($t_{2g}^4\ e_g^2$)[b]	4·3	6·8	2·5

(a) Data on $LaCoO_3$ are not given since Co^{3+} ion is present in both high and low spin states (see discussion)

(b) Can be any of the following states: $^5T_2+^3T_2$, $^3T_1$, ^3E, $^3A_2$

there are complications due to the presence of both high spin ($t_{2g}^4\ e_g^2$) and low spin (t_{2g}^6) states of the Co^{3+} ion since in this solid, $\triangle_{cf} \simeq \triangle_{ex}$. Accordingly, we see bands which can be ascribed to the low (2·8 eV) and high (1·0 and 4·0 eV) spin states in the valence band. The final state in the case of the low-spin Co^{3+} ion is $^2T_{2g}$. The two bands in the case of the high spin ion can be assigned to the removal of an e_g and a t_{2g} electron resulting respectively in $t_{2g}^4\ e_g^1$ and $t_{2g}^3\ e_g^2$ configurations; each of these configurations can give rise to more than one final state and it is difficult to assign the exact state. $LaNiO_3$ with Ni^{3+} in the d^7 configuration can give rise to several final states and we see at least two bands in the XPES around 1·0 and 2·8 eV (table 1). Of these, the first band may be due to $(^3T_2 + ^3T_1)$ state; the band at 2·8 eV would then be due to one of the five possible final states with the $t_{2g}^4\ e_g^2$ configuration.

All the oxide perovskites show bands around 5 and 7 eV which can be assigned to metal-oxygen π and σ bands (Riga *et al* 1977). The positions of these bands show some interesting trends (table 1). It is known that in $LaMnO_3$ and $LaFeO_3$ $\triangle_{cac}^{\pi} < \triangle_{cac}^{\sigma} < \triangle_c$ where $\triangle_{cac}^{\pi}$ and $\triangle_{cac}^{\sigma}$ are the respective cation-anion-cation overlap integrals and $\triangle_c$ is the critical overlap integral which determines the nature of *d*-electron behaviour (Goodenough 1966). In localised electron systems like $LaMnO_3$ and $LaFeO_3$, $\triangle_{cac}^{\sigma} < \triangle_c$, while in collective *d*-electron systems like $LaNiO_3$, $\triangle_{cac}^{\sigma} > \triangle_c$. Accordingly, we find that the energy difference between π and σ bands is much smaller in $LaFeO_3$ and $LaMnO_3$ (1·5 and 1·4 eV respectively) than in $LaNiO_3$ (2·5 eV). $LaVO_3$ and $LaCrO_3$ fall in between since $\triangle_{cac}^{\sigma} \simeq \triangle_c$ (table 1). In the valence band of metallic $LaNiO_3$ we see a band at an energy considerably lower (2·2 eV) than the Fermi level. Such bands are not seen in insulators like $LaCrO_3$ and $LaFeO_3$. This low energy band in $LaNiO_3$ may be ascribed to a plasmon.

The core levels of La as well as transition metals found by XPES are summarised in table 2. The La core level bands show satellites around 4 eV from the main peak and this is assigned to $O(2p) \rightarrow La(4f)$ charge transfer (Wertheim *et al* 1972; Burroughs *et al* 1976; Howng and Thorn 1978). The 13 eV and 17 eV satellites seen in the lanthanum as well as $O(1s)$ peaks may be electron energy loss peaks (eq. $O(2s) \rightarrow O(2p)$). The La core level binding energies in $LaBO_3$ compounds do not change appreciably with the B ion. We do not also find any systematics in $O(1s)$ binding energy in the $LaBO_3$ series. The binding energies E of the $3p$ and $2p$ levels of transition metal ions show an interesting relationship with the nuclear charge Z (atomic number). In figure 2, we have shown plots of ln E versus ln Z in the $LaBO_3$ oxide perovskites. The values of E in the perovskites are close to those in the transition metal sesquioxides B_2O_3 as can be seen from figure 2. We see that the ln E—ln Z plots are linear. This linearity can be understood in terms of the relation $E = x(Z - Z_0)^2$; the x term allows for the quantum defect and varies for different energy levels while Z_0 is constant for all the levels (Rao *et al* 1979). In a relatively narrow range of Z, we would expect a linear relation between ln E and ln Z.

In figure 3 we have plotted the difference in $2p_{3/2}$ and $2p_{1/2}$ binding energies of the transition metal ions against the nuclear charge. We find that the spin-orbit splitting varies linearly with the nuclear charge, a behaviour also shown by transition metal sesquioxides. This is somewhat surprising since spin-orbit splitting would be expected to vary as Z^4. The linear relationship found here indicates strong deviations from the spherical coulomb potential.

Table 2. Core level energies (eV) in $LaBO_3$ compounds

	Transition metal ion[a]				Lanthanum levels[b]		Oxygen 1s[e]
B	3*p*	$2p_{3/2}$[a]	$4d_{5/2}$[b]	4*p*[c]	$3d_{5/2}$[c]	$3d_{3/2}$[d]	
V	40·7	516·6 (7·5)	102·7 (3·1)	196·8 (4·0)	834·5 (4·1, 12·6)	851·5 (4·2, 12·8)	530·0 — —
Cr	43·2	576·0 (10·1)	101·1 (2·0)	194·4 (3·3)	834·4 (3·3, 12·5)	851·4 (3·3, 13·0)	529·6 (13·8, 17·6)
Mn	48·3	640·9 (12·0)	101·5 (2·6)	—	834·1 (4·1, 12·3)	851·1 (4·0, 13·5)	529·3 — —
Fe	55·2	710·5 (13·5)	101·2 (2·8)	194·9 (3·5)	833·7 (4·0, 12·9)	850·9 (4·0, 12·5)	529·0 (13·5, 17·8)
Co	60·6	779·6 (15·6)	101·5 (2·6)	194·7 (4·0)	833·6 (4·0, 12·8)	850·6 (4·0, 12·5)	528·8 — —
Ni	67·1	—	101·1 (2·7)	194·6 (4·0)	833·8 (3·7, 12·3)	850·8 (3·7, 13·0)	528·9 (14·0, 17·0)

(a) We could not obtain 3*s* energies due to closeness of these bands to La (4*d*) bands. The values in the parenthesis refer to the difference in energy between $2p_{3/2}$ and $2p_{1/2}$ levels or $4d_{5/2}$ and $4d_{3/2}$ levels.

(b) There are satellites in the region 3·5–4 eV and 10–13 eV from the $4d_{3/2}$ bands.

(c) Position of satellites from the main band are shown in the parenthesis. We also see satellites around 4 eV in the $4d_{5/2}$ band.

(d) There is an additional satellite in the region of 15·7–16·7 eV.

(e) The *O* (1*s*) peak shows satellites around 13 eV and 17 eV in some of the compounds.

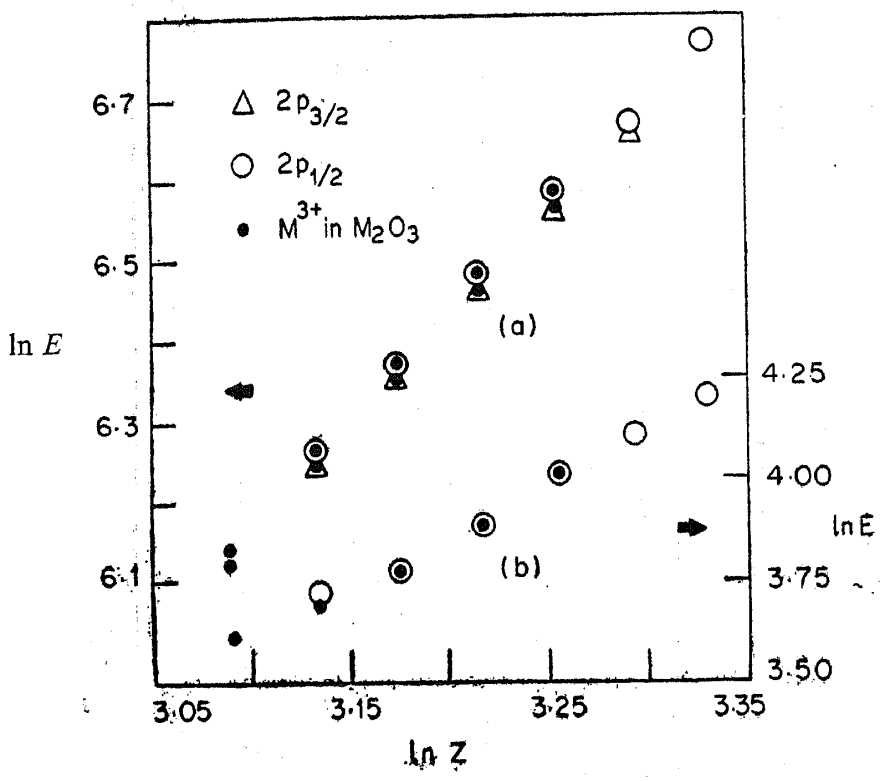

Figure 2. **a.** Plot of the logarithm of binding energies of $2p_{3/2}$ (triangles) and $2p_{1/2}$ (circles) levels against logarithm of nuclear charge (Z) in $LaBO_3$ compounds. **b.** Plot of the logarithm of binding energy of $3p$ level against ln Z in $LaBO_3$ compounds. Crosses denote values in the corresponding transition metal sesquioxides, B_2O_3.

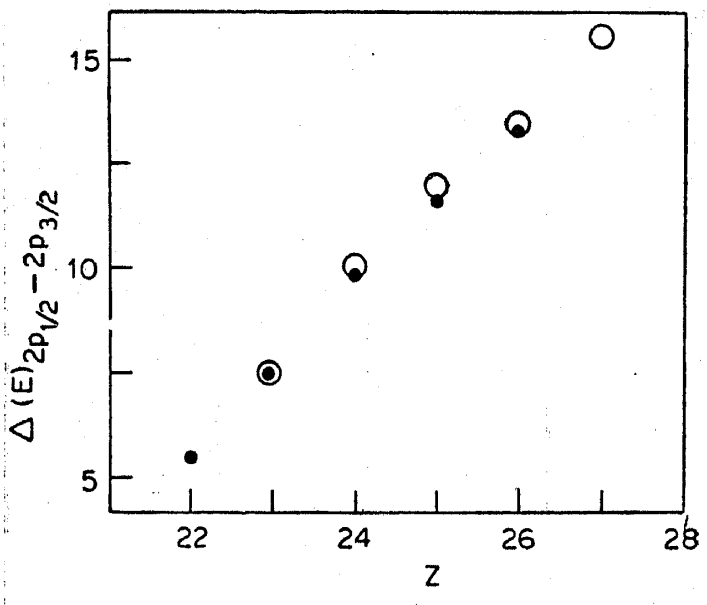

Figure 3. Plot of the spin-orbit splitting of the $2p$ band against Z in $LaBO_3$. Crosses denote values in the corresponding transition metal sesquioxides B_2O_3.

We have measured the chemical shifts of lanthanum in the x-ray L_{III} absorption spectra in the $LaBO_3$ compounds. Interestingly enough, these shifts show some systematics with the transition metal ion. In figure 4, we have plotted the chemical shift $\triangle E$ against atomic number Z of the transition metal and also the spin S of the transition metal ion. We find that $\triangle E$ shows a minimum in the case of Fe^{3+}. It has been shown that the electrical resistivity and activation energy for conduction of these compounds show such variations with Z (Ganguly *et al* 1976). This is because, electronic properties of these perovskites are determined by the spin configuration of the transition metal ion as mentioned earlier. $LaFeO_3$ with the highest value of S (2·5), therefore, shows a maximum in electrical resistivity and activation energy, while $LaNiO_3$ and $LaTiO_3$ with $S=1/2$ show the lowest values. Accordingly, we see that plot of the chemical shift against the spin S (or log ρ) shows proportionality between the two. It is indeed interesting that the chemical shift of La is sensitive to such changes in electronic properties of these perovskite oxides. This may be because of the competition between La–O and B–O bonding prevalent in the perovskites (Bhide *et al* 1973; Rao 1974). The charge on the La^{3+} ion increases as the B–O

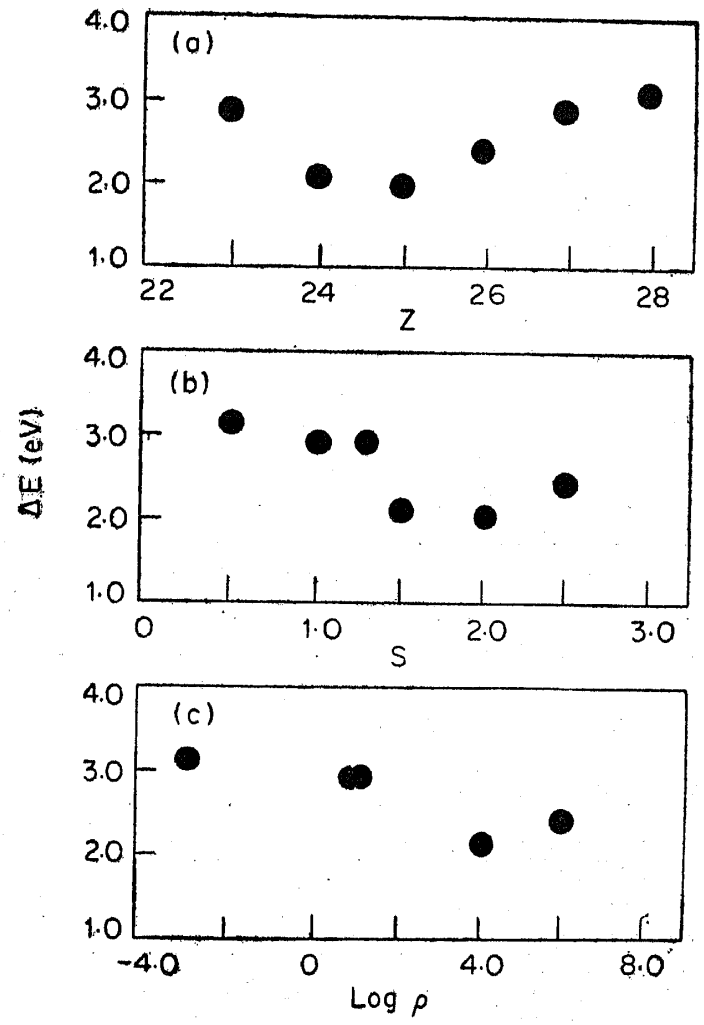

Figure 4. Plot of the chemical shift of La in the x-ray absorption spectra of $LaBO_3$ compounds against (**a**) Z (of *B*); (**b**) spin of the *B* ion and (**c**) logarithm of electrical resistivity of the solid at 298K.

Table 3. Core levels of Fe and Co in $LnFeO_3$ and $LnCoO_3$.

$LnFeO_3$				$LnCoO_3$			
Ln	3*p*	$2p_{3/2}$*	*O*(1*s*)	Ln	3*p*	$2p_{3/2}$*	*O*(1*s*)
La	55·2	710·2 (13·9)	529·0	La	60·6	779·6 (15·6)	528·8
Eu	55·1	710·2 (14·5)	529·6	Nd	61·2	780·25 (15·2)	530·3
Ho	56·2	710·7 (13·7)	529·5	Y	—	780·0 (15·6)	528·8
Yb	55·3	710·5 (13·7)	529·5	—	—	—	—

*The values in the parenthesis refer to the difference in energy between $2p_{3/2}$ and $2p_{1/2}$ levels.

Table 4. Chemical shifts (eV) of Fe and Co in x-ray absorption spectra in $LnFeO_3$ and $LnCoO_3$

$LnFeO_3$		$LnCoO_3$	
Ln	ΔE, eV	Ln	ΔE, eV
La	11·0	La	10·8
Eu	10·7	Nd	10·8
Yb	10·8	Gd	10·8
—	—	Yb	10·8

sigma bond gets stronger. This trend in the La chemical shifts of $LaBO_3$ is consistent with the trend in metal-oxygen π and σ bands discussed earlier.

In order to find out the effect of the Ln cation on the core levels of $LnBO_3$, we have examined the XPES of some rare earth ortho-ferrites and -cobaltites and the results are shown in table 3. The transition metal core levels as well as oxygen 1*s* binding energies do not seem to be sensitive to the rare earth ion. It appers that the variation in electronic properties of $LnBO_3$ compounds with Ln (Ganguly *et al* 1976) is not reflected in the core level binding energies. X-ray *K*-absorption spectra of these ortho-ferrites and -cobaltites show that the chemical shifts of Fe and Co also do not vary significantly with rare earth ion (table 4). The fact that the binding energies of the transition metal core electrons in XPES are essentially the same in $LnBO_3$ (independent of Ln) and B_2O_3 indicates that differences in bonding between the perovskites and oxides of corundum structure are not manifested in these levels.

3.2. *Solid solutions of oxide perovskites*

Valence bands of the $LaNi_{1-x}Co_xO_3$ system in XPES as well as UVPES are shown in figure 5. The spectra clearly show that the valence band of the solid solutions $LaNi_{0·7}Co_{0·3}O_3$ and $LaNi_{0·3}Co_{0·7}O_3$ show features of both $LaNiO_3$ and $LaCoO_3$. Shifts of the bands with respect to the Fermi level are negligible. It is interesting that the valence band of an alloy formed by $LaNiO_3$ and $LaCoO_3$, to a first approximation, have *d* bands associated with individual atomic species. Furthermore, it makes no difference whether the solid solution is a metal or a semiconductor as found in $LaNi_{0·7}Co_{0·3}O_3$ and $LaNi_{0·3}Co_{0·7}O_3$. These results on oxide alloys, where the *d* electrons are conduction electrons, are essentially similar to the typical metallic alloys

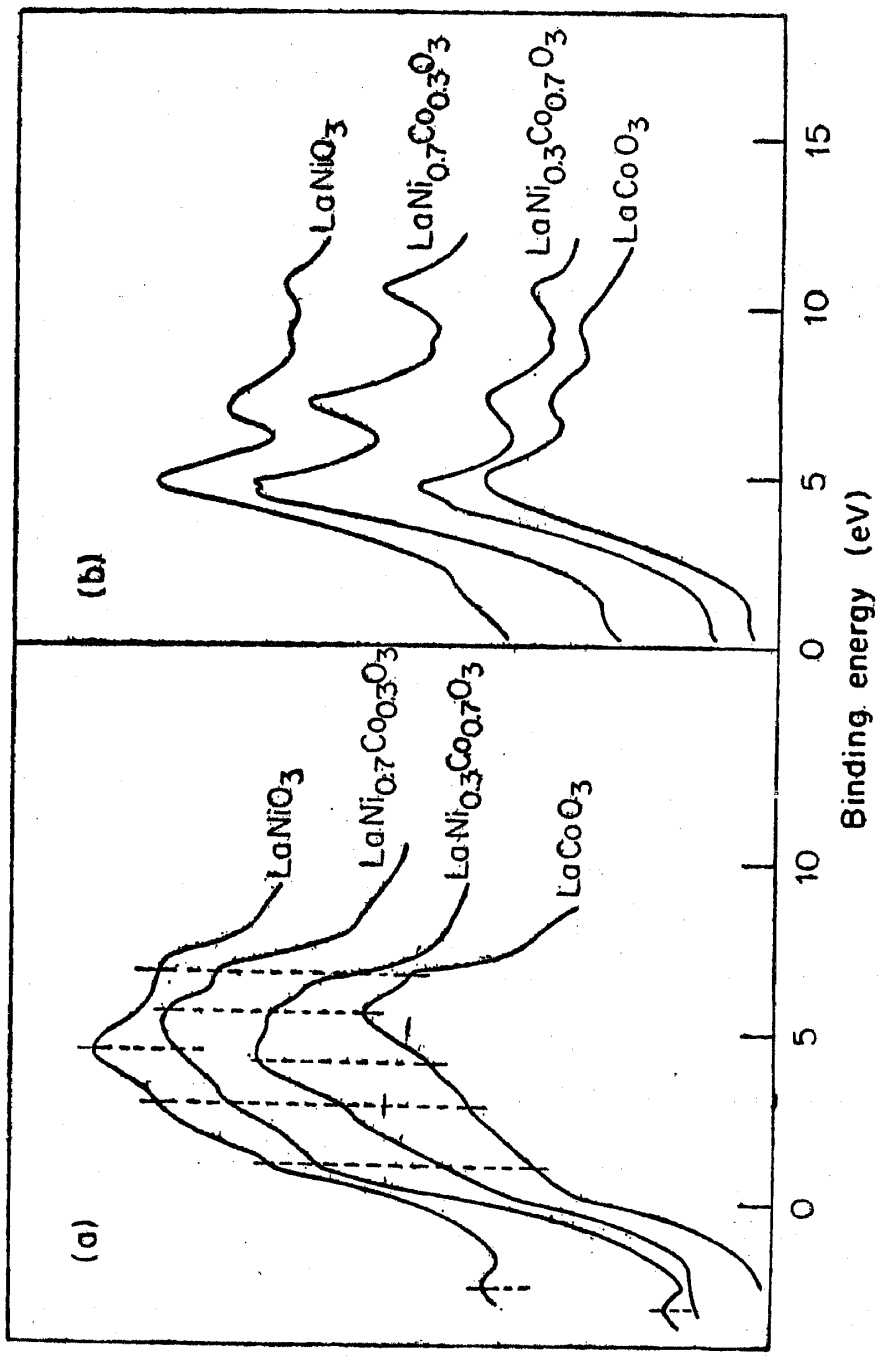

Figure 5. Valence bands of the $LaNi_{1-x}Co_xO_3$ system: (a) XPES; (b) UVPES (HeII)

where conduction electrons are *s* electrons. It appears that the rigid band description of conduction bands is applicable to the systems studied here rather than the coherent potential approximation. Solid solutions of $LaNiO_3$ with $LaFeO_3$ also essentially show additivity features of the valence bands of the component oxides (figure 6a). The π and σ bands due to metal-oxygen bonding, however, show some variation in the alloys. Thus, the separation between π and σ bands in $LaNiO_3$ (2·5 eV) decreases when it alloys with $LaCoO_3$. In the extreme case of the solid solutions formed by $LaCoO_3$ and $LaFeO_3$, we again see that the additivity of valence bands holds (figure 6b), but the π and σ metal-oxygen bands show differences.

Core level binding energies of the solid solutions are shown in table 5. The data show that the transition metal core level binding energies do not get affected in the solid solutions compared to the parent perovskites. Chemical shifts of the transition

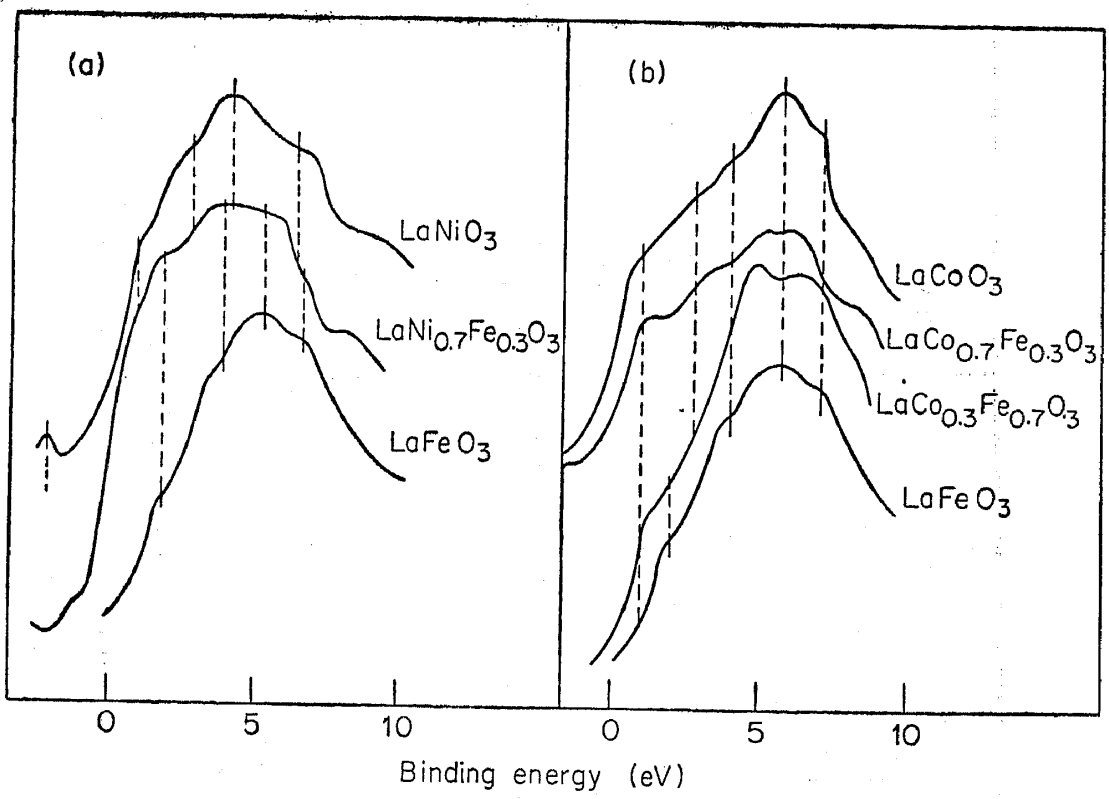

Figure 6. XPES valence bands of (a) $LaNi_{1-x}Fe_xO_3$ and (b) $LaCo_{1-x}Fe_xO_3$.

Table 5. Core level energies (eV) in solid solutions of $LaBO_3$ compounds

	Transition metal levels (eV)			Lanthanum levels (eV)*			Oxygen
	$3p$	$2p_{3/2}$	$2p_{1/2}$	$4d_{5/2}$**	$4p_{3/2}$	$3d_{5/2}$**	$1s$
$LaNi_{0.7}Co_{0.3}O_3$	Ni^{3+} 67·3	—	873·0	101·4 (2·5)	194·7	834·0 (17·0)	528·7
$LaNi_{0.3}Co_{0.7}O_3$	Co^{3+} 60·5	779·4	795·0	101·5 (2·5)	194·4	833·3 (17·0)	528·2
$LaNi_{0.7}Fe_{0.3}O_3$	Ni^{3+} 67·1	(7)	—	101·0 (2·7)	194·7	833·4 (17·0)	528·7
$LaCo_{0.7}Fe_{0.3}O_3$	—	Fe^{3+} 710·5 Co^{3+} 779·5	Fe^{3+} 724·0 Co^{3+} 795·0	101·0 (2·5) — —	194·6	833·6 (17·0)	528·9
$LaCo_{0.3}Fe_{0.7}O_3$	—	Fe^{3+} 710·5	Fe^{3+} 724·0	101·7 (2·8)	194·6	833·8 (16·8)	528·8

* Positions of satellites from the main peaks are similar to those in table 2.
** Values in parenthesis give the energy difference between $d_{5/2}-d_{3/2}$.

Table 6. Chemical shifts of *K*-absorption edges of nickel, cobalt and iron in $LaBO_3$ compounds

Compound	Chemical shifts (eV)		
	Nickel	Cobalt	Iron
$LaNiO_3$	11·0	—	—
$LaNi_{0·7}\ Co_{0·3}\ O_3$	11·1	10·7	—
$LaNi_{0·3}\ Co_{0·7}\ O_3$	11·1	10·7	—
$LaCoO_3$	—	10·8	—
$LaNi_{0·7}\ Fe_{0·3}\ O_3$	10·7	—	10·8
$LaFeO_3$	—	—	11·0
$LaFe_{0·7}\ Co_{0·3}\ O_3$	—	10·8	11·0
$LaFe_{0·3}\ Co_{0·7}\ O_3$	—	10·7	10·8

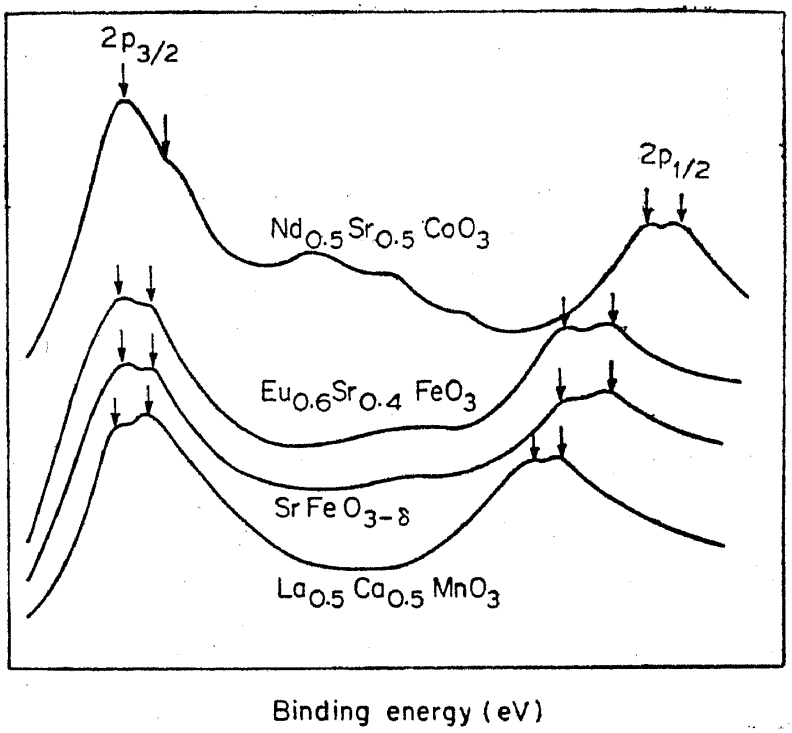

Figure 7. Transition metal 2*p* bands showing presence of 3+ and 4+ states. The first peak is due to 3+ state.

metal ions in the x-ray *K* absorption spectra also do not change in the solid solutions compared to those in the parent compounds (table 6). This would indicate that the effective charge on the transition metal ions does not differ greatly between the component oxides and their solid solutions.

3.3. *Multiple valence oxides*

Study of the perovskite oxides containing transition metal ions in two oxidation states by XPES has been successful in identifying the oxidation states. In figure 7 we have shown the 2*p* bands of a few typical mixed valence oxides. We see that both the

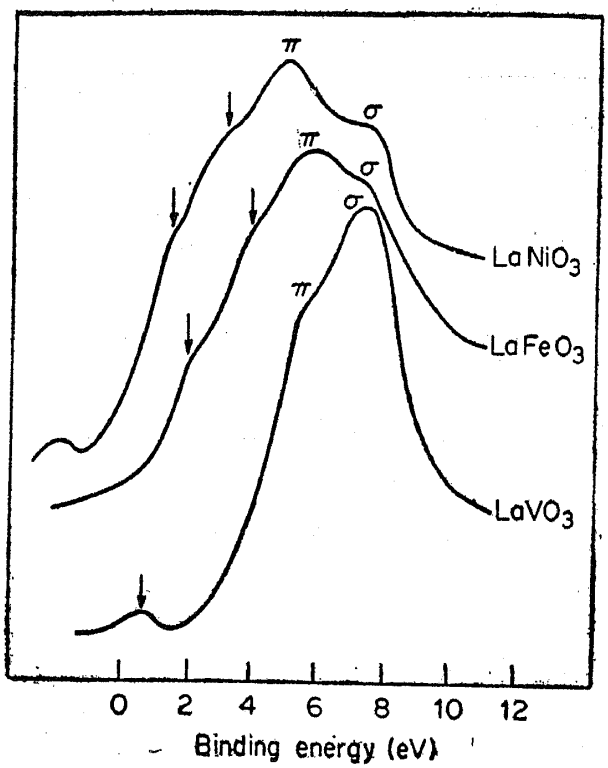

Figure 8. Mn($3p$) bands showing 3+ and 4+ states.

Table 7. Core level binding energies (eV) of Mn, Fe and Co in mixed valence oxides

Compound		$2p_{3/2}$	$2p_{1/2}$	$3p$
$LaMnO_3$*	Mn^{3+}	640·9	652·9	48·3
	Mn^{4+}	642·1	654·1	49·4
$La_{0·7}Ca_{0·3}MnO_3$	Mn^{3+}	640·8	652·7	48·2
	Mn^{4+}	641·8	653·8	49·2
$La_{0·5}Ca_{0·5}MnO_3$	Mn^{3+}	641·1	652·6	48·4
	Mn^{4+}	642·0	653·7	49·4
Mn_2O_3		641·2	652·9	48·3
MnO_2		641·9	653·5	49·5
$SrFeO_{3-\delta}$	Fe^{3+}	710·0	723·2	55·4
	Fe^{4+}	711·0	724·2	56·2
$Eu_{0·6}Sr_{0·4}FeO_3$	Fe^{3+}	709·6	723·1	54·9
	Fe^{4+}	710·8	724·0	56·0
Fe_2O_3	Fe^{3+}	710·3	723·6	55·2
$SrCoO_{3-\delta}$	Co^{3+}	779·8	795·3	60·4
	Co^{4+}	780·6	795·8	61·2
$Nd_{0·5}Sr_{0·5}CoO_3$	Co^{3+}	780·0	795·0	60·6
	Co^{4+}	781·0	796·0	61·6
$NdCoO_3$	Co^{3+}	780·1	795·5	60·5

*15% Mn^{4+} was present in the sample

$2p_{3/2}$ and $2p_{1/2}$ bands are doublets with the lower energy band arising from the 3+ state and the higher energy band arising from 4+ state. Transition metal $3p$ bands similarly show the 3+ and 4+ions distinctly as typified by manganese oxides in figure 8. The valence bands also show the existence of multiple oxidation states clearly although the assignments are not as straightforward due to the closeness of bands arising from different final state effects. Thus, $LaMnO_3$ (containing 15% manganese 4+) and $La_{0.5}Ca_{0.5}MnO_3$ show features of Mn^{4+} and Mn^{3+} just as in MnO_2 and Mn_2O_3. In table 7 we have tabulated the core level binding energies of a number of mixed valence oxides alongwith those of some reference oxides to show how well XPES can identify the different oxidation states. This is particularly important in compounds like $Ln_{0.5}Sr_{0.5}CoO_3$ where it is difficult to identify Co^{3+} and Co^{4+} states by other methods like Mössbauer spectroscopy. This is because the hopping time of the electron between the Co^{3+} and Co^{4+} ions is smaller than 10^{-6} sec, the latter being the life time of the nuclear excited state determining the time scale in Mössabauer spectra. Since the time scale in ESCA is of the order of 10^{-16} sec, complications due to electron hopping frequency do not arise.

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