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Charge Transfer Satellites in X-Ray Photoelectron Spectra of Lanthanum Compounds†

P VISHNU KAMATH* & D D SARMA
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012

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Satellite structures arising from the O(2*p*)→La(4*f*) charge transfer in the X-ray photoelectron spectra of a number of La compounds have been studied and correlated with structural data on the compounds. Trends in relative intensities of the satellites are interpreted in terms of the dependence on metal-ligand overlap.

Charge transfer satellites are commonly found in the X-ray photoelectron spectra of organic molecules[1], first row transition metal compounds[2] and rare earth compounds[3]. Weak satellites have also been found next to the metal core level peaks of second and third row transition metal oxides[4]. The existence of charge transfer satellites next to the ligand core level peaks has also been established recently in several oxides[4,5], chlorides and sulphides[6] of metals. In order to explain the nature of charge transfer satellites, especially the observed trends in the relative intensities in related series of compounds, a simple model based on sudden approximation and non-zero overlap between metal and ligand orbitals has recently been proposed from our laboratory[4]. According to this model the relative intensities of satellites in transition metal compounds increase initially with the metal-ligand overlap, go through a maximum and then decrease. However, data on satellites in a large class of related compounds of a single metal which can be used to verify this prediction are not available in literature. Thus we considered it important to carry out one such investigation. For this purpose, compounds of La seemed to be the most suitable as they show a well defined satellite ~4 eV away from the main 3*d* signal; moreover, there are many well known related series of La compounds with varying lattice parameters and crystal structures. We report herein the satellite intensities in the following compounds:

(i) $LaAl_{1-x}Fe_xO_3$ with $x = 0.0$, 0.025, 0.05, 0.25, 0.50 and 1.0; (ii) $LaMO_3$ series where M is a first row transition metal from V to Ni and La_2MO_4 (M = Ni, Cu); and (iii) $La(OH)_3$ and La_2O_3 in crystalline and amorphous forms.

Materials and Methods

X-ray photoelectron spectra were recorded with an ESCA 3 Mark II spectrometer which has been described elsewhere[7]. The samples were finely ground and spread over a thin mesh so as to minimize charging effects. All the samples were heated to 900 K *in vacuo* to cause dehydration, using a variable temperature probe. Heating was continued till narrow reproducible O(1*s*) spectra were obtained. The spectra were recorded using AlKα radiation ($h\nu = 1486.6$ eV). The positions of the satellite peaks were measured with respect to the main peak, while no attempt was made to obtain accurate absolute binding energies of various peaks.

Compounds of composition $LaAl_{1-x}Fe_xO_3$ were prepared by coprecipitation of the ions as hydroxides, and then by heating at about 1200°C for 24-36 hr. Preparation of $LaMO_3$ and La_2MO_4 series of compounds has been described previously[8]. Amorphous $La(OH)_3$ was obtained by adding excess of liquor ammonia to $LaCl_3$ solution, while crystalline $La(OH)_3$ was obtained by boiling La_2O_3 in water for several hours. Decomposition of $La(OH)_3$ at 800 K produced amorphous La_2O_3. X-ray diffraction patterns of all the compounds were recorded with a Phillips X-ray diffractometer using CuKα source.

A detailed analysis of the spectra was carried out to evaluate the relative intensities of the satellites. The recorded spectrum was first background reduced, and then decomposed into two component peaks. The component peaks were constructed symmetrically, by an examination of the lower binding energy and the higher binding energy flanks of the background reduced spectrum. The $AlK\alpha_{3,4}$ contribution of La $3d_{3/2}$ spin orbit split component in the higher binding energy tail of the La $3d_{5/2}$ feature was suitably substracted. The component peaks were then shifted relative to one another, till the error between the background reduced spectrum and the constructed spectrum was minimized. This decomposition allowed us to evaluate the satellite intensity in terms of the ratio of the areas of the two-component peaks reliably.

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Results and Discussion

$LaAl_{1-x}Fe_xO_3$: All the six compounds ($x=0.0$, 0.025, 0.05, 0.25, 0.5 and 1.0) studied presently were obtained in single phase with sharp X-ray diffraction patterns. $LaAlO_3$ is known to be a rhombohedral perovskite, while $LaFeO_3$ an orthorhombically distorted perovskite. All the compounds in this series have been indexed according to the cubic structure; the resulting refined parameters are listed in Table 1 and plotted as a function of x in Fig. 1. A sudden increase in the lattice parameter between $x=0.25$ and 0.5 possibly indicates a transition from the rhombohedral to the orthorhombic distortion in this range of x-values.

Some typical spectra of $3d_{5/2}$ region of La in $LaAl_{1-x}Fe_xO_3$ series presented in Fig. 2 reveal that the satellite intensity varies considerably with x. The plot of relative intensities of the satellite as a function of the lattice parameter, shown in Fig. 2b indicates that the relative intensity goes through a maximum in the intermediate value of $x=0.5$ ($a=3.896$ Å). This is in accordance with the results predicted from the earlier model[4], if we assume that the averaged La($4f$) – O($2p$) overlap varies monotonically with the unit cell volume. However this assumption is somewhat difficult to ascertain, particularly in view of the change in the structure of these compounds around $x=0.25$, and a detailed knowledge of La – O distances will be required for a more complete understanding. It is still noteworthy that this system provides the first example of satellite intensity going through a maximum in a related series of compounds.

$LaMO_3$: In this series, we have investigated the satellite intensity in the La($3d$) region of compounds with M = V, Cr, Mn, Fe, Co and Ni. $LaCoO_3$ and $LaNiO_3$ are rhombohedral perovskites, while the other compounds are orthorhombic. In view of these structural differences, it is somewhat difficult to make comparison between the lattice parameters of these compounds. However, a plot of the relative intensities of the satellites in these compounds against the lattice parameter a (Fig. 3a) clearly shows a trend of maximum satellite intensity at an intermediate value of a. However, this seems to fail entirely for the case of Mn (see Fig. 3a) where a minimum in the satellite intensity is observed. This we believe is due to the very large value of the parameter b in the case of $LaMnO_3$. Thus, a plot of the relative intensities of the satellites as a function of the parameter b (Fig. 3b) shows a smooth variation, just as in the case of $LaAl_{1-x}Fe_xO_3$ series.

We have also investigated two compounds with K_2NiF_4 structure: La_2CuO_4 and La_2NiO_4. It is seen

Table 1—Pseudo-cubic Lattice Parameters of the Compounds in the Series $LaAl_{1-x}Fe_xO_3$ and Their Satellite Intensities

x	a(Å)	I_s/I_o (%)
0.0	3.790	70.5
0.05	3.7983	78.2
0.25	3.8314	77.3
0.5	3.8958	82.8
1.0	3.9346	79.2

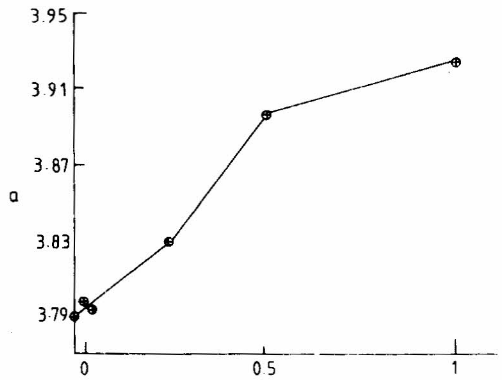

Fig. 1—Plot of the pseudo-cubic lattice parameters of the series of compounds $LaAl_{1-x}Fe_xO_3$ as a function of composition x.

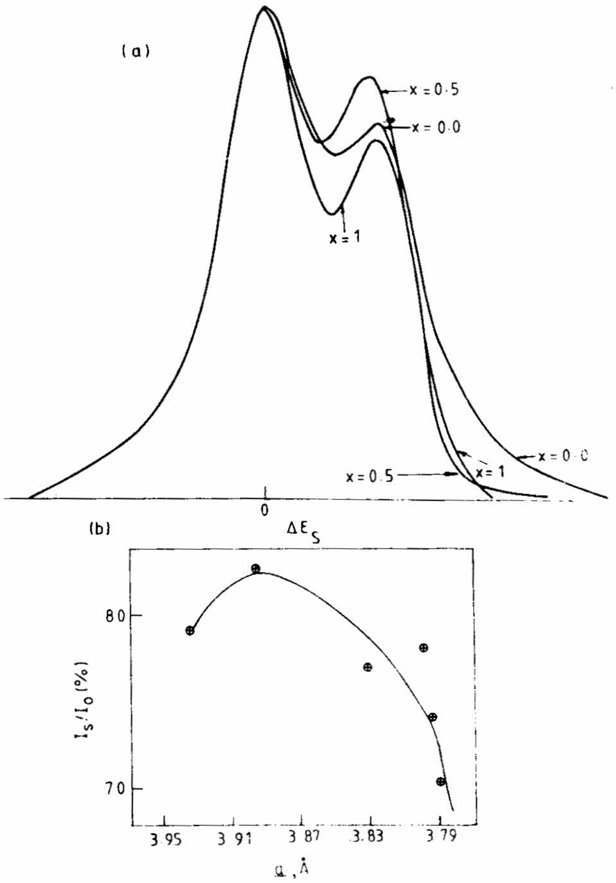

Fig. 2 (a) Background reduced X-ray photoelectron spectra in $3d_{5/2}$ region of La for the compounds $LaAl_{1-x}Fe_xO_3$ where $x=0$, 0.5 and 1.0. (b) Plot of the satellite intensities in the $3d_{5/2}$ region of La as a function of the pseudo-cubic lattice parameters, for the series $LaAl_{1-x}Fe_xO_3$.

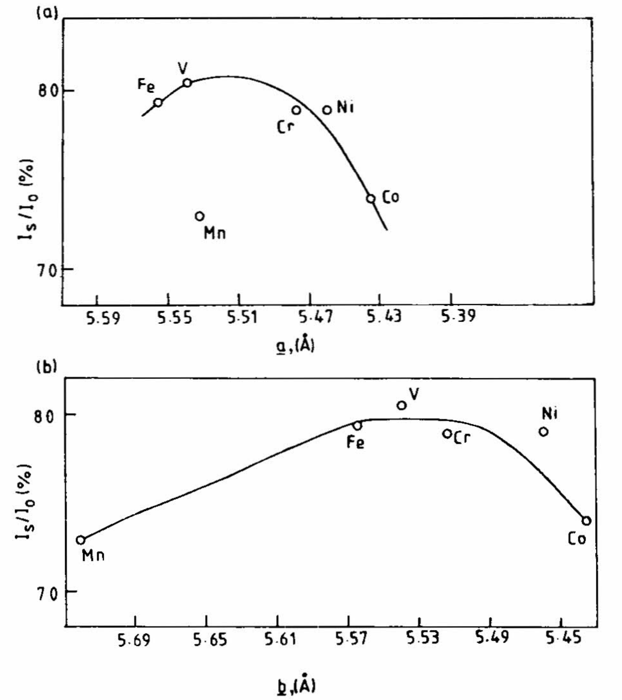

Fig. 3—(a) Plot of the satellite intensities in the $3d_{5/2}$ region of La as a function of the lattice parameter *a*, for the compounds of the series $LaMO_3$ (M = first row transition metal). (b) Plot of the satellite intensities in the $3d_{5/2}$ region of La as a function of the lattice parameter *b*, for the compounds of the series $LaMO_3$ (M = first row transition metal).

that La_2CuO_4 with a shorter *a* parameter exhibits a larger satellite intensity than La_2NiO_4. However, both La_2NiO_4 (84%) and La_2CuO_4 (90%) have larger satellite intensities (Fig. 3a) than the compounds in the $LaMO_3$ perovskite series. This is possibly due to the larger metal-ligand overlap owing to the short *a* parameter in the case of La_2MO_4.

$La(OH)_3$ and La_2O_3: From the above discussion, it becomes evident that small changes in lattice parameters and crystal structure can exhibit considerable changes in the intensity of the satellite via variation of the overlap between the metal and ligand orbitals. To investigate this point further, we have examined the satellite intensity in crystalline and amorphous forms of $La(OH)_3$ and La_2O_3. The energy separations and the relative intensities of the satellite in these compounds are given in Table 2. Interestingly the crystalline forms of $La(OH)_3$ and La_2O_3 show higher satellite intensities than the amorphous forms. This difference probably arises as a result of some change in local structure around the La^{3+} ions in the two forms. However it is difficult to ascertain the exact differences at the moment.

Table 2—Satellite Intensities and Energy Separations of Crystalline and Amorphous $La(OH)_3$ and La_2O_3

Form	E_{sat}(eV)	I_s/I_o (%)
	$La(OH)_3$	
Amor.	2.9	62.9
Cryst.	3.2	71.1
	La_2O_3	
Amor.	4.2	85.3
Cryst.	4.2	91.7

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