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M. Piacentini

Istituto di Struttura della Materia del CNR, Frascati, Italy

V. Grasso and S. Santangelo

Istituto di Struttura della Materia, Università di Messina, Messina, Italy

M. Fanfoni

Scuola Internazionale Superiore di Studi Avanzati, Miramare, Trieste, Italy

S. Modesti

Dipartimento di Fisica, Università di Roma "La Sapienza", Roma, Italy

A. Savoia

Laboratori Nazionali dell'INFN, Frascati, Italy.

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With the partial yield technique we measured the absorption spectra of several core levels in FePS_3 and NiPS_3 . The $M_{2,3}$ spectra of Fe and Ni are interpreted as localized transitions $3p^{63d^m}-3p^{53d^{m+1}}$ of the transition metal ion, split into a multiplet by final state multiconfiguration interaction. The $P L_{2,3}$, $S L_{2,3}$, and $S L_1$ spectra are similar to each other and are interpreted in terms of the projected density of states of the conduction bands derived from the states of the $(P_2S_6)^{4-}$ cluster.

Introduction

The transition metal chalcogeno-phosphates MPX_3 (M stands for a transition metal ion and X is either S or Se) form a large family of layered compounds with very interesting properties. In particular, these materials can be intercalated with alkali ions and so they are good candidates in Li-based batteries¹⁻³. However, their intercalation capability changes with the transition metal ion. For example, in the case of chemical intercalation, NiPS_3 is the most active material, while ZnPS_3 is completely inert⁴. The S-based compounds crystallize in the monoclinic system and have similar lattice parameters^{5,6}. Their different behavior with respect to intercalation has been related to the degree of ionicity of the transition metal ion¹. We feel that it depends strongly also on the number of available d states.

The electronic band structure of the transition metal chalcogeno-phosphates has not been calculated yet. Piacentini et al.⁷ proposed a semiempirical molecular orbital scheme for the $(P_2S_6)^{4-}$ cluster in NiPS_3 . Group theory was used to derive the symmetrized

combinations of the P 3s,3p and the S 3s,3p states. After identifying the bonding and antibonding combinations, an energy level sequence of the valence states was proposed. Finally, the energies of the levels were obtained empirically from the comparison with the valence band X-ray photoemission spectra (XPS). This approach gave a reliable sequence of the valence states, but it could not give an accurate description of the localized transition metal 3d states and of the lowest conduction states, based primarily on the transition metal 4s and 4p levels and on the P and S $3p_z$ levels⁹. Hints on the conduction bands density of states were obtained by a comparative analysis of the reflectivities of several MPS_3 compounds measured up to 35 eV⁸.

We have undertaken a series of researches on the electronic properties of the MPS_3 compounds with the aim of understanding the changes in the valence and conduction states due to the intercalation process. In this paper we present the soft X-ray absorption spectra of pure FePS_3 and NiPS_3 measured at the $P L_{2,3}$, $S L_{2,3}$, $S L_1$, and Fe (Ni) $M_{2,3}$ thresholds. The phosphorus and sulphur $L_{2,3}$ absorption spectra

are very alike in the two compounds and between each other, indicating that they do not depend on the transition metal ion, but that they represent the density of the first empty states of the $(\text{P}_2\text{S}_6)^{4-}$ cluster. From the relative intensities of the structures, we think that the lowest conduction band is formed mostly by P s-like states. Instead, the transition metal $M_{2,3}$ edges are atomic-like and strongly affected by final state configuration interaction.

Experimental Set-up

The experiments were performed on the "Grasshopper" beam line of PULS at the Frascati INFN National Laboratories¹⁰. The radiation emerging from the ADONE storage ring was collected by a 4° grazing incidence, cylindrically bent mirror and focused onto the entrance slit of the Baker Mfc. Grasshopper monochromator. The monochromator was equipped with a Baush and Lomb 600 l/mm replica grating. Operating with 20 μm slits we had .2 Å constant resolution. The radiation from the monochromator was refocused onto the sample by a 2° grazing incidence cylindrical mirror bent into a toroid. The absorption was measured with the partial yield technique using a double pass PHI cylindrical mirror analyzer (CMA). The CMA axis was normal to the incident radiation and the sample was mounted at $\sim 45^\circ$, p-polarization. We collected several spectra at different kinetic energies of the photoelectrons in order to discriminate between the direct photoemission structures from true absorption peaks.

In our set-up we did not have a reference signal, so we could not normalize the yield spectra, $Y(\hbar\omega)$, to the instantaneous photon flux, $I_0(\hbar\omega)$. In order to correct for the variation of I_0 , that was a smooth function of the photon energy $\hbar\omega$, as well as of time, first we subtracted, and then we normalized our spectra to the pre-edge background. In fact, the total yield can be written as :

$$Y(\hbar\omega) = A I_0(\hbar\omega) (\mu_b(\hbar\omega) + \mu_c(\hbar\omega)), \quad (1)$$

where A is a proportionality constant and the absorption coefficient has been divided into two contributions, the first arising from the background due to all the upper states (μ_b) and the second from the core level under study (μ_c). We extrapolated smoothly the pre-edge shape of $A I_0(\hbar\omega) \mu_b(\hbar\omega)$ in order to obtain the normalized absorption

$$\frac{\mu_c}{\mu_b} = \frac{Y(\hbar\omega)}{A I_0(\hbar\omega) \mu_b(\hbar\omega)} - 1. \quad (2)$$

As an example, in fig.1 we show the measured P

$L_{2,3}$ yield spectrum of NiPS_3 taken at 4 eV kinetic energy. The strong peak at 142 eV is the direct photoemission peak of the P 2p states, as it shifts to 139 eV in the spectrum measured at 0.8 eV kinetic energy. The dashed line in fig.1 represents the background curve, extrapolated from the pre-edge region, that was used in eq.2.

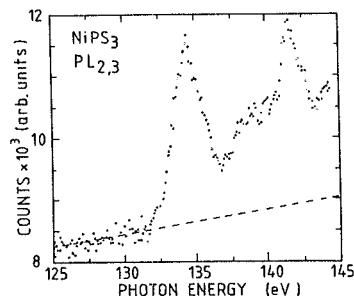


Fig. 1 - P $L_{2,3}$ yield spectrum in NiPS_3 (dots) taken at 4 eV kinetic energy. The dashed line represents the smooth background extrapolated from the pre-edge region, used to normalize the yield spectra according to eq. 2.

In fig.2 we present the normalized absorption spectra of the P $L_{2,3}$, S $L_{2,3}$, and S L_1 core states in FePS_3 and NiPS_3 . The energy scales of the spectra have been renormalized, and the zeroes aligned, according to the relation

$$E = \hbar\omega - E_b, \quad (3)$$

where E_b is the binding energy of the core levels referred to the top of the valence states of the $(\text{P}_2\text{S}_6)^{4-}$ cluster. The values of E_b , that are reported in Tab. 1, have been determined assuming that the valence band XPS spectrum of ZnPS_3 , reported in Ref. 8, yields the $(\text{P}_2\text{S}_6)^{4-}$ valence density of states up to -10 eV for all these materials. In FePS_3 and NiPS_3 , where the photoemission from the transition metal 3d states overlaps the top of the valence bands, we

Table 1 - Binding energies (in eV) of the principal core levels in NiPS_3 (upper lines) and in FePS_3 (lower lines). The zero of energy has been referenced to the top of the valence states of the $(\text{P}_2\text{S}_6)^{4-}$ cluster, as explained in the text and in Ref. 12.

	P	S	M
2s	188.3	225.5	
	225.5	
2p _{3/2}	130.6	161.2	
	131.0	161.3	
3p			66.2
			52.3

used the S-P $3p_{x,y}$ structure at -6 eV binding energy^{8,12} as a reference.

In fig.3 we present the $M_{2,3}$ absorption spectra of Fe and Ni in FePS_3 and NiPS_3 , respectively. Since strong atomic effects occur at these thresholds, we did not renormalize the energies and we used a constant background in eq. 2.

Only in the P $L_{2,3}$ spectra we could see clearly the direct photoemission peak (fig.1). In the other spectra it is not as much evident and it may be responsible for some of the higher energy weak structures. The Fe $M_{2,3}$ spectrum in FePS_3 showed the diffraction second order P $L_{2,3}$ structures above 65 eV. Such features are reported in the inset of fig.3 to show that they overlap, and probably affect slightly, the Ni $M_{2,3}$ spectrum in NiPS_3 .

Discussion

a) The $(\text{P}_2\text{S}_6)^{4-}$ Structures.

It is remarkable that the spectra of the core states of FePS_3 shown in fig.2 are practically the same as those of NiPS_3 . In addition, the main features of the P $L_{2,3}$, S $L_{2,3}$ and S L_1 spectra in both compounds occur at almost the same renormalized energies, but with different relative intensities. Both observations are strong indications that these spectra are affected only slightly by the transition metal ion and that they represent the

projected densities of states of the $(\text{P}_2\text{S}_6)^{4-}$ clusters.

In fig.2 the energy zeroes lie at the onset of the core levels absorptions. The presence of the localized 3d states of the transition metal ion and the possibility of charge transfer transitions at the fundamental threshold make it very difficult to ascertain the existence of core excitons associated with these edges. The P $L_{2,3}$ threshold in black phosphorus is formed by two, very sharp peaks at 130.33 and 131.20 eV, assigned to the spin-orbit partners of the 2p core excitons¹³. Similar peaks, about at the same energies, have been observed at the P $L_{2,3}$ threshold in InP ¹⁴. In our case, the phosphorus $L_{2,3}$ edge is formed by a single, strong peak at 134.8 eV, 2 eV wide, followed by a smooth continuum with some weak features superimposed.

The sulphur $L_{2,3}$ and L_1 spectra begin with a weak, broad structure centered at about 4 eV, where the P $L_{2,3}$ spectrum has the strong peak. The S $L_{2,3}$ spectrum then rises to a marked peak located in a region where the P $L_{2,3}$ absorption shows only weak features. Also the sulphur $L_{2,3}$ absorption spectra of several transition metal sulphides show weak pre-edge structures, interpreted as transitions from the spin-orbit split S 2p states to the transition metal empty d bands^{15,16}. Hybridization with sulphur s (and possibly d) levels makes these transitions observable. Such an assignment was based on the variation of the experimental structures with the transition metal and, in the case of TaS_2 , with the crystal structure¹⁵. In addition, the observed features agreed well with the calculated densities of the empty d bands¹⁵. We did not observe any of these effects in the case of the MPS_3 compounds, in particular a drastic change in shape from Ni to Fe, associated with the different occupancy of the d states in the two ions.

In several sulphur and phosphorus compounds, the S (P) L_2 - L_3 spin-orbit partners are well resolved¹³⁻¹⁵, unlike the case under study of the transition metal chalcogeno phosphates. Weak features, present in particular on the first structure of the S $L_{2,3}$ spectrum, may be due to the spin-orbit splitting, as well as to the density of final states. The density of the conduction states proposed previously from the study of the fundamental reflectivity spectra, is more structured than our results show. The lack of evident splitting in our spectra is not due to poor experimental resolution. The width of the P $L_{2,3}$ direct photoemission peak, shown in fig.2, is due to the CMA bandpass of 1.5 eV. Nevertheless, the 2p splitting is clearly observable. We rather believe that it depends on the combined effects of the overlap of several spin-orbit split structures and of lifetime broadening of the core states. Finally, the S L_1 peak is much

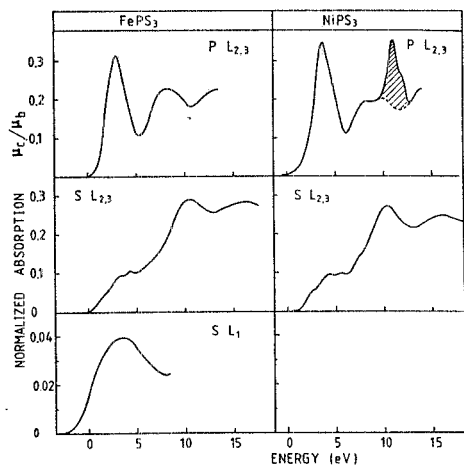


Fig. 2 - Absorption spectra of the P $L_{2,3}$, S $L_{2,3}$, and S L_1 core states of FePS_3 (left panels) and NiPS_3 (right panels). The P $L_{2,3}$ spectrum of NiPS_3 shows also the direct photoemission peak. The dashed curve under this peak represents the most probable absorption spectrum, as inferred by a comparison with the yield spectrum taken at 0.8 eV kinetic energy.

broader than the S and P $L_{2,3}$ features, probably for the faster Auger decay of the 2s hole with respect to the 2p holes.

All the above clues indicate that the core spectra that we have measured correspond to the projected density of empty states of the $(\text{P}_2\text{S}_6)^{4-}$ cluster. The relative intensities of the strongest structures suggest also the atomic contributions of the phosphorus (sulphur) atomic wavefunctions to the final crystal states.

The structure at about 4 eV in fig.2 is much stronger in the P than in the S $L_{2,3}$ spectra with respect to the following smooth absorption. Following the formulation of the projected density of states in X-ray absorption, based on a tight binding scheme¹⁷, we think that the lowest bands are formed mostly from s-like states centered around the phosphorus atoms. Regions of the Brillouin zone far from the center probably contribute also with sulphur s-like and p-like states. Instead, at higher energies, around 12 eV in fig.2, the situation seems reversed, as the S spectrum shows a much stronger peak.

In a simplified model of the energy level sequence of the MPS_3 compounds, the fundamental gap was thought to arise from the bonding-antibonding splitting of the P $3p_z$ states^{4,7,9}. According to the present results, the contribution of such states to the lowest conduction band is very small. A similar situation was encountered already in the III-VI layer compounds, such as GaS. Piacentini et al.⁷ have pointed out the similarity between the $(\text{P}_2\text{S}_6)^{4-}$ cluster in the MPS_3 compounds and the (Ga_2S_6) cluster in GaS. Both clusters are formed by two metalloid atoms strongly bound together with covalent bonds along the c axis. Each metalloid atom is then connected with three sulphur atoms lying in the external faces of the single layer. In the MPS_3 compounds the cluster has octahedral coordination, while in GaS it has a trigonal prismatic structure. Neglecting the interactions between the sulphur atoms lying in the two external sheets, we should expect similar properties for the two clusters. Also for GaS the first conduction band can be naively associated with the antibonding Ga $4p_z$ orbitals. However, the calculations of Nagel et al.¹⁸ and Robertson¹⁹ have shown that the lowest conduction band does not have Ga p_z character, but rather that it derives mostly from the (antibonding) Ga 4s orbitals, because of the hybridization between the 4s and $4p_z$ states of Ga. Experimental evidence of this was achieved by measuring the X-ray dichroism of the Ga K edge in GaS¹⁷. The similarity between the (Ga_2S_6) and the $(\text{P}_2\text{S}_6)^{4-}$ clusters supports our conclusion that the lowest conduction band in NiPS_3 and FePS_3 is formed mostly by the P 3s antibonding orbitals.

b) The Transition Metal $M_{2,3}$ Thresholds.

The $M_{2,3}$ spectra of Fe and Ni in FePS_3 and NiPS_3 , shown in fig.3, differ significantly from each other and from the P and S $L_{2,3}$ edges. Instead, they resemble very much the $M_{2,3}$ absorptions of Fe and Ni in several other ionic compounds, such as their halides and oxides^{20,21}, suggesting that the transition metal ion M^{++} spectra represent an intra-atomic character of the excitation, irrespective of the ligand species. Thus, the sharp fine structures are interpreted in terms of the transition metal

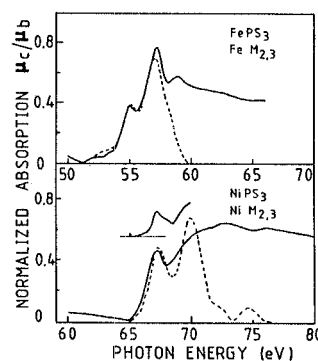


Fig. 3 - Absorption spectra of the Fe (upper curve) and Ni (lower curve) $M_{2,3}$ core states in FePS_3 and NiPS_3 , respectively. The dashed curves reproduce the spectra calculated by Yamaguchi et al.²² for the respective halides. The inset in the NiPS_3 panel is the second-order P $L_{2,3}$ spectrum as measured in the Fe $M_{2,3}$ spectrum in FePS_3 .

ion intra-atomic transition $3p^6 3d^m - 3p^5 3d^{m+1}$ ($m=6$ for Fe^{++} , and $m=8$ for Ni^{++}), that is split into a multiplet structure by multiconfiguration interaction of the final state $3p^5 3d^{m+1}$. Recently, Shin et al.²¹ have analyzed successfully the $M_{2,3}$ absorption spectra of several transition metal compounds in the framework of the ligand field theory, taking the localized character of the excitation and the covalency of the 3d orbitals with the surrounding ligands as well as the crystal field into consideration. We believe that their results hold in the present case too, in view of the fact that also for the d-d transitions at the fundamental absorption edge there is a very good agreement between the structures found in NiPS_3 and FePS_3 and the Ni (Fe)-halides^{7,8}. For comparison, in fig. 3 we show also the Fe^{++} and Ni^{++} absorption spectra calculated by Yamaguchi et al.²² for the transition metal halides. Finally, we want to notice that our $M_{2,3}$ spectrum of Fe differs significantly from the $M_{2,3}$ spectrum of Fe in the low-spin compound FeS_2 ²³.

Conclusions

We measured the L_1 edge of S, the $L_{2,3}$ edges of both S and P and the $M_{2,3}$ spectra of Fe and Ni in FePS_3 and NiPS_3 respectively, using the partial yield technique. The $M_{2,3}$ spectra are assigned to the localized transitions $3p^6 3d^m - 3p^5 3d^{m+1}$ of the M^{++} ions. The similarity between each other of the P and S core spectra suggests that they represent the conduction band density of states of the $(\text{P}_{26}\text{S}_6)^{4-}$ cluster. The different intensities of the structures are attributed to the different atomic contributions to the final states.

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Note added in proof. After submission of the manuscript, a paper on a related subject has appeared²⁴. The partial yield spectra of the P $2p$ edge as well as the resonant photoemission spectra are consistent with our measurements (the latter will be the subject of a later publication).

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