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EXPERIMENTAL STUDIES OF THE VALENCE AND CONDUCTION STATES
OF THE TRANSITION METAL THIOPHOSPHATES

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The transition metal thiophosphates belong to a large family of layered compounds with the general formula MPX_3 , where M indicates a divalent transition metal ion and X represents a chalcogen atom. These materials can be intercalated with alkali ions, between other species, and are well suited for cathodes in high capacity batteries based on Li^+ transport (1). We have investigated in detail the valence bands of $MnPS_3$, $FePS_3$ and $NiPS_3$ with the resonant photoemission technique and their lowest conduction bands by means of soft X-ray absorption from several core levels.

The experiments have been performed using the Grasshopper beam line of the Italian synchrotron radiation facility PULS at the Frascati National Laboratories run by the Istituto Nazionale di Fisica Nucleare. Single crystals were cleaved inside the photoemission ultrahigh vacuum chamber. The soft X-ray absorption measurements were performed with the partial yield technique. We investigated also the weak d-d transitions on the transition metal ion occurring below the fundamental threshold (2) using a Perkin Elmer 330 spectrophotometer.

The MPS_3 compounds can be envisaged as formed by a lattice of M^{2+} ions and $(P_2S_6)^{4-}$ groups. Their valence bands derive mostly from the $(P_2S_6)^{4-}$ states. However, the energy distribution curves (EDC) measured in photoemission in the valence band region contain also structures originating from the configurational multiplet splitting due to the ionization of the transition metal d states (d^n-d^{n-1}), as well as from satellite structures. In order to discriminate between the different possibilities of assignment of the experimental structures, we used the resonant photoemission technique by measuring several EDC's at different photon energies around the transition metal 3p absorption threshold (Fig. 1). We observed that some features show rapid intensity changes, that we followed by means of constant-initial-state (CIS) photoemission spectra.

The CIS structures can be related with corresponding features present in the 3p absorption spectra. These behaviors are a fingerprint of the localized nature of the transitions that involve the 3d electrons of the transition metal ion. The other structures that do not resonate can be assigned to the valence states of the $(P_2S_6)^{4-}$ clusters. Good agreement is found between the latter structures and the calculated densities of states ^(3,4).

The soft X-ray absorption spectra of the phosphorus $L_{2,3}$ (sulphur $L_{2,3}$) levels in $MnPS_3$, presented in Fig. 2, are similar to those of $FePS_3$ and $NiPS_3$ and are interpreted in terms of the projected density of states of the lowest conduction bands. The contribution to the lowest conduction bands from the $(P_2S_6)^{4-}$ states does not seem to change significantly with the compound. The differences between the phosphorus and sulphur $L_{2,3}$ thresholds are attributed to the different amount of mixing of phosphorus and sulphur atomic orbitals to the crystal conduction states.

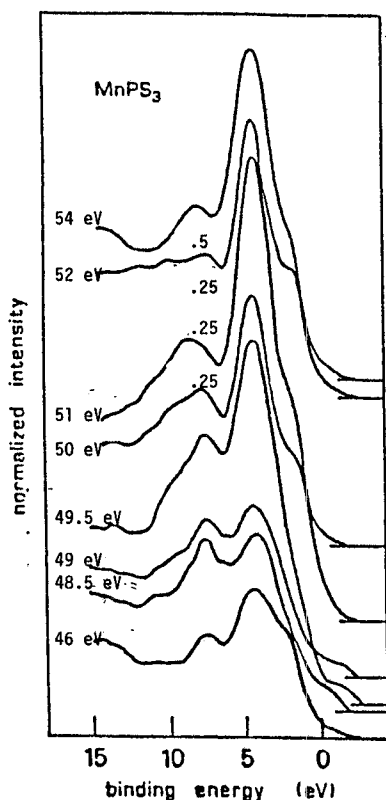


Fig. 1 - EDC spectra of $MnPS_3$ at several photon energies around the Mn 3p threshold, showing the resonant nature of several structures.

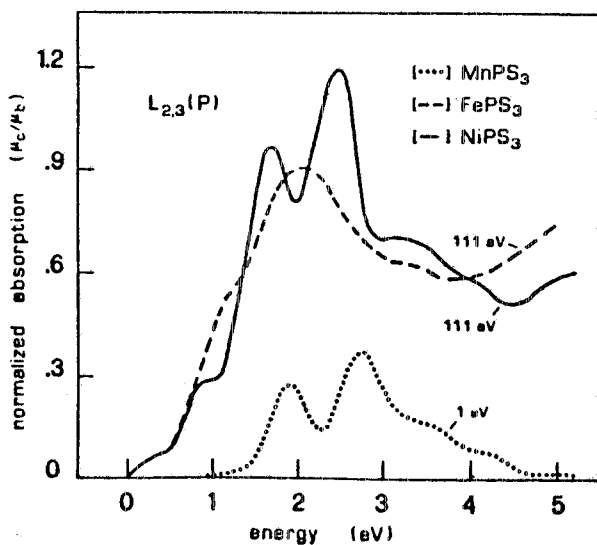


Fig. 2 - Phosphorus $L_{2,3}$ absorption spectra of $MnPS_3$, $FePS_3$ and $NiPS_3$ measured with the partial yield technique.

Weak structures are found in the near infrared and visible absorption spectra of the MPS_3 compounds ($M=Mn, Fe, Co, Ni$) below their fundamental absorption thresholds. We interpreted these features as d-d transitions

in terms of the ligand field theory.

All the above observations give further support to the ionic picture of these materials. The valence states derive mostly from the $(P_2S_6)^{4-}$ clusters while the d states of the transition metal ions are strongly localized and cannot be treated as band-like states.

References:

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