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Reduction Sites of Transition-Metal Phosphorus Trichalcogenides, MPX_3

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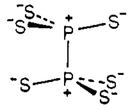
By examining a number of experimental observations on MPX_3 and also by carrying out tight-binding band calculations on $FePS_3$, it was shown that the acceptor levels of MPX_3 responsible for their alkali-metal intercalation processes are low-lying partially filled metal 3d orbitals.

Transition-metal phosphorus trichalcogenides MPX_3 (M = first-row transition metal; X = S, Se) are layered materials,[1] which may be considered as salts of M^{2+} and $P_2X_6^{4-}$ ions.[2-4] The perspective view and the Newman projection of a hexachalcogenohypophosphate ion $P_2X_6^{4-}$ are shown in **1a** and **1b**, respectively. In an MPX_3 slab each M^{2+} ion is surrounded by three $P_2X_6^{4-}$ ions as depicted in **2**, and with two X atoms from each $P_2X_6^{4-}$ ion, every M^{2+} ion is octahedrally coordinated by six X atoms.



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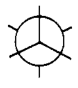

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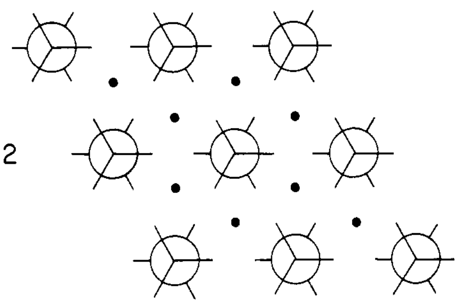

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MPX_3 compounds are interesting because of their quasi-two-dimensional properties and their application as cathode materials in lithium batteries.[5] It is known that lithium and metallocene intercalation reactions of MPX_3 are both redox reactions, in which the guest species gives up an electron to the MPX_3 host and is intercalated as a cation.[2,5e,6] Despite a number of studies, however, no satisfactory picture has yet emerged concerning the reduction sites of MPX_3 (i.e., low-lying empty levels of MPX_3 that accept the electron). In fact, except for the 3d levels of M^{2+} ions, nearly all possible empty levels of MPX_3 have been proposed as acceptor levels (e.g., the 4s and 4p orbitals of M^{2+} ions,[5b,7] the σ antibonding orbitals of P–P bonds,[8] and the sulfur 3d orbitals[9] for MPS_3). Metal 3d levels have been excluded from consideration primarily because of the following two observations: (a) Optical absorption measurements appear to show that MPX_3 compounds are broad-band semiconductors.[5a,d] (b) Chemical intercalation of lithium seems to affect the magnetic properties of MPX_3 very little.[5d]

Table I. Exponents ζ_μ and the Valence-Shell Ionization Potentials $H_{\mu\mu}$ for Slater-Type Orbitals χ_μ[a,b]

χ_μ	ζ_μ	ζ_μ'	$H_{\mu\mu}$, eV
Fe 4s	1.90		−8.4
Fe 4p	1.90		−5.0
Fe 3d	5.35 (0.5505)	2.0 (0.6260)	−12.2
P 3s	1.88[c]		−20.2[d]
P 3p	1.63[c]		−12.5[d]
S 3s	2.12[c]		−20.1[d]
S 3p	1.83[c]		−13.3[d]

[a] The d orbitals of Fe are given as a linear combination of two Slater-type orbitals, and each is followed by the weighting coefficient in parentheses.[17] [b] A modified Wolfsberg–Helmholz formula was used to calculate $H_{\mu\nu}$.[18] [c] Reference 12a. [d] Reference 19.

However, exclusion of metal 3d orbitals as acceptor levels leads to serious conceptual problems. In what might be referred to as the weak-interaction model,[8] covalent interactions between metal and X atoms in MPX_3 are considered negligible. Thus, the electronic structure of an MPX_3 slab can be approximated by flat 3d, 4s, and 4p bands of M^{2+} ions superposed with the s,p-block bands of $P_2X_6^{4-}$ ions. With the metal 3d orbitals excluded, possible acceptor levels of MPX_3 can be either the 4s and 4p bands of M^{2+} ions or the empty bands of $P_2X_6^{4-}$ ions derived from the σ antibonding orbitals of P–P and P–X bonds (σ_{P-P}^* and σ_{P-X}^*, respectively). In the weak-interaction model the σ_{P-P}^* level is considered as low lying in energy, since the P–P bond length of ~2.2 Å found in $P_2X_6^{4-}$ ions is regarded as long and therefore is weak. However, this bond length is typical of single P–P bonds found in other phosphorus compounds.[10] In addition our extended Hückel[11] calculations on $P_2S_6^{4-}$ show that the LUMO (primarily σ_{P-P}^*) lies as much as 15 eV above the HOMO (primarily sulfur lone-pair orbital). Therefore, it is really questionable that any bands arising from σ_{P-P}^* and σ_{P-X}^* can be low enough in energy

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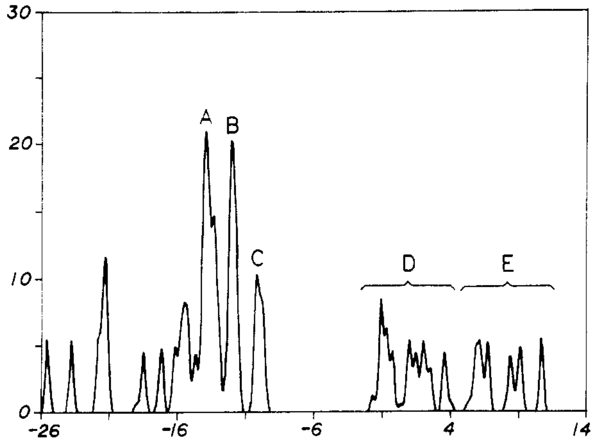

Figure 1. Total density of states of $FePS_3$, where the abscissa is in eV and the ordinate is in number of electrons per eV per unit cell.

to be good acceptor levels. We also note that metal 4s orbitals are too high in energy to be good acceptor levels. For instance, the neutral transition-metal elements Mn, Fe, Ni and Zn have their 4s orbitals about 10 eV above their 3d levels.[12]

It is interesting to observe that $ZnPS_3$ and $CdPS_3$, which contain d^{10} ions (i.e., Zn^{2+} and Cd^{2+}), hardly react with *n*-butyllithium.[5] $FePS_3$ and $NiPS_3$ with d^6 and d^8 ions, respectively, are found to be good cathode materials and react with *n*-butyllithium.[5] On the other hand, $MnPS_3$, which has d^5 ions, slowly reacts with *n*-butyllithium.[5] These findings suggest that low-lying partially filled 3d orbitals behave as acceptor levels but have been explained in terms of the energy gaps of MPX_3 determined from their apparent optical absorption edges (e.g., the apparent band gaps of $FePS_3$, $NiPS_3$, $MnPS_3$, and $ZnPS_3$ are 1.5, 1.6, 3.0, and 3.4 eV, respectively).[5a] These data hint that MPS_3 with the smaller energy gap would have the lower lying acceptor levels and hence would be a better cathode material. Those apparent band gaps, however, cannot refer to the band gap between the valence (highest occupied) and conduction (lowest unoccupied) bands of $P_2S_6^{4-}$ ions, since such a gap would be nearly independent of the nature of metal according to the weak-interaction model.[8] Nor can the apparent band gaps of MPS_3 (for M^{2+} ions other than d^{10}) be related to the energy difference between the valence band of $P_2S_6^{4-}$ ions and the 4s band of M^{2+} ions, because such an energy gap would be smallest for $ZnPS_3$.[12] These conclusions are consistent with the electrical resistivities of $MnPS_3$ ($\sim 10^9$ Ω cm) and $NiPS_3$ ($\sim 10^9$ Ω cm).[5d] Those resistivity values are rather large for semiconductors and are similar in magnitude despite the difference of 1.4 eV in their apparent band gaps. Namely, $MnPS_3$ and $NiPS_3$ do not appear to be semiconductors as far as their electrical resistivity values are concerned.

To gain some insight into the electronic structures of MPX_3 compounds and therefore answer some of their puzzling problems, we calculated the band electronic structure of an $FePS_3$ slab by employing the tight-binding band scheme[13] based upon the extended Hückel method.[11] The atomic parameters used in the present calculations are summarized in Table I.

Results and Discussion

Since M^{2+} ions are octahedrally coordinated in MPX_3, one expects that the metal 3d-block bands are represented by three bands derived from the t_{2g} level of M^{2+} (i.e., t_{2g} subbands) lying below two bands derived from the e_g level of M^{2+} (i.e., e_g subbands). Figure 1 shows the total density of states of an $FePS_3$

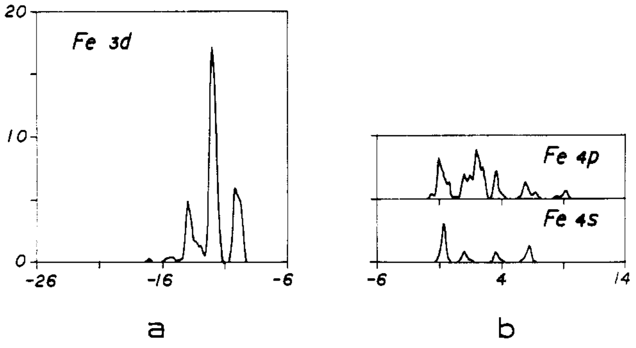

Figure 2. Iron orbital density of states of $FePS_3$: (a) 3d orbital; (b) 4s and 4p orbitals. The abscissa is in eV, and the ordinate of (a) is in number of electrons per eV per unit cell. In (b), every interval of the ordinate refers to five electrons per eV per unit cell.

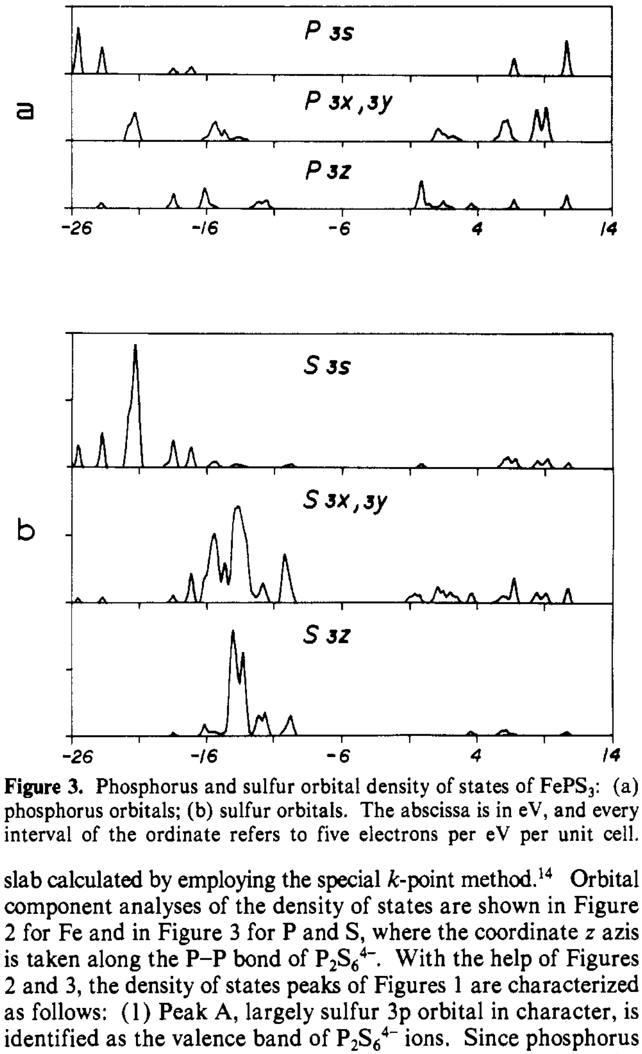

Figure 3. Phosphorus and sulfur orbital density of states of $FePS_3$: (a) phosphorus orbitals; (b) sulfur orbitals. The abscissa is in eV, and every interval of the ordinate refers to five electrons per eV per unit cell.

slab calculated by employing the special *k*-point method.[14] Orbital component analyses of the density of states are shown in Figure 2 for Fe and in Figure 3 for P and S, where the coordinate *z* azis is taken along the P–P bond of $P_2S_6^{4-}$. With the help of Figures 2 and 3, the density of states peaks of Figures 1 are characterized as follows: (1) Peak A, largely sulfur 3p orbital in character, is identified as the valence band of $P_2S_6^{4-}$ ions. Since phosphorus orbital character is lacking, peak A is primarily derived from sulfur lone-pair orbitals. (2) Peak B, largely composed of metal 3d orbitals with only small contribution of sulfur 3p orbitals, is considered as the t_{2g} subband. Peak C, in which sulfur 3p-orbital character is nearly as large as metal 3d contribution, is therefore assigned as the e_g subbands. Phosphorus character is very small in peaks B and C. In particular, this means that the sulfur

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(12) For the neutral transition-metal elements Mn, Fe, Ni and Zn, the 4s orbital is calculated to be about 10 eV higher in energy than the 3d orbital. On going from Fe to Zn in the first-row transition-metal series, the 4s-orbital energy is gradually lowered in energy by 1 eV. See: (a) Clementi, E.; Roetti, C. *Atomic Data Nucl. Data Tables* **1974**, *14*, 177. (b) Fischer, C. F. *Atomic Data* **1972**, *4*, 302.

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(14) We employed the 6*k* point set. The wave vectors k_i and their weighting factors w_i are given as follows: $k_1 = (^1/_9, {}^1/_9)a^*$, $w_1 = {}^1/_9$; $k_2 = (^2/_9, {}^2/_9)a^*$, $w_2 = {}^1/_9$; $k_3 = (^4/_9, {}^4/_9)a^*$, $w_3 = {}^1/_9$; $k_4 = (^1/_3, {}^1/_9)a^*$, $w_4 = {}^2/_9$; $k_5 = (^5/_9, {}^1/_9)a^*$, $w_5 = {}^2/_9$; $k_6 = (^4/_9, {}^2/_9)a^*$, $w_6 = {}^2/_9$. For details of the special *k*-point method, See: (a) Chadi, D. J.; Cohen, M. L. *Phys. Rev. B: Solid State* **1973**, *8*, 5747. (b) Monkhorst, H. L.; Pack, J. D. *Phys. Rev. B: Solid State* **1976**, *13*, 5188. (c) Baldereschi, A. *Phys. Rev. B: Solid State* **1973**, *7*, 5212.

3p-orbital character of the e_g subbands arises from sulfur lone-pair orbitals. (3) The major orbital components of the D peaks are metal 4s and 4p orbitals, while those of the E peaks are phosphorus and sulfur orbitals. Thus, the E peaks are associated with the σ_{P-P}^* and σ_{P-S}^* orbitals of $P_2S_6^{4-}$ ions. (4) The densities of state peaks that occur in the energy region below peak A are largely associated with the 3s orbitals of sulfur and phosphorus.

It is clear from Figure 1 that the 4s, 4p bands of Fe^{2+} ions (D) and the antibonding bands of $P_2S_6^{4-}$ ions (E) are too high in energy to be good acceptor levels and be responsible for the apparent absorption edge of $FePS_3$. Thus, the metal 3d-block bands (B and C), which are partially filled[15] with high-spin d^6 ions, must be responsible for the acceptor capability and also for the absorption edge.

Contrary to the expectation of the weak-interaction model,[8] the widths of the t_{2g} and e_g subbands (2.0 and 1.5 eV, respectively) are not negligible. In addition, the latter have very strong sulfur lone-pair character. All of these indicate that covalent interactions between iron and sulfur are strong. This conclusion is consistent with the observation[16] that the $10D_q/B$ ratios determined for $MnPS_3$ and $NiPS_3$ are exceptionally large, thereby suggesting a high degree of covalent bonding between metal and sulfur atoms.

Unlike the t_{2g} subbands, the e_g subbands have strong sulfur lone-pair character; therefore, the e_g subbands C are a lot more compatible with the valence band A than are the t_{2g} subbands B. Thus, optical absorption from A to C would be very intense compared with that from A to B and would be responsible for the apparent fundamental absorption edge of $FePS_3$. Bands A and C are estimated to be separated by about 1.8 eV, in reasonable agreement with the apparent band gap 1.5 eV of $FePS_3$.[5a]

The t_{2g} subbands are largely metal 3d orbital in character so that electron addition into these bands would lead to a sensitive change in the properties of M^{2+} ions. On the other hand, metal 3d-orbital character does not dominate in the e_g subbands, so electron addition into these bands may not significantly modify the properties of M^{2+} ions unless the amount of electron addition is large enough. This aspect might be quite relevant in interpreting the intercalation behavior of $NiPS_3$.[7]

The t_{2g} subbands are primarily metal 3d orbitals in nature, while the e_g subbands are metal 3d orbitals and sulfur lone-pair orbitals in character. Therefore, electron addition into those bands could not fundamentally change the properties associated with the strength of the P–P and P–S bonds such as their stretching vibrational frequencies. In fact, infrared spectra of Li_xFePS_3 and Li_xNiPS_3 show[5b] that the ν_{P-P} mode appears at a constant frequency (442 and 440 cm^{-1} for Li_xFePS_3 and Li_xNiPS_3, respectively).

Concluding Remarks

On the basis of the band structure of $FePS_3$ examined in our study, the following qualitative picture may be proposed for the band electronic structures of other MPX_3 compounds: The positions of the valence and conduction bands of $P_2X_6^{4-}$ ions (A and E, respectively) would be little affected by the nature of M^{2+}. With respect to those bands, the positions of the t_{2g} subbands, the e_g subbands, and 4s and 4p bands of M^{2+} ions (B–D, respectively) would shift toward lower and higher energy for metal atoms M on the right and left of Fe, respectively.

From the present study, it is inevitable to conclude that acceptor levels responsible for intercalation reactions of MPX_3 are low-lying partially filled 3d-block bands. It is the optical absorption from the valence band A to the e_g subband C that is responsible for the apparent fundamental absorption edge of MPX_3 with metal ions other than d^{10}.

As already pointed out, one of the two major reasons why metal 3d levels have not been considered as acceptor levels is the apparent observation that chemical intercalation of lithium affects the magnetic properties of MPX_3 very little.[5d] However, this observation is not unequivocal: Although experimental difficulties are present, magnetic susceptibilities of Li_xNiPS_3 in the paramagnetic region are found to decrease with x.[5d] Furthermore, the ^{31}P study of Li_xNiPS_3 shows[7a] that nonmagnetic $NiPS_3$ slabs must occur for $x > 0.5$ at least. In view of the present study, it would be difficult to accept that magnetic susceptibilities of MPX_3 would not vary upon lithium intercalation, unless we are dealing with a genuinely new magnetic phenomenon with MPX_3 systems. Further experimental and theoretical studies are in progress to clarify this problem.

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Registry No. $FePS_3$, 20642-11-9.

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Notes

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Reaction of Potassium Vapor with Tungsten Trioxide Crystals

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Tungsten trioxide is a crystalline solid composed of corner-shared WO_6 octahedra in an essentially cubic array. Ternary compounds with potassium, tungsten, and oxygen are numerous and varied in structure.[1-10] In the tungstates, $K_2W_nO_{3n+1}$, tungsten has a formal +6 valence. In the nonstoichiometric bronzes, K_xWO_3, valence varies according to the amount of potassium incorporated into a somewhat complex hexagonal or tetragonal corner-shared WO_6 octahedral network. Two bronzes of interest

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