

NATURE OF THE OXIDIZING CENTRES IN TRANSITION METAL PHOSPHORUS TRISULFIDES MPS_3 ($M = Fe, Ni$)

R. BREC, G. A. FATSEAS and G. OUVARD

Laboratoire de Chimie des Solides, U.A.-CNRS 279, Université de Nantes, 2, rue de la Houssinière, 44072 Nantes Cédex (France)

M.-H. WHANGBO

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204 (U.S.A.)

Summary

On the basis of $FePS_3$ and $NiPS_3$ band structure, it has been demonstrated that electron donation corresponding to lithium intercalation in these layered structures has to take place on low-lying, partially-filled, 3d-block bands. Past ^{31}P NMR studies on the Li_xNiPS_3 have been reassessed and are shown to be quite consistent with nickel reduction. Mössbauer spectroscopy studies suggest the occurrence of highly reduced iron sites with unusual characteristics.

Introduction

Transition metal phosphorus trisulfides (MPS_3 with $M =$ first row transition metal) are interesting phases because of their quasi-two-dimensional properties and their potential application as cathode materials in lithium batteries [1, 2]. It has been shown in many instances that the MPS_3 compounds are oxidizing materials and that electron donors (lithium, metallocenes, ...) can reduce them, the guest species being intercalated in the MPS_3 host lattice as a cation [3, 4]. The MPS_3 phases can be considered as metal and phosphorus double sulfides, but because of their room temperature cationic exchange abilities [5, 6], they can also be viewed as salts of M^{2+} and $(P_2S_6)^{4-}$ ions. Thus, in a slab, each M^{2+} ion is surrounded by three $(P_2S_6)^{4-}$ anions, as depicted in Fig. 1, and with two S atoms from each $(P_2S_6)^{4-}$, every M^{2+} cation is octahedrally coordinated by six S atoms. Since the host structure is reduced upon lithium intercalation, the nature of the reduction sites, i.e., low-lying empty levels of the MPS_3 that accept the electrons, is raised.

Because no clear picture had emerged concerning the identification of the oxidizing centres in the MPS_3 compounds, and in spite of a certain number of experiments, Whangbo [7] and Mercier [8] carried out tight binding

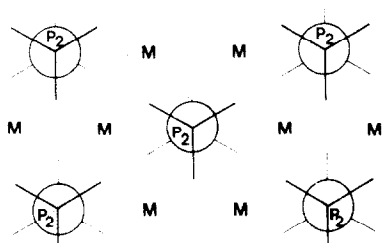


Fig. 1. Schematic projection of MPS_3 slab structure showing $(P_2S_6)^{4-}$ and M^{2+} ionic distribution.

band calculations. After a brief review of $FePS_3$ and $NiPS_3$ band structures, a reassessment of past ^{31}P NMR results shows good agreement with cationic reduction in the Li_xNiPS_3 intercalates. Recent Mössbauer spectroscopy studies on Li_xFePS_3 series confirm the role of the transition metal as the oxidizing centre, the reduced iron exhibiting an unexpected isomer shift value.

Band structure of $FePS_3$ and $NiPS_3$

Figure 2(a) shows the total density of states of an $FePS_3$ slab calculated by employing the special k-point method [7]. Orbital component analysis of that density indicates that:

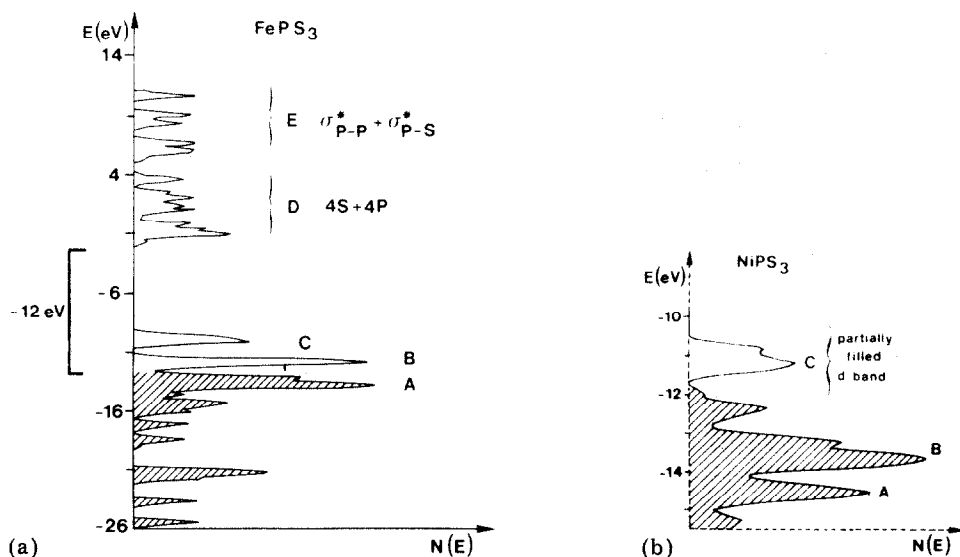


Fig. 2. (a) Total density of state of $FePS_3$. (b) Density of states of $NiPS_3$ (only low lying bands are represented), from ref. 8.

(i) peak A, largely sulfur 3p orbital in character, is identified as the valence band of $(P_2S_6)^{4-}$ ions;

(ii) peak B is largely composed of metal 3d orbitals and considered as the t_{2g} sub-band;

(iii) peak C, in which sulfur 3p orbital character is nearly as large as the metal 3d contribution, is assigned as the e_g sub-band;

(iv) at higher energy, the major orbital components of the D peaks are metal 4s and 4p orbitals, while those of the E peaks are associated with the σ^*_{P-P} and σ^*_{P-S} orbitals of $(P_2S_6)^{4-}$ ions; and

(v) the density of states 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 Fig. 2(a) that the metal 3d-block bands (B and C), which are partially filled with high-spin d^6 ions, must be responsible for the electron-acceptor capability.

The low lying density of state bands of $NiPS_3$ are shown in Fig. 2(b). The component analysis shows that:

(i) peak A is identified as the valence band of $(P_2S_6)^{4-}$ ions;

(ii) peak B is considered as the t_{2g} sub-band, above which a small peak is a bonding contribution of the P-P type; all these bands are filled, the B one corresponding to t_{2g}^6 configurations; and

(iii) at higher energy, peak C is assigned to sub-band e_g and is thus the first, low lying, partially-filled level (d^8 ion).

As pointed out for $FePS_3$, the accepting levels in $NiPS_3$ for electron reduction are constituted by the Ni^{2+} d orbitals. In both cases, intercalation of reducing species must, hence, lead to the transition metal in a highly reduced state, with characteristics that can be determined in the Li_xNiPS_3 and the Li_xFePS_3 series through relevant spectroscopic studies.

Properties of Li_xNiPS_3 ($0 \leq x \leq 1.45$)

Systematic studies of the bulk electronic properties of Li_xMPS_3 , such as the Knight shift of the ^{31}P host nuclei as a function of the intercalation ratio, enable information to be obtained on the modification of the electronic properties of the host resulting from the change in its magnetic properties. The ^{31}P NMR spectra of the Li_xNiPS_3 series have shown [9] important and interesting modifications. In a pure $NiPS_3$ matrix, the ^{31}P line shape appears as a Pake doublet (peaks A in Fig. 3) that does not seem to change in the early stage of lithium intercalation ($x < 0.5$ in Li_xNiPS_3). Its shape, position, and relaxation time ($T_1 \approx 16$ ms) are identical over the entire concentration range. It has been shown that, as a result of its broadening and shift, this peak disappears suddenly at 155 K, *i.e.*, close to the anti-ferromagnetic ordering temperature of $NiPS_3$. For a lithium concentration of $x \approx 0.5$, a new line (peak B) appears. The latter has the same shift as ^{31}P in $CdPS_3$, and a T_1 value that is two orders of magnitude longer than that of peak A and identical with that in the cadmium derivative. This new line, B, progressive-

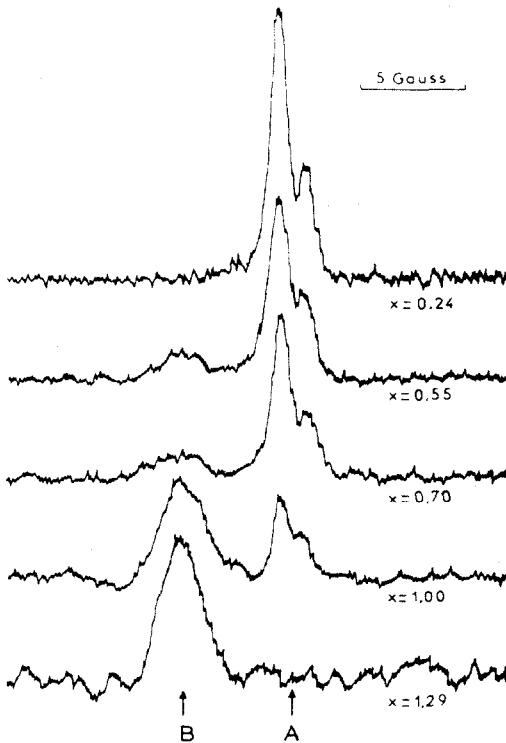
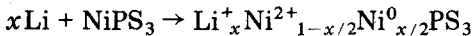


Fig. 3. ^{31}P NMR line shape in Li_xNiPS_3 intercalates ($0 \leq x \leq 1.45$).

ly grows at the expense of line A, and does not disappear at $T_N \approx 155$ K, as does line A. Indeed, it is still present at 4 K. These results lead to the conclusion that a diamagnetic phase has occurred upon lithium intercalation. Since no cell change is observed upon lithium intercalation in Li_xNiPS_3 , and since the accepting levels are the e_g band of Ni^{2+} , it is possible to say that in Li_xNiPS_3 some microdomains must exist retaining the original magnetic properties of NiPS_3 (with unreduced Ni^{2+}) and some diamagnetic microdomains containing reduced Ni^0 atoms. The reduction process may hence be written as:



The unchanged properties of the matrix in the $0 < x < 0.5$ concentration range is a curious phenomenon. It may, in part, be explained by the detection threshold of the NMR technique, and in part by the fact that $x\text{Li}$ are needed to produce $x/2 \text{Ni}^0$, which further lowers this threshold. Also, it has been found [10] that an electronic transfer with slow kinetics takes place during lithium intercalation in FePS_3 , and this phenomenon may also certainly act in the intercalation in NiPS_3 . Another possibility is that the reduced nickel is statistically scattered within the structure, and only gathers

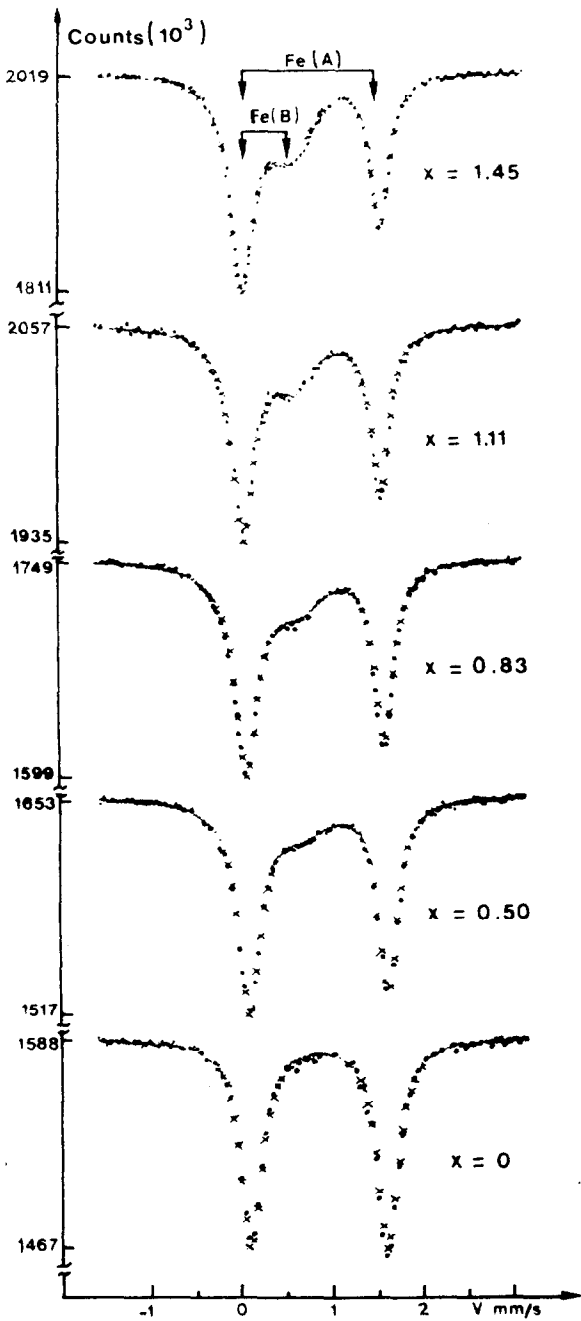


Fig. 4. Room temperature Mössbauer spectra of Li_xFePS_3 intercalates ($0 \leq x \leq 1.45$).

in detectable microdomains when some critical concentration around $x \approx 0.5$ is reached.

These results are consistent with magnetic data that show [3] a decrease in the susceptibility with an increase in the lithium content.

Properties of Li_xFePS_3 ($0 \leq x \leq 1.42$)

In the Li_xFePS_3 series, the assumed oxidizing species, Fe^{2+} , can be directly observed by using Mössbauer spectroscopy. The spectra obtained at room temperature for the Li_xFePS_3 series are given in Fig. 4. For $x = 0$, a quadrupole doublet is observed (site Fe(A), $\delta = 0.86 \text{ mm s}^{-1}$ and $\Delta = 1.52 \text{ mm s}^{-1}$), and for $x \neq 0$, the lithium intercalates give rise to a second iron doublet attributed to a second site of reduced iron, called Fe(B), whose relative intensity increases with x . Fe(A) hyperfine parameters remain almost the same in the whole concentration range ($\delta = 0.86 \text{ mm s}^{-1}$ and $\Delta = 1.55 \text{ mm s}^{-1}$ for the $\text{Li}_{1.45}\text{FePS}_3$ sample). Those for Fe(B) decrease slightly from $\delta = 0.47 \text{ mm s}^{-1}$ and $\Delta = 0.52 \text{ mm s}^{-1}$ in $\text{Li}_{0.50}\text{FePS}_3$ to $\delta = 0.43 \text{ mm s}^{-1}$ and $\Delta = 0.48 \text{ mm s}^{-1}$ in $\text{Li}_{1.45}\text{FePS}_3$. A rather unexpected result is obtained here, for previous Mössbauer data from lithium intercalate chalcogenides, oxides, and halogenides have shown that the electron donation is always reflected by an increase in the isomer shift. In effect, as ^{57}Fe , $\langle \Delta R^2 \rangle$ is negative, δ increase when $|\phi_s(\text{O})|^2$ decreases, *i.e.*, when the electrons are filling predominantly Fe-3d like bands. However, it must be pointed out that these previous studies always dealt with the reduction of iron in a high oxidation state, whereas in this study, iron is already present as Fe^{2+} in the starting FePS_3 .

In a phenomenological approach, it may be assumed that reduction of Fe(A) to Fe(B) in Li_xFePS_3 involves only the population of the 3d and 4s orbitals. According to the results of Walker *et al.* [11], the decrease of δ from $\sim 0.85 \text{ mm s}^{-1}$ for Fe(A) to $\sim 0.45 \text{ mm s}^{-1}$ for Fe(B) corresponds to the change in a free iron configuration from $3d^64s^{0.2}$ to $3d^74s^{0.8}$. Since the increased 3d orbital population would increase δ via its screening effect upon the 3s orbital, the decrease of δ on going from $3d^64s^{0.2}$ to $3d^74s^{0.8}$ must be due to an increased 4s orbital population, whose effect must dominate over the 3d orbital screening effect. The iron 3d orbitals would be more extended in a crystal with substantial covalent bonding than with strong ionic bonding, therefore the isomer shift of the former would be less sensitive to a change in the 3d orbital population. In fact, for the reduction of Fe^{3+} to Fe^{2+} , the increase of δ is 0.4 mm s^{-1} for iron sulfides but $\sim 1.0 \text{ mm s}^{-1}$ for strongly ionic compounds. Another factor to consider is the overlap distortion of core orbitals, which is known to strongly influence the isomer shift and may play a role in the Li_xFePS_3 intercalates.

The initial stage of intercalation shows that about two lithium atoms are needed to produce one Fe(B) site, as if the oxidation state of Fe(B) is zero. This result is in agreement with observations made for nickel in Li_xNiPS_3 , and therefore suggests that the oxidation/reduction process on lithium intercalation in these phases is the same.

Conclusion

NiPS₃ and FePS₃ are cathodic materials able to function as secondary positives in lithium batteries. Because the cations are present with the low oxidation state of II in the original phases, reversible reduction to a lower state appears difficult to envisage. However, following band structure calculations and further physical experiments, electron transfer was found to occur on the transition metal leading to highly reduced nickel and iron species gathered in microdomains in the Li_xMPS₃ intercalates.

References

- 1 A. H. Thompson and M. S. Whittingham, *Mater. Res. Bull.*, 12 (1977) 741.
- 2 A. Le Méhauté, G. Ouvrard, R. Brec and J. Rouxel, *Mater. Res. Bull.*, 12 (1977) 1191.
- 3 G. Ouvrard, *Thesis*, Nantes, France, 1980.
- 4 J. P. Audière, R. Clément, Y. Mathey and C. Mazières, *Physica*, 99B (1980) 133.
- 5 R. Clément, *J. Chem. Soc., Chem. Commun.*, (1980) 647.
- 6 R. Clément, O. Garnier and Y. Mathey, *Nouv. J. Chim.*, 6 (1981) 13.
- 7 M.-H. Whangbo, R. Brec, G. Ouvrard and J. Rouxel, *Inorg. Chem.*, 24 (1985) 2459.
- 8 H. Mercier, *Thesis*, Orsay, France, 1985.
- 9 C. Berthier, Y. Chabre and M. Minier, *Solid State Commun.*, 28 (1978) 327.
- 10 G. Ouvrard, M.-H. Whangbo, G. Fatseas and R. Brec, *Solid State Ionics*, submitted for publication.
- 11 L. R. Walker, G. K. Wertheim and V. Jaccarino, *Phys. Rev. Lett.*, 6 (1961) 98.