

Correlation Between the Structural Disorder Studied by EXAFS and the Magnetic Properties of Intercalated MnPS_3

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Abstract. Intercalation of various cations into layered MnPS_3 induces some disorder in the local structure of Mn(II) cations, observable by EXAFS at the manganese K edge. The amplitude of this disorder effect is correlated with the amplitude of the 'weak ferromagnetism' also observed at low temperature in the intercalates.

Key words: Layered phosphochalcogenides, magnetic properties, EXAFS.

1. Introduction

Transition-metal hexathiohypodiphosphates MPS_3 , where M is a divalent metal, form a class of lamellar semiconductors [1, 2] with a structure related to that of CdCl_2 .

It has been shown in the past few years that these materials give rise to an unusual intercalation process of cationic species from their aqueous solution with a loss of M^{2+} cations by the layers to balance electric charges [3]. In this manner, a large variety of species could be inserted into MnPS_3 , including in particular potassium, cobalticinium, *n*-octyl-ammonium and methyltris(octyl)ammonium. Magnetic susceptibility measurements have shown that MnPS_3 is a strongly coupled two-dimensional antiferromagnet [4, 5]. Intercalation was found to reduce antiferromagnetic interactions and, in addition, the susceptibility of the intercalates increased dramatically below about 40 K. This effect was observed on all the intercalated derivatives mentioned above [6] and it was interpreted as the onset of 'weak ferromagnetism' below a critical temperature in these materials. A few selected results extracted from [6] and [8] are recalled in Figure 1 to emphasize the 'intermediate behaviour' of the methyltris(octyl) ammonium intercalate. Complete understanding of these unusual phenomena would require detailed structure determination of the intercalates, but suitable crystals of these materials have never been obtained. Our previous EXAFS study [7] of MnPS_3 and of its cobalticinium intercalate $\text{Mn}_{0.83}\text{PS}_3(\text{Co}(\text{C}_5\text{H}_5)_2)_{0.34}$ was thus the first structural investigation yielding information on the short-range order around the manganese ions. The most salient result was that intercalation of CoCp_2^+ induced an important local disorder, especially for the second shell of the radial distribution corresponding to the Mn—P and Mn—Mn distances. In an attempt to establish a correlation between such a local disorder

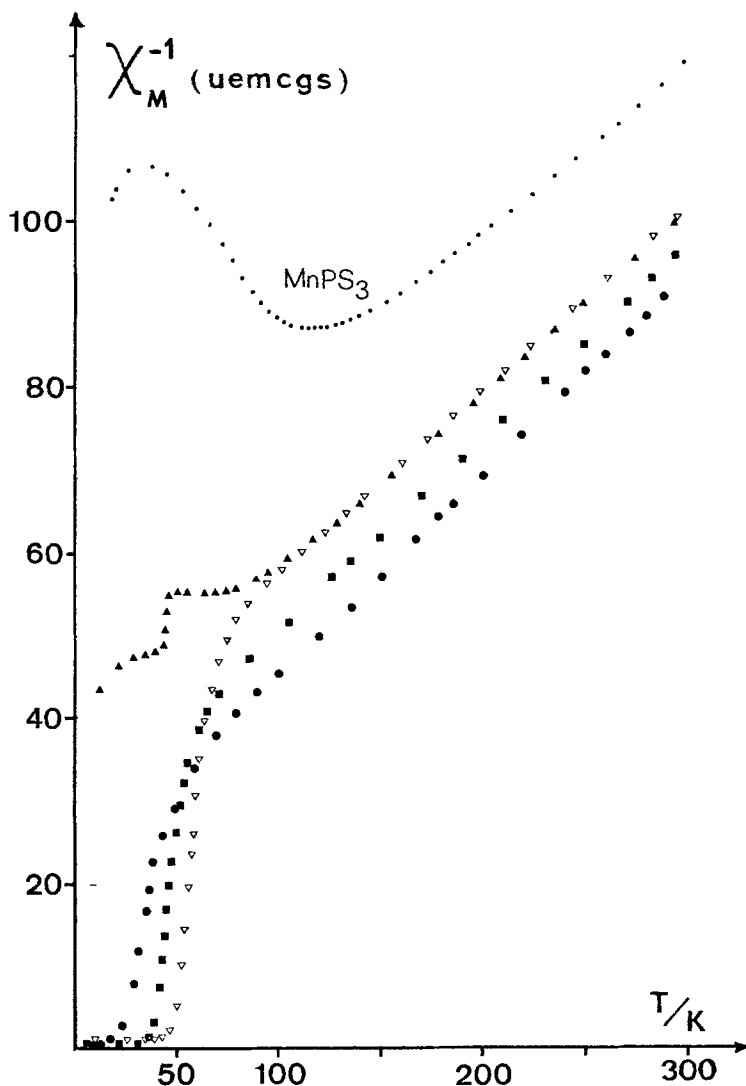


Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility of (·) MnPS_3 and of several intercalates $\text{Mn}_{1-x}\text{PS}_3\text{G}_{2x}(\text{H}_2\text{O})_y$. (\blacktriangle) $G = \text{methyltris(octyl)N}^+$ (I); (∇) $G = n(\text{octyl)N}^+$ (II); (\bullet) $G = \text{K}^+$ (III); (\blacksquare) $G = \text{CoCp}_2^+$ (IV).

and the magnetic transition of the material, an EXAFS study of the methyltris(octyl)-ammonium intercalate of MnPS_3 was undertaken, with the hope that the weaker magnetization of the low temperature form of this material would correspond to a local disorder intermediate between that of MnPS_3 and of the cobalticinium intercalate. In addition, two other intercalates were also studied to test the consistency of the previous results [7].

2. Experimental Section and Data Analysis

The synthesis of MnPS_3 from the pure elements was carried out by the procedure already described in [1]. Interaction of K^+ , n -octyl NH_3^+ and methyltris(octyl) N^+ cations was

achieved, as described in [3], by contact of MnPS_3 with an aqueous solution of the guest cation.

Intercalation was ascertained by X-ray powder patterns and elemental analysis. Results were in full agreement with data already published [3]. The materials obtained remain quite well ordered, as they exhibit sharp hkl reflexions. Indexation of representative intercalates are given in Table I. The EXAFS spectra of the intercalates $\text{Mn}_{0.89}\text{PS}_3(\text{methyltris}(\text{octyl})\text{-N}^+)_{0.22}0.3\text{H}_2\text{O}$, $\text{Mn}_{0.89}\text{PS}_3(n\text{-octylNH}_3^+)_{0.22}0.3\text{H}_2\text{O}$ and $\text{Mn}_{0.89}\text{PS}_3(\text{K}^+)_{0.4}(\text{H}_2\text{O})$ (noted **I**, **II** and **III**, respectively) were recorded at room temperature under the same conditions as those already described in [7] for MnPS_3 and the cobalticinium intercalate (noted **IV**). Measurements were carried out at LURE, the French synchrotron radiation laboratory, on the EXAFS I [9] and EXAFS II [10] spectrometers.

Data analysis of EXAFS spectra followed the standard procedure [11] including transformation of the X-ray absorption spectra of the EXAFS spectra $K^*\chi(k)$, Fourier transformation to obtain the radial distribution functions $F(R)$ and least-squares data fitting of the filtered $k^*\chi(k)$ to the standard plane wave EXAFS formula [11a] with theoretical amplitudes and phase-shift functions [12]. As in [7], the fitting was made in two steps in order to include the first two peaks of the radial distribution (Figure 2).

3. Results and Discussion

The modulus of the radial distribution functions of Intercalates **I**, **II** and **III** are presented in Figure 2. Previous results obtained for MnPS_3 and the cobalticinium intercalate (**IV**) are also recalled in Figure 2 for clarity.

The two main peaks on the curve for MnPS_3 correspond to the Mn—S distances (peak *A*) and to the unresolved Mn—P and Mn—Mn distances (peak *B*) [7]. Two main factors are obvious from Figure 2: firstly, the amplitude of the second peak (*B*) of Intercalates **II** and **III** is dramatically reduced with respect to that of pure MnPS_3 , as already observed for Intercalate **IV**. In contrast, the decrease of peak *B* is much less pronounced in the case of Intercalate **I**.

Beside these qualitative facts, quantitative structural data have been obtained for each material, in particular the distances between manganese and its neighbours and also the mean deviation value σ in these distances. Figures 3a–c illustrate the good agreement of the three-shell fits with experimental data for MnPS_3 and Intercalates **I** and **II**. Detailed results of the fits are gathered in Table II.

The parameter σ represents the width of the distribution of distances in a shell. Its variation for the second shell is characteristic of the increase of the local disorder around Mn(**II**) cations. As in [7], this increase of local disorder can be evaluated by the expression $\Delta\sigma = (\sigma^2(\text{intercalate}) - \sigma^2(\text{MnPS}_3))^{0.5}$. These values are listed in Table III.

The important result of this study is that the disorder effect induced by intercalation is less important in the (methyltris(octyl)N⁺) compound than in the three other intercalates. This observation is clearly shown qualitatively in Figures 2 and 3 and also quantitatively in Table III.

If we now return to the magnetic properties of these compounds (Figure 1), the striking fact is that the amplitude of the jump of the susceptibility around the transition temperature is correlated to the amplitude of the local disorder around the manganese ions. The transition between a paramagnetic and a weak ferromagnetic phase in the intercalates is, therefore, clearly correlated to the structural disorder induced in the host layers by the guest cations. This fact, which could have been fortuitous on the basis of the results of [7] alone, is now

Table I

(a) Indexation of $\text{Mn}_{0.83}\text{PS}_3(\text{CoCP}_2)_{0.37}\text{H}_2\text{O}$ at 20°C. Cell dimensions: $a = 6.117 \text{ \AA}$, $b = 10.59 \text{ \AA}$, $c = 12.53 \text{ \AA}$, $\beta = 109.0$.

Spacing/Å			
Obs.	Calcd.	<i>hkl</i>	Intensity
11.85	11.847	001	m
5.926	5.925	002	m
3.952	3.950	003	w
3.014	3.015	130	s
2.965	2.962	004	w
2.892	2.892	200	w
2.809	2.809	131	vs
2.519	2.519	132	s
2.317	2.318	202	m
2.221	2.221	133	w
1.765	1.766	060	s
1.745	1.746	061	s
1.692	1.692	330	m
1.612	1.612	331	w

(b) Indexation of $\text{Mn}_{0.89}\text{PS}_3(\text{Metris}(\text{Octyl})\text{N})_{0.22}0.3\text{H}_2\text{O}$ at 20°C. Cell dimensions: $a = 6.10 \text{ \AA}$, $b = 10.55 \text{ \AA}$, $c = 19.51 \text{ \AA}$, $\beta = 109.0$.

Spacing/Å			
Obs.	Calcd.	<i>hkl</i>	Intensity
18.47	18.45	001	s
9.23	9.22	002	s
6.161	6.156	003	m
4.610	4.612	004	w
3.003	3.008	130	s
	3.002	201	s
2.885	2.888	131	s
	2.884	200	s
2.714	2.718	201	m
2.529	2.530	202	m
1.759	1.758	060	m
1.748	1.750	061	m

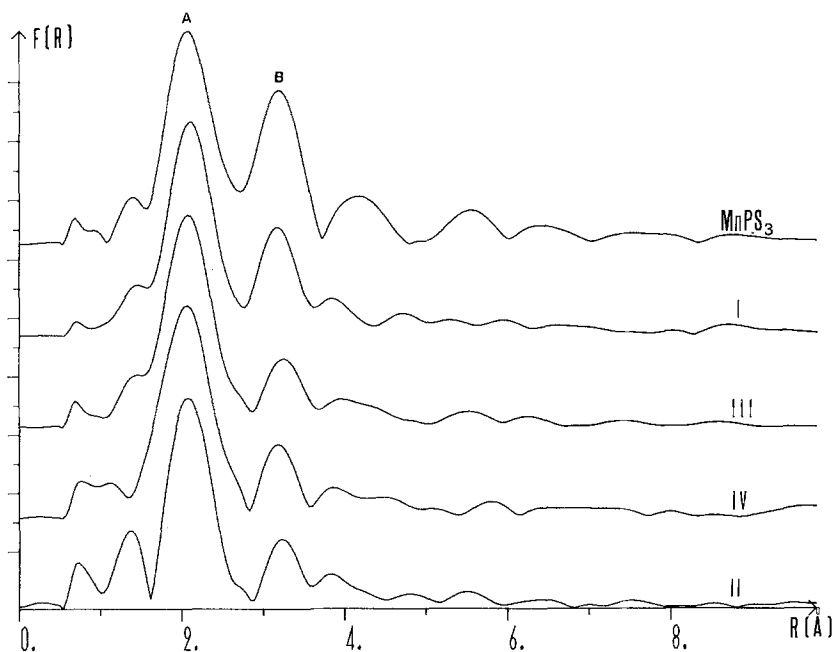


Fig. 2. Modulus of the EXAFS Radial Distribution Functions $|F(R)|$ around Mn in MnPS_3 and the four intercalates. (I) $\text{Mn}_{0.89}\text{PS}_3(\text{methyltris}(\text{octyl})\text{N}^+)_{0.22}$; (II) $\text{Mn}_{0.89}\text{PS}_3(n\text{-octylNH}_3^+)_{0.22}$; (III) $\text{Mn}_{1.80}\text{PS}_3(\text{K}^+)_{0.40}$; (IV) $\text{Mn}_{0.83}\text{PS}_3(\text{Co}(\text{C}_5\text{H}_5)_2^+)_{0.34}$. Distances on this graph do not correspond to reality, as the curves are not corrected for phase shifts.

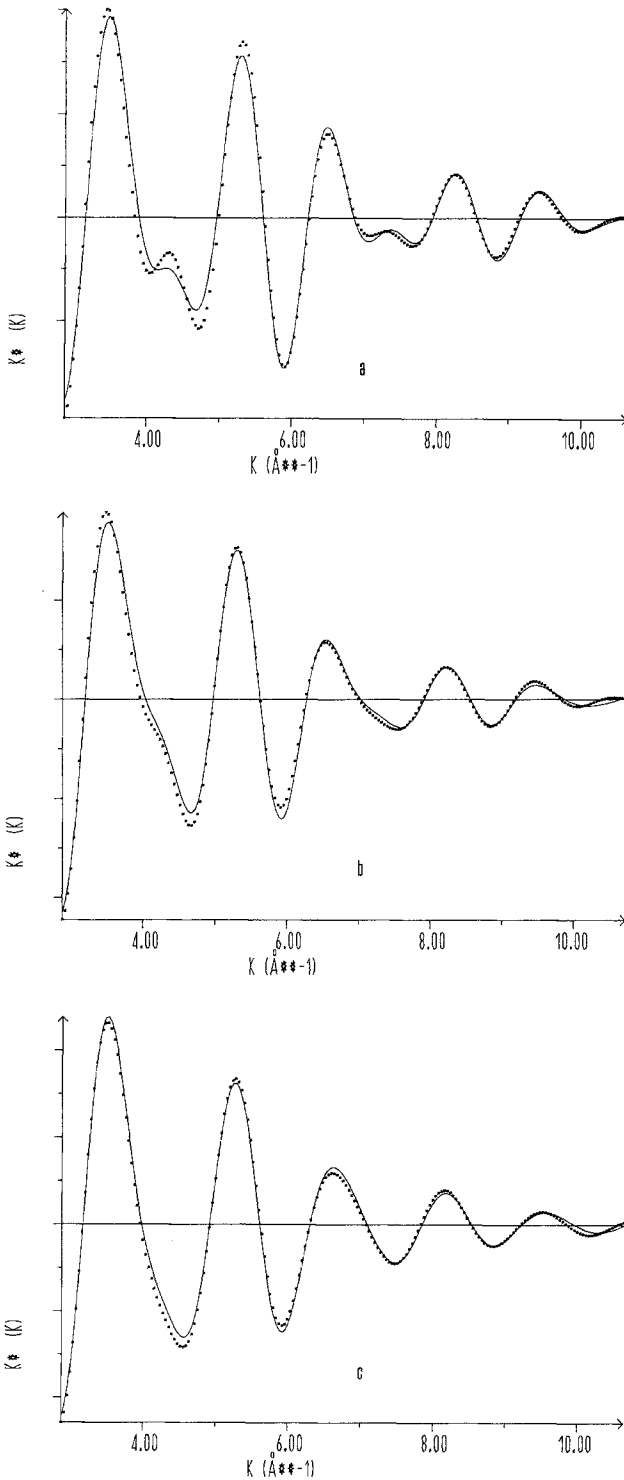


Fig. 3. Least squares fits (full) line of the filtered EXAFS spectra. (a) MnPS_3 ; (b) $\text{Mn}_{0.89}\text{PS}_3(\text{methyltris(octyl)N}^+)_{0.22}$; (c) $\text{Mn}_{0.89}\text{PS}_3(\text{n-octylNH}_3^+)_{0.22}$.

Table II. Structural parameters extracted from EXAFS spectra with the fitting procedure described in ref. [7]. The numbers of neighbours N are fixed. The errors estimated by MINUIT, the fitting program, are 0.02 Å for $R_{\text{Mn-S}}$, 0.04 Å for $R_{\text{Mn-P}}$ and $R_{\text{Mn-Mn}}$, 0.01 Å for σ

	N	$\sigma/\text{Å}$	$R/\text{Å}$			
Mn-S	6	0.08	2.58	MnPS ₃		
Mn-Mn	3	0.08	3.50			
Mn-P	6	0.08	3.66			
Mn-S	6	0.10	2.58	Mn _{0.89} PS ₃ (methyltris(octyl)N) _{0.22} (H ₂ O) _{0.3}	(I)	
Mn-Mn	3	0.11	3.49			
Mn-P	6	0.11	3.70			
Mn-S	6	0.10	2.57	Mn _{0.89} PS ₃ (<i>n</i> -octylNH ₃) _{0.22} (H ₂ O) _{0.3}	(II)	
Mn-Mn	3	0.15	3.50			
Mn-P	6	0.15	3.70			
Mn-S	6	0.10	2.57	Mn _{0.80} PS ₃ (K) _{0.40} (H ₂ O) _{1.0}	(III)	
Mn-Mn	3	0.15	3.52			
Mn-P	6	0.15	3.73			
Mn-S	6	0.10	2.57	Mn _{0.83} PS ₃ (Co(C ₅ H ₅) ₂) _{0.34} (H ₂ O) _{0.3}	(IV)	
Mn-Mn	3	0.16	3.51			
Mn-P	6	0.16	3.71			

Table III. Selected data for Intercalates I, II, III and IV: Values of $\Delta\sigma$ which quantize the increase of disorder due to intercalation. Magnetic susceptibility values under the weak ferromagnetic transition, measured at ~ 1000 G. Composition parameter x of the intercalates Mn_{1-x}PS₃G_{2x}(H₂O)_y. Interlayer spacing of the intercalates (6.5 Å for MnPS₃). ($d = c \sin \beta$).

Intercalate	$\Delta\sigma/\text{Å}$	$\chi_{\mu\text{emegs}}^{-1} T < T_c$	$x (\pm 0.01)$	$d/\text{Å}$
(I)	0.07	50	0.11	18.47
(II)	0.13	~ 0.8	0.11	10.38
(III)	0.13	~ 0.8	0.20	9.50
(IV)	0.14	~ 0.5	0.17	11.85

firmly established. Another interesting point is that the rate of intralayer vacancies x in the intercalates is not a crucial factor for the magnetic transition problem, at least in the range studied, since the variation of x is not correlated to $\Delta\sigma$ or to the magnetic behaviour (Table III). For example, the two compounds Mn_{0.89}PS₃(*n*-octylHN₃⁺)_{0.22} and Mn_{0.80}PS₃(K⁺)_{0.40} lie at the limits of the studied range of x values but are quite similar from both the magnetic and structural point of view. However, x has a considerable influence on the transition temperature: it is obvious from Figure 1 that the higher the manganese vacancy rate, the lower the transition temperature.

The next question arising is why the methyltris(octyl)ammonium cation induces less disorder in the layers than cobalticinium, for instance. An important factor could be the charge/volume ratio of the guest species. Table III displays the values of the interlayer spacings of the various intercalates and it is obvious that the methyltris(octyl) ammonium cation is much more bulky than the others. The electric field around this cation is, therefore, much lower, hence the perturbation acting on the P⁴⁺—S²⁻ dipoles of the MnPS₃ layers.

In conclusion, the present results support the idea that intercalation induces a magnetic transition because it renders neighbouring manganese sites structurally different from each other, whereas they are quasi-equivalent in pure MnPS₃. Spin canting and weak ferromagnetism can then occur through classical mechanisms, antisymmetric exchange and single-ion anisotropy energy, as for instance in the β form of manganese sulfide [13].

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