High-T_c Magnets in a Series of Substituted Pyridinium−FePS$_3$ Layered Intercalates

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A series of new FePS$_3$ layered intercalation compounds having the general formula Fe$_{1-x}$PS$_3$G$_{2x}$ (where G stands for a monocation) has been prepared by cation exchange with several pyridinium derivatives. The occurrence of intralayer Fe^{2+} vacancies is evidenced by ^{57}Fe Mössbauer spectroscopy. The magnetic properties of these well-crystallized intercalates are shown to depend dramatically on the nature of the guest species. Some intercalates remain antiferromagnets as in pristine FePS$_3$, but those with pyridinium, *N*-methylpyridinium, and methylviologen as the guest species acquire a spontaneous magnetization below a critical temperature which can be as high as 88 K. The magnetization of the methylviologen intercalate is particularly strong. The magnetization in all cases displays a strong remanence due to single ion anisotropy of the Fe^{2+} ions and to the Ising character of the magnetic interaction.

Introduction

In the past 10 years, considerable effort has been devoted to the synthesis of molecular based materials exhibiting ferro- or ferrimagnetism.[1−4] Following the pioneering work on the ferromagnetic decamethylferricenium tetracyanoethylene charge-transfer compound,[5] a great many organometallic and organic compounds of various dimensionalities have been synthesized. Although most compounds usually have extremely low Curie temperatures, a dramatic step toward high-T_c magnets has been recently achieved with the synthesis of the V(TCNE)$_x$·y(CH$_2$Cl$_2$) room-temperature molecular based magnet[6] and of three-dimensional chromocyanides.[7,8]

Though intercalation reactions appear quite far from molecular chemistry, we believe that they provide a strategy which can bring original contributions to the area of magnetic materials. For example, our group has recently synthesized an MnPS$_3$ intercalation compound containing a hyperpolarizable asymmetric chromophore, which is a new multiproperty material associating spontaneous magnetization and nonlinear optical properties.[9,10] This article extends previous work on FePS$_3$ and describes a series of new intercalates prepared by ion exchange, which exhibit unusual magnetic properties in the temperature range 77−90 K.

Transition-metal hexathiohypodiphosphates MPS$_3$, where M stands for a metal in the (+II) oxidation state, form a family of lamellar semiconductors[11,12] or Mott insulators[13] (for a review see refs 14−16). Several MPS$_3$ compounds display a unique reactivity, as they are able to exchange a fraction of their intralayer M^{2+} cations with a great variety of cationic species which occupy the interlayer galleries.[17,18]

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The magnetic properties of the MPS$_3$ compounds have been extensively studied.[10,19–24] The pristine materials order antiferromagnetically below a relatively high critical temperature T_c (78 K for M = Mn, ≈117 K for M = Fe) and the magnetic structures have been determined.[25–27] In the early 1980s, one of us showed that intercalating MnPS$_3$ resulted in a dramatic modification of the magnetic properties,[28,29] to such an extent that the intercalate exhibited spontaneous magnetization below a critical temperature of around 40 K. The role played by intercalation has been only recently understood, the key feature being that the intralayer metallic vacancies created by the ion-exchange intercalation process are ordered, an effect that destroys the balance between the antiparallel spins.[30–32] Similar phenomena have also been observed by Joy et al.[33]

Ion-exchange intercalation in FePS$_3$ has been much less developed. This compound is interesting for two reasons: the magnetic interactions between Fe^{2+} ions are stronger than those between Mn^{2+} ions, and the electronic structure of the Fe^{2+} ions is strongly anisotropic, which causes the magnetic behavior of FePS$_3$ to be of an Ising type.[22,23] We have shown in 1990 that an FePS$_3$ intercalate of pyridine and pyridinium acquired spontaneous magnetization below 92 K.[34] More recently, Joy et al. prepared a series of amine–FePS$_3$ intercalates which behave as antiferromagnets.[35] Whereas these authors claim that Fe^{2+} ions are released along with insertion, Bhowmick et al. recently published a study of the methyl- and ethylamine intercalates of FePS$_3$, in which they concluded that reduced sites were created due to electron transfer accompanying intercalation.[36]

As it is well-known that the intercalation chemistry of amines into layered compounds is a complex matter, depending in particular on the water content of the employed amines,[14] we have attempted to achieve intercalation in FePS$_3$ by pure ion exchange.

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Experimental Section

FePS$_3$ in the form of powder and monocrystalline thin platelets was synthesized from the elements as reported earlier.[11,12]

Pyridinium chloride and methylviologen dichloride were purchased and used without further purification. 4-Picolinium and 3,5-lutidinium chlorides were prepared by treating the parent amines in ethylic ether with a stream of gaseous hydrogen chloride, filtering off the white precipitate and washing it with ether. *N*-methylpyridinium and *N*-3,5-trimethylpyridinium iodides were prepared by refluxing the parent amines with a stoichiometric amount of iodomethane in dichloromethane for 3 h. The precipitated salts were filtered, washed with dichloromethane, and checked by ^{1}H NMR.

Synthesis of the FePS$_3$ Intercalates. *Pyridinium (pyH)*: In a typical experiment, 150 mg of FePS$_3$ powder was treated with a concentrated solution of 3 g of pyH$^+$Cl$^-$ in 2 mL ethanol for 24 h at 60 °C under nitrogen. The powder was then washed with ethanol, dried, and handled in air. The same procedure was employed to intercalate FePS$_3$ monocrystalline platelets.

4-Picolinium and 3,5-lutidinium: FePS$_3$ powder (150 mg) was introduced into an ampule containing a solution of 500 mg of picolinium (or lutidinium) chloride in 3 mL of ethanol. The ampule was then sealed under vacuum and heated for 2 days at 120 °C. The same procedure was also employed to insert *N*-3,5-trimethylpyridinium, using a 1:1 water–ethanol mixture as the solvent.

Methylviologen: FePS$_3$ powder (150 mg) was treated with a solution of 500 mg of methylviologen dichloride in 3 mL of methanol (instead of ethanol which partially reduces methylviologen to its blue monocation). The mixture was heated at 60 °C over 6 h in a Schlenk tube under argon.

N-Methylpyridinium: As direct ion-exchange failed, even at 140 °C, intercalation of *N*-methylpyridinium was carried out in two steps: (i) preinsertion of tetraethylammonium ions as previously described;[18] (ii) treatment of the obtained preintercalate (150 mg) with 500 mg of *N*-methylpyridinium iodide in 5 mL of ethanol at 60 °C over 3 days.

Magnetic Measurements. Most magnetic measurements have been carried out on powdered samples of typical weight 15 mg using a Metronique Ingenierie SQUID magnetometer. Single crystals of the pyridinium intercalate (≈5 mg) have been studied using a homemade sample holder of plexiglass which allows orientation of platelets either parallel or perpendicular to the magnetic field. Magnetization was measured as a function of temperature (usually between 120 and 5 K) and as a function of an applied magnetic field. The magnetic susceptibility of the pyridinium intercalate was also measured between 20 K and room temperature with a Faraday balance equipped with an Oxford Instrument cryostat.

Mössbauer Spectrometry Experiments. The Mössbauer spectra were obtained on a constant-acceleration spectrometer with a 25-mCi source of ^{57}Co in a rhodium matrix. The calibration was made with a metallic iron foil at room temperature. The experimental line width was typically 0.22 mm s^{-1}. The absorber was a sample of ≈100 mg of each FePS$_3$ intercalate synthesized in this work, in the form of polycrystalline powder, enclosed in a capsule ≈2 cm in diameter. All measurements were made at room temperature. The typical counting time was ca. 6 h. A least-squares computer program was used to fit the Mössbauer parameters.

Results

The intercalates were characterized by powder X-ray diffraction using a Siemens diffractometer. Complete intercalation was ascertained by the disappearance of the 00*l* reflection of pure FePS$_3$. Due to preferential orientation, the samples display only sharp 00*l* reflections which allow straightforward calculation of the basal spacing. Results are gathered in Table 1. All values lie in the range 9.7–9.9 Å (6.42 Å for pure FePS$_3$). The increase of the basal spacing upon inter-

Table 1. Analytical Data and Interlayer Spacing of the FePS$_3$ Intercalates

intercalate	spacing (Å)	analytical data (wt %)					
		Fe	P	S	C	N	H
Fe$_{0.88}$P$_{0.99}$S$_3$(pyridinium)$_{0.24}$	9.88	22.2	14.0	43.7	7.9	1.47	1.26
Fe$_{0.83}$P$_{0.99}$S$_3$(methylviologen)$_{0.14}$	9.72	21.7	14.6	43.9	11.0	1.80	1.38
Fe$_{0.89}$P$_{0.95}$S$_3$(4-picolinium)$_{0.20}$	9.88	24.7	14.4	47.0	8.06	1.25	0.89
Fe$_{0.89}$P$_{0.95}$S$_3$(3,5-lutidinium)$_{0.25}$	9.93	22.7	14.7	46.15	10.4	1.60	1.25
Fe$_{0.91}$P$_{0.99}$S$_3$(N-methylpyridinium)$_{0.22}$	9.86	23.4	14.1	44.35	7.54	1.40	1.39
Fe$_{0.88}$P$_{0.95}$S$_3$(N,3,5-trimethylpyridinium)$_{0.24}$	9.93	25.5	14.2	46.2	9.85	1.50	1.04

Table 2. Indexation of the X-ray Diffraction Pattern of the Fe$_{0.83}$PS$_3$(methylviologen)$_{0.14}$ Intercalate
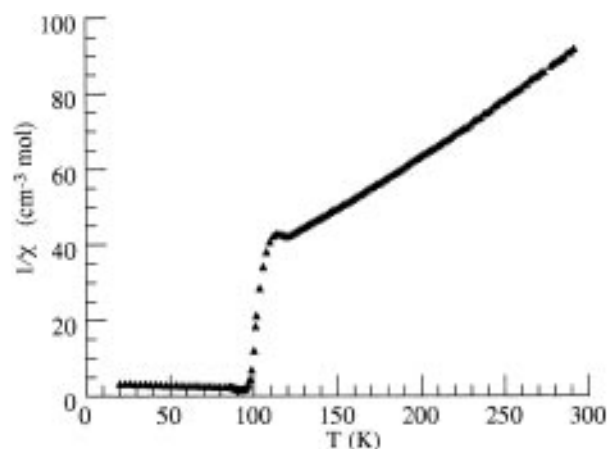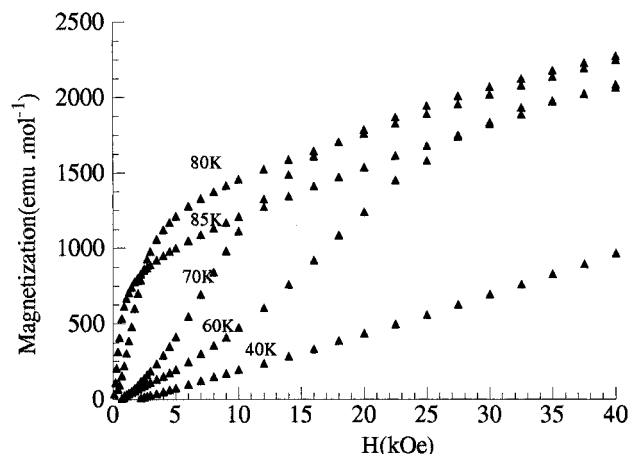
cell dimensions	
$a = 5.983$ Å	$c = 10.498$ Å
$b = 10.374$ Å	$\beta = 112.29°$

spacing, Å			
obsd	calcd	*h k l*	intens
9.725	9.714	0 0 1	s
5.180	5.187	0 2 0	w
4.860	4.857	0 0 2	s
3.238	3.238	0 0 3	s
2.933	2.933	1 3 0	s
2.768	2.768	2 0 0	m
2.663	2.663	1 3 1	s
2.427	2.428	0 0 4	w
2.313	2.313	1 3 2	m
2.092	2.088	2 0 2	m
1.729	1.729	0 6 0	s
1.702	1.702	0 6 1	s
1.619	1.619	0 0 6	w

Figure 1. Temperature dependence of the reciprocal magnetic susceptibility of the Fe$_{0.88}$P$_{0.99}$S$_3$(pyH)$_{0.24}$ intercalate (per mole of Fe).

Figure 2. Dependence of the magnetization (per mole of Fe) of the Fe$_{0.88}$P$_{0.99}$S$_3$(pyH)$_{0.24}$ intercalate versus applied magnetic field at various temperatures.

calation is therefore about 3.4 Å, and comparison with the van der Waals dimensions of the guest species strongly suggests that the latter lie with their average molecular plane parallel to the layers. X-ray diffraction photographs of the methylviologen and pyridinium intercalates were also obtained using a Seeman Bohlin camera. The compounds exhibit sharp *hkl* reflections which can be indexed using a monoclinic unit cell derived from that of FePS$_3$, expanded in the *c* direction. A detailed indexation is provided in Table 2 for the methylviologen intercalate. It is worth emphasizing that no superlattice reflections were observed, in contrast to the case of certain MnPS$_3$ intercalates.[30,31]

Elemental analyses of the intercalates (Table 1) suggest a formula where the uptake of positive charges is systematically accompanied by a loss of Fe^{2+} ions. Several analyses carried out on different batches show that the precision on all stoichiometry figures is about ± 0.02. In the case of lutidinium, trimethylammonium, and 4-picolinium, a small loss of phosphorus seems to be significant.

The infrared spectra of the intercalates all display two strong bands at 605 and 555 cm^{-1} arising from the splitting of the the ν(PS$_3$) asymetric stretching band which occurs at 570 cm^{-1} in pure FePS$_3$. In addition, the spectra show a number of bands assigned to the inserted organic cations.

Magnetic Properties of the Intercalates. *Pyridinium intercalate:* The temperature dependence of the magnetic susceptibility of the Fe$_{0.88}$P$_{0.99}$S$_3$(pyridinium)$_{0.24}$-(solv)$_y$ intercalate is shown in Figure 1. The susceptibility undergoes a steep increase on cooling between 100 and 92 K and remains nearly constant below that temperature. However, measurement of the field dependence of the magnetization at various temperatures below T_c indicate a quite complex behavior (Figure 2). When the temperature is close to T_c, the magnetization

increases rapidly for low values of the applied field, then reaches a saturation regime with a constant slope. As the temperature is lowered, increasing values of the applied field are required to reveal the magnetization.

The magnetization (M) of the pyridinium intercalate (powder) has also been studied in very low and in zero fields. Results are shown in Figure 3. The field-cooled magnetization (FCM) curve obtained by cooling down in a field of 10 Oe shows a rapid increase of M below 90 K. Switching off the field at 40 K and warming show that the remnant magnetization is very strong up to T_c. The zero-field-cooled magnetization (ZFCM), obtained upon warming a sample cooled to 40 K in zero field, remains equal to zero until the temperature approaches T_c.

Anisotropy measurements were carried out at 80 K on single platelets oriented parallel or perpendicular to the external magnetic field. The field dependence of the
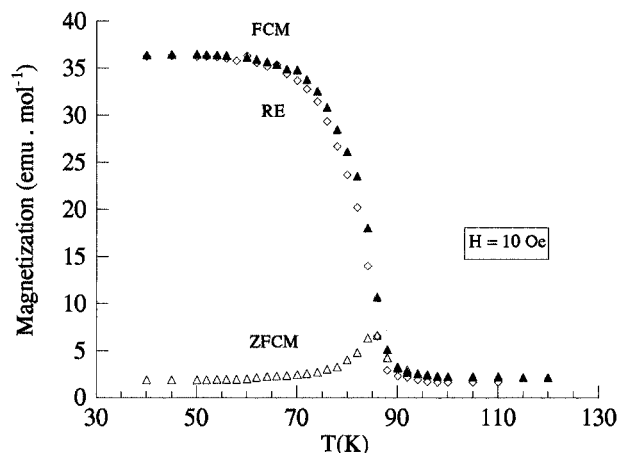
Figure 3. Temperature dependence of the magnetization of $Fe_{0.88}P_{0.99}S_3(pyH)_{0.24}$ within a field of 10 Oe. The field-cooled magnetization (FCM) was measured upon cooling within the field. The zero-field-cooled magnetization (ZFCM) was measured after cooling in the zero field and then warming within the field. The remnant magnetization (RE) was measured after cooling within the field and then warming in zero field.
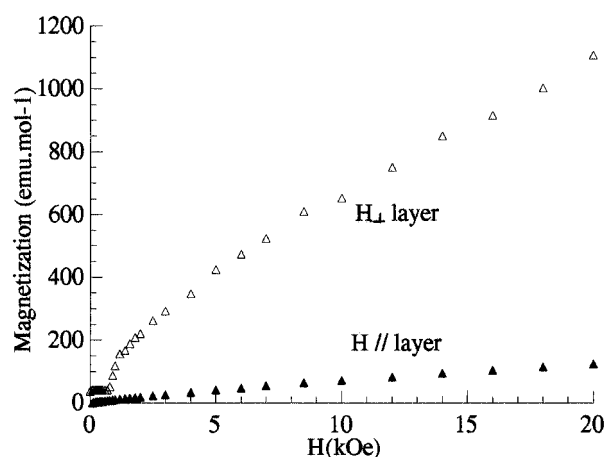

Figure 5. Temperature dependence of the magnetization of $Fe_{0.83}P_{0.99}S_3(MV)_{0.14}$ within a field of 10 Oe. The field-cooled magnetization (FCM) was measured upon cooling within the field. The zero-field-cooled magnetization (ZFCM) was measured after cooling in the zero field and then warming within the field. The remnant magnetization (RE) was measured after cooling within the field and then warming in zero field.

Figure 4. Dependence of the magnetization at 80 K of a single platelet of the $Fe_{0.88}P_{0.99}S_3(pyH)_{0.24}$ intercalate versus magnetic field applied perpendicular ($H_\perp$) or parallel (||) to the platelet at 80 K.

Figure 6. Dependence of the magnetization (per mole of Fe) of the $Fe_{0.83}P_{0.99}S_3(MV)_{0.14}$ intercalate versus applied magnetic field at 40 and 70 K.

magnetization, shown in Figure 4 for both orientations, demonstrates considerable anisotropy. The magnetization is very weak when the slabs are parallel to the applied magnetic field, even for strong values. In contrast, a rapid increase of M occurs around 800 Oe in the perpendicular orientation. These results suggest that the axis of easy magnetization is nearly perpendicular to the slabs.

Methylviologen intercalate: The temperature dependence of the magnetization of the powdered methylviologen intercalate has been studied in the same manner as the pyridinium one. Results are shown in Figure 5. The profile of the FCM, RM, and ZFCM curves is very similar to the profile given by the pyridinium intercalate. The critical temperature of the methylviologen intercalate is only 77 K but the magnitude of the field cooled and remnant magnetization appears stronger.

The field dependence of the magnetization below T_c was studied at both 70 and 40 K. Results are shown in Figure 6. With respect to the pyridinium case, the $M(H)$ curves reach a true plateau and the saturation magnetization is stronger than for the pyridinium intercalate.
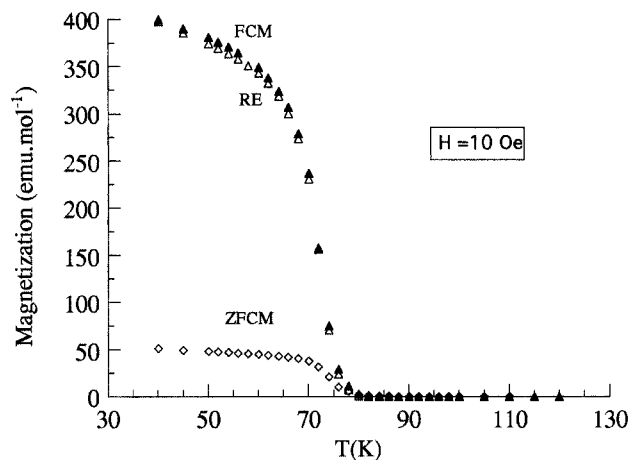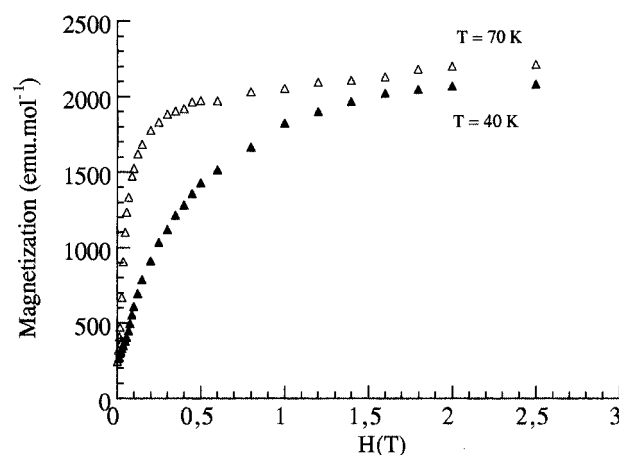
A value of 2000 emu/mol of Fe has been measured, which represents about 10% of the value if all the Fe^{2+} spins were parallel. The $M(H)$ curves are less sluggish than those given by the pyridinium material, but nevertheless at 40 K the plateau is not reached until an external field of 1 T is applied.

Hysteresis of the methylviologen intercalate was studied at 70 K by cycling the applied field between +5000 and −5000 G. The intercalate exhibits a hysteresis loop, with a width of about 200 Oe (Figure 7).

N-Methylpyridinium intercalate: The temperature dependence of the magnetization of the N-methylpyridinium intercalate in a field of 30 Oe (FCM, RM, and ZFCM) is shown in Figure 8. A magnetic transition occurs around 82 K, but the values of the magnetization are smaller than for the above two intercalates. The field dependence of the magnetization has been studied at 70 K (Figure 9). The $M(H)$ curve reaches a plateau and a saturation magnetization of about 700 emu/mol of Fe.

4-Picolinium, 3,5-lutidinium, and tetraethylammonium intercalates. The tetraethylammonium intercalate used as an intermediate in the synthesis of the N-methylpyridinium intercalate has been studied as
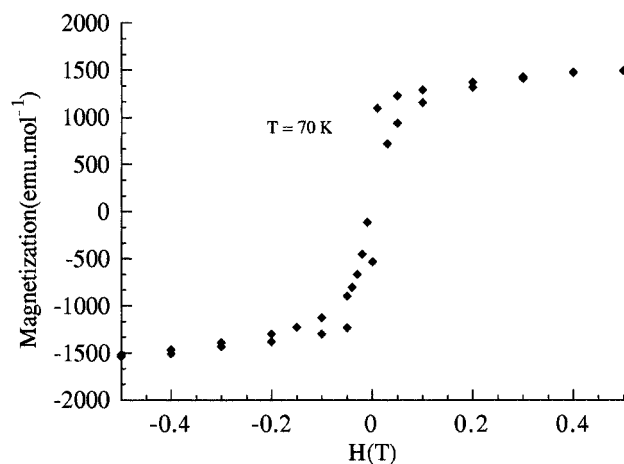
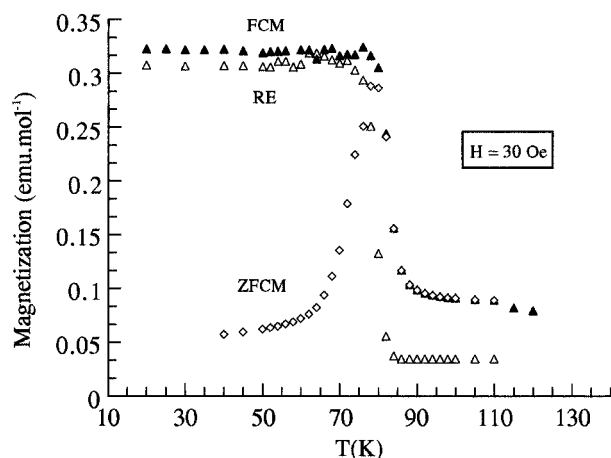**Figure 7.** Hysteresis loop of the $Fe_{0.83}P_{0.99}S_3(MV)_{0.14}$ intercalate at 70 K.

Figure 8. Temperature dependence of the magnetization of $Fe_{0.91}P_{0.99}S_3(N\text{-MepyH})_{0.22}$ within a field of 30 Oe. The field-cooled magnetization (FCM) was measured upon cooling within the field. The zero-field-cooled magnetization (ZFCM) was measured after cooling in the zero field and then warming within the field. The remnant magnetization (RE) was measured after cooling within the field and then warming in zero field.
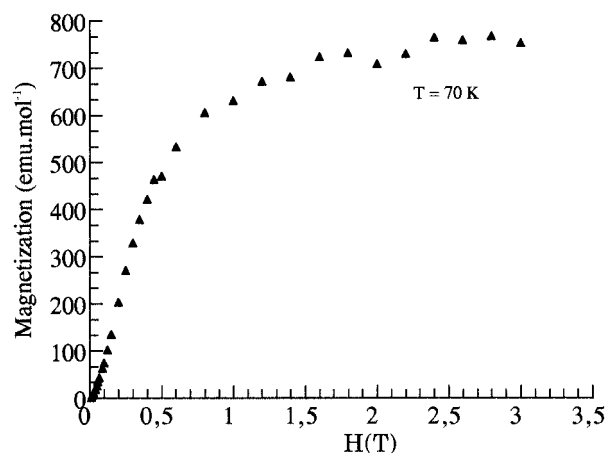

Figure 9. Dependence of the magnetization of the $Fe_{0.91}P_{0.99}S_3$-(N-MepyH)$_{0.22}$ intercalate versus applied magnetic field at 70 K.

well as the 4-picolinium and 3,5-lutidinium intercalates. In the three cases, however, no spontaneous magnetization has been detected. These intercalates behave as antiferromagnets. The FCM measured upon cooling the 4-picolinium intercalate in a field of 30 Oe is shown in
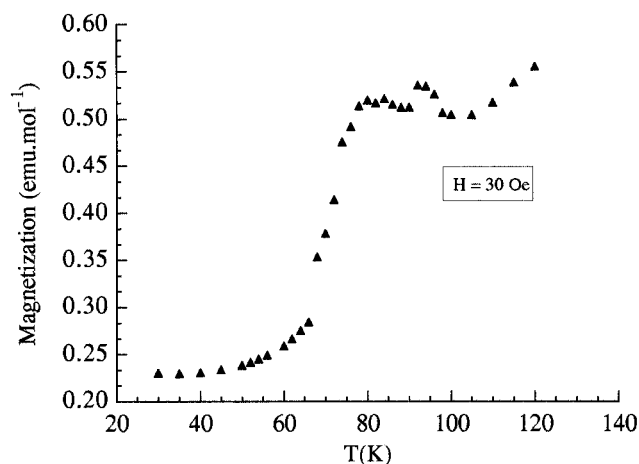

Figure 10. Temperature dependence of the magnetization of $Fe_{0.89}P_{0.95}S_3(4\text{-picolinium})_{0.20}$ within a field of 30 Oe. The field-cooled magnetization (FCM) was measured upon cooling.

Figure 10 as a representative example of the behavior of these three compounds.

Mössbauer Spectra. The Mössbauer spectrum of $FePS_3$, shown in Figure 11a, consists of a single doublet characterized by an isomer shift (IS) of 0.868 mm/s and a quadrupole splitting (QS) of 1.522 mm/s, in agreement with previously published data.[37] These values correspond to Fe(II) ions occupying equivalent sites. The spectra of the intercalates at room temperature are shown in Figure 11b−e. They all exhibit two doublets, labeled A and B. The relative intensity of these doublets strongly depends on the nature of the intercalate, but their IS and QS (Table 3) remain almost constant throughout the series. The IS of both A and B are very close to the IS observed in pure $FePS_3$, but their QS are very different (typically 1.65 mm/s for A and 2.34 mm/s for B). Therefore, A is almost identical with the doublet of pure $FePS_3$, whereas B reveals another kind of Fe(II) ions in a more distorted site. The relative populations of A and B indicated in Table 3 do not take in account small residues due to a weak signal around $\delta \approx 0.4$ mm/s, which may arise from very small amounts of Fe^{3+} ions. We emphasize the fact that the residue is very low for the methylviologen intercalate, which affords the largest magnetization, whereas the residue is maximum for the 3,5-lutidinium intercalate, which do not exhibit any magnetization. This is a strong argument to support the assertion that the strong magnetization measured for the methylviologen intercalate cannot be attributed to iron oxide impurities.

Interpretation and Discussion

This work shows that $FePS_3$ intercalates can be synthesized by ion exchange and that no assistance is required for the Fe^{2+} ions to leave the host lattice. This avoids the use of a basic medium to carry out the synthesis and allows one to insert organoammonium cations "free of amine".

Mössbauer Spectra and Structure of the Host Lattice. Mössbauer spectroscopy provides evidence for the presence of two different kinds of iron atoms in the intercalated $FePS_3$ host lattice, as was already ob-

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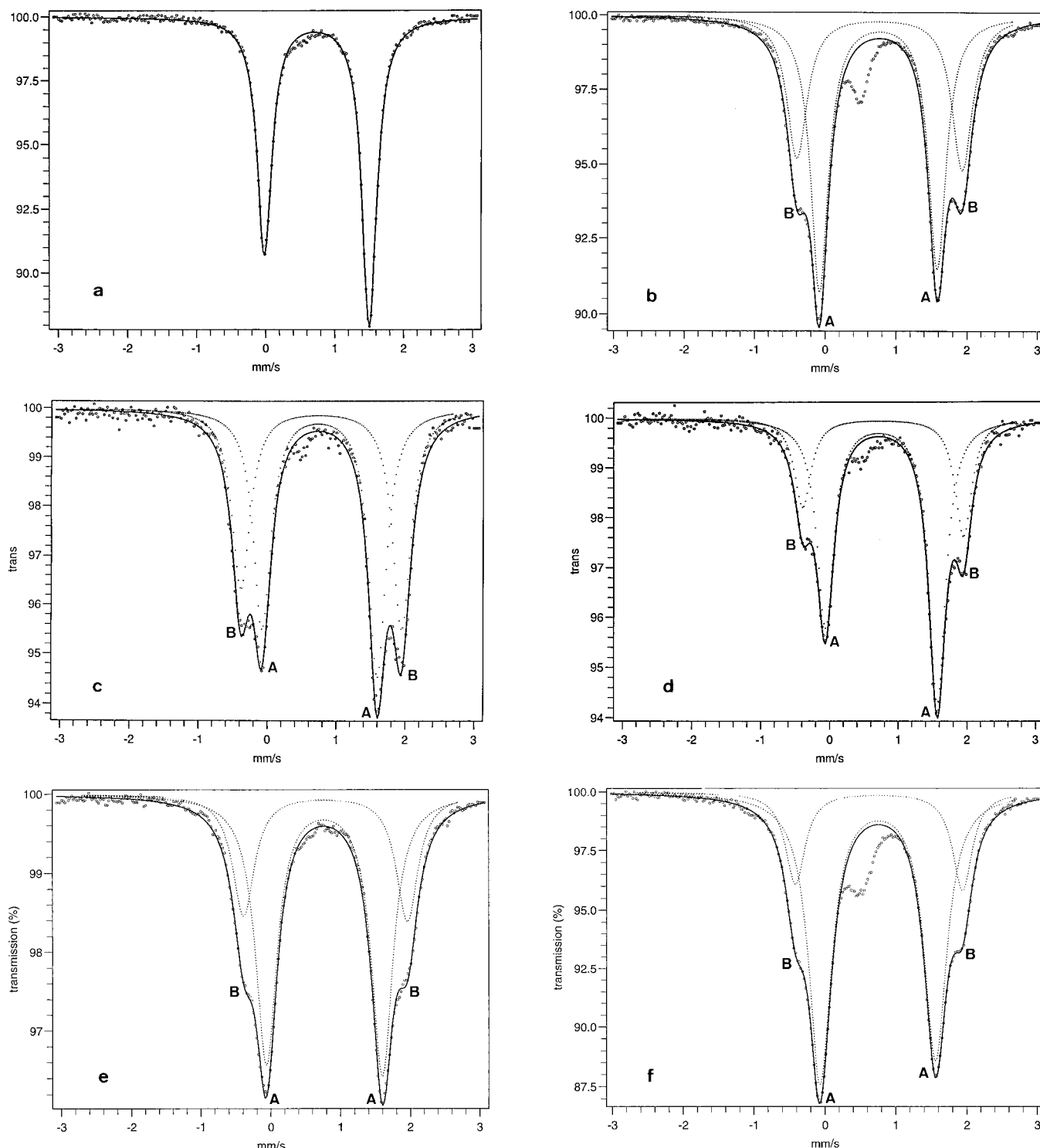
Figure 11. ^{57}Fe Mössbauer spectra of FePS$_3$ (a) and of some intercalates with the following guest species: pyridinium (b); methylviologen (c); 4-picolinium (d); methylpyridinium (e); 3,5-lutidinium (f).

served.[35,38] A relationship can be established between the Mössbauer data and the amount of iron vacancies in the slabs. As mentioned above, the A doublet can be attributed to the Fe^{2+} ions in the same environment as in the pure phase. The following paragraph suggests that the B doublet arises from those Fe^{2+} ions located next to an iron vacancy.
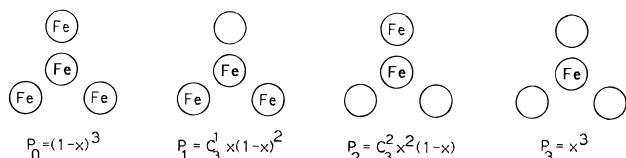
If the Mössbauer data are examined in light of the analytical data of the intercalates, it appears that the ratio of the intensity of B to the intensity of A increases along with the amount of the iron loss, that is along with the amount of intralayer iron vacancies (denoted

by x in the Fe$_{1-x}$PS$_3$ formulation). Therefore the quadrupole splitting of a particular Fe^{2+} ion can be thought of as being modified by the presence of a vacancy next to it, because of symmetry modification. In pure FePS$_3$, each Fe^{2+} ion is surrounded by three other Fe^{2+} ions. In the intercalate, the probability of existence of zero, one, two, or three vacancies (P_0, P_1, P_2, and P_3, respectively) around a particular Fe^{2+} ion can be expressed as a function of the amount x of vacancies by a binomial

(38) Léaustic, A.; Audière, J. P.; Lacroix, P.; Clément, R.; Lomas, Michalowicz, A.; Dunham, W.; Francis, A. H. *Chem. Mater.* **1995**, *7*, 1103.

Table 3. Parameters Extracted from the ^{57}Fe Mössbauer Spectra of Pure FePS$_3$ and of the Ammonium Intercalates

compound	δ (mm/s)	ΔE_q (mm/s)	% of A and B	R (%)
FePS$_3$	0.868	1.522	100 (A)	<1
Fe$_{0.88}$P$_{0.99}$S$_3$(pyridinium)$_{0.24}$	0.876	1.661	61 (A)	4
	0.891	2.230	39 (A)	
Fe$_{0.83}$P$_{0.99}$S$_3$(methylviologen)$_{0.14}$	0.882	1.674	54 (A)	1
	0.905	2.331	46 (B)	
Fe$_{0.91}$P$_{0.99}$S$_3$(N-methylpyridinium)$_{0.22}$	0.888	1.660	68 (A)	<1
	0.908	2.349	32 (B)	
Fe$_{0.89}$P$_{0.95}$S$_3$(4-picolinium)$_{0.20}$	0.877	1.630	70 (A)	5
	0.903	2.337	30 (B)	
Fe$_{0.89}$P$_{0.95}$S$_3$(3,5-lutidinium)$_{0.25}$	0.868	1.729	64 (A)	5.5
	0.885	2.358	36 (B)	
Fe$_{0.88}$P$_{0.95}$S$_3$(N,3,5-trimethylpyridinium)$_{0.24}$	0.887	1.634	70 (A)	2.5
	0.914	2.362	30 (B)	

Scheme 1^a

$$P_0 = (1-x)^3 \qquad P_1 = C_3^1\, x(1-x)^2 \qquad P_2 = C_3^2\, x^2(1-x) \qquad P_3 = x^3$$

^{a} x: probability of a metallic site of the host lattice to be vacant. $1 - x$: Probability of a metallic site to be occupied by an iron atom.

law, provided the vacancies are distributed randomly (Scheme 1). If $x = 0.1$, the expressions given in Scheme 1 lead to values of 0.73, 0.24, 0.01, and 0.001 for P_0, P_1, P_2, and P_3, respectively. These values become 0.51, 0.38, 0.1, and 0.01 for $x = 0.2$.

The largest amount of vacancies experimentally found is $x = 0.17$ in the case of the methylviologen intercalate. Therefore, only P_0 and P_1 will have nonnegligible values. In other words, only two types of Fe^{2+} ions can be efficient absorbers for population reasons: those Fe^{2+} ions surrounded by three other Fe^{2+} ions (responsible for doublet A) and those surrounded by two Fe^{2+} ions plus a vacancy (responsible for doublet B with an increased quadrupole splitting because of local deformation). More quantitatively, we can compare the probability figures to the relative intensity of the A and B doublets. Thus, in the case of the 4-picolinium intercalate ($x = 0.11$), $P_0 = 0.70$ and $P_1 = 0.26$. Integration of the Mössbauer doublets after deconvolution gives A 70% and B 30%. The agreement may seem less good for the methylviologen intercalate ($x = 0.17$), $P_0 = 0.57$ and $P_1 = 0.35$, whereas the relative intensity of the doublets are A 54% and B = 46%. However, doublet B might also contain the small contribution of those Fe^{2+} ions surrounded by two vacancies. If this was the case, $P_1 + P_2 = 0.42$, very close to the experimental data.

Magnetic Properties. The results described in this work are in sharp contrast with those of Joy et al.[35] These authors have recently shown that several amine–FePS$_3$ intercalates behave as antiferromagnets but nevertheless exhibit superparamagnetic properties due to the formation of small particles of Fe$_2$O$_3$ as an impurity. In contrast, we claim that the methylviologen–, pyridinium–, and methylpyridinium–FePS$_3$ intercalates described in this work are genuine magnets. A number of arguments support this assertion.

As pointed out above, syntheses involving ammonium salts take place in slightly acidic media, whereas syntheses carried out with amines[35] take place in basic media, which favors precipitation of iron ions as insoluble hydroxides or oxides. The Mössbauer spectra

of our intercalates actually indicate the presence of a small amount of Fe^{3+} ions, but these ions do not seem to play a significant role in determining the magnetization, as those intercalates that afford the largest magnetization possess the smallest amounts of Fe^{3+} ions. Moreover, several intercalates (picolinium, etc.) do not exhibit any magnetization, despite the presence of a certain amount of Fe^{3+} ions. Other arguments are found in the characteristics of the magnetic properties themselves. The saturation magnetization of the methylviologen intercalate is strong, its remnance is very high. Above all, this intercalate exhibits hysteresis, and this would not be the case if the magnetization was merely reflecting the presence of superparamagnetic iron oxide particles. The strong anisotropy of the magnetization observed on a platelet of the pyridinium intercalate is another feature that cannot be accounted for by the hypothesis of very small particles of impurities. On the contrary, this large anisotropy strongly suggests that the 2D Ising nature of the magnetic interaction[22] in pristine FePS$_3$ is preserved in the intercalates studied in this work. The strong remnant magnetization observed for the pyridinium, methylviologen, and methylpyridinium intercalation compounds confirm their Ising character, which underlines the relationship between the parent layered materials and their intercalates.

A striking characteristic of the magnetic properties is the sluggish character observed when the field dependence of the magnetization is studied at temperatures well below T_c. This is particularly pronounced for the pyridinium compound. The possibility of weak *inter*layer antiferromagnetic interactions that would have to be overcome by the applied field is ruled out by the zero-field magnetization curves which demonstrate that the magnetization appears on cooling even in a very small external field. It is therefore likely that this "sluggish" character is due to a low mobility of the Bloch walls separating the Weiss domains and to the strong anisotropy of the Fe^{2+} ions which makes it difficult to change the direction of the spins. The smaller effect observed with the methylviologen intercalate may be due to the larger amount of iron vacancies in this case, which decreases the overall magnetic interaction and also causes T_c to shift toward lower temperature.

The question finally arises as why does intercalation change the overall antiferromagnetic ordering of pure FePS$_3$ into a different one characterized by the occurrence of spontaneous magnetization. It must be stressed that the saturation magnetization observed represents only a fraction (10% for the methylviologen compound)

of the magnetization that would be achieved if all the iron spins were parallel. Therefore intercalation only introduces some kind of noncompensation. We have recently shown that the magnetization which occurs at low temperature in the tetramethylammonium MnPS$_3$ intercalate was related to the superlattice formed by the intralayer Mn^{2+} vacancies created during intercalation. These vacancies destroy the balance between the upward and downward spins that prevails in the pure MnPS$_3$. One signature of the superlattice was the appearance of relatively intense extrareflections in the X-ray diffraction pattern of this intercalate. In the case of the methylviologen and pyridinium−FePS$_3$ intercalates, X-ray diffraction does not show any extrareflection that could indicate the occurrence of a superlattice. Therefore, despite the fact that ion-exchange intercalation seems at first sight to alter MnPS$_3$ and FePS$_3$ in the same manner, another explanation has to be sought in the case of FePS$_3$.

It must be recalled at this point that the magnetic structures of FePS$_3$ and MnPS$_3$ are very different. Whereas any Mn^{2+} ion in MnPS$_3$ is antiferromagnetically coupled to its three nearest neighbors, the Fe^{2+} ions participate in competitive couplings. In a layer of FePS$_3$, each Fe^{2+} ion is ferromagnetically coupled with two of the three nearest neighbors, and antiferromagnetically with the third (the cations are located at the corners of a honeycomb lattice). In a recent detailed study of the magnetism of FePS$_3$, Joy et al. have emphasized the fundamental role played by single-ion anisotropy in determining the Weiss constant of this compound.[22] The Weiss constant of FePS$_3$ single crystals is found to be positive or negative, depending on the parallel or perpendicular orientation of the magnetic field with respect to the plane of the platelet. This dependence has been ascribed by these authors to crystal field effects arising because of trigonal elongation of the FeS$_6$ octahedra. This interpretation implies that chemical factors that would affect the geometry of the FeS$_6$ octahedra should also be able to modify the relative importance of the ferromagnetic versus antiferromagnetic interactions. Therefore, it can be tentatively sug-

gested that certain guest species such as pyridinium and methylviologen cations, which have an electron-accepting character, sufficiently interact with the sulfur atoms of the layers to cause slight geometry changes that would favor the ferromagnetic interactions at the expense of the antiferromagnetic ones. The largest magnetization is obtained when the guest species is methylviologen, which is well-known to be a strong electron acceptor. Actually it is obvious from the facile synthesis of this intercalate that methylviologen has a strong chemical affinity toward FePS$_3$.

Conclusion

In view of the abundant literature for over 20 years dealing with magnetism in the MPS$_3$ layered compounds, it appears that complex phenomena occur, particularly in the case of FePS$_3$. The present work reinforces the interest in these systems, as it demonstrates that the magnetic properties of FePS$_3$ may be strongly affected by the intercalation of specific molecular species, even when the latter proceeds through an ion-exchange route. In some cases, the intercalates exhibit a genuine spontaneous magnetization up to a quite high critical temperature, and there seems to be a relation between the chemical nature of the inserted species and the intensity of the magnetization. Although a definite mechanism cannot be given yet, the role played by intercalation seems to be different for FePS$_3$ than it is for MnPS$_3$. In particular, work will be undertaken to study the influence of chemical guest species having a greater electron accepting power, such as cationic phthalocyanines, with the perspective of achieving greater magnetization.

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