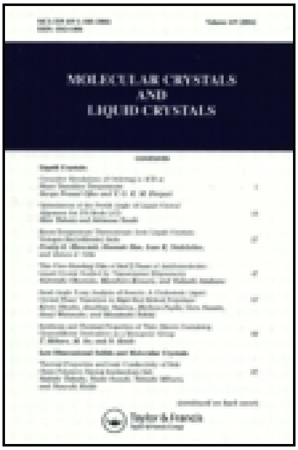

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The $NiPS_3$-Cobaltocene intercalation compound: A new ferromagnet

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The $NiPS_3$-Cobaltocene intercalation compound: a new ferromagnet

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The layered $NiPS_3$-Cobaltocene intercalation compound is shown to acquire spontaneous magnetization below 70 K, although $NiPS_3$ orders antiferromagnetically. An XPS study of this intercalate is described, which shows that the electronic density at the Ni, P and S atoms is increased upon intercalation.

Keywords: Intercalation; $NiPS_3$; XPS; Ferromagnets

INTRODUCTION

Intercalation of molecular cations into layered $MnPS_3$ and $FePS_3$[1-3] is known to cause dramatic changes in their magnetic properties[4,5]. Whereas the pristine materials order in an antiferromagnetic way[6-9], some of their intercalates acquire a magnetization below a critical temperature that can be as high as 90K ($FePS_3$ methylviologen)[5]. Mn- and $FePS_3$ intercalates are synthesized by an ion exchange process[10], which involves the departure of intralayer M^{2+} cations and subsequent uptake of cations in between the galleries[11]. In the case of the $MnPS_3$ intercalates, the intralayer vacancies have been shown to be responsible for the appearance of the magnetization[12].

The intercalation of cobaltocene into $NiPS_3$ was first reported by our group

15 years ago[13], but the electronic structure and magnetic properties of the intercalate have not been studied in depth. This communication decribes an XPS study of the intercalate and a detailed investigation of its magnetic properties. Intercalation of cobaltocene into $NiPS_3$ leads to a ferromagnet with $T_c \approx$ 60 K, although the intercalation process does not involve any loss of nickel.

EXPERIMENTAL

A cobaltocene intercalate (hereafter denoted 1) has been prepared by reaction of $NiPS_3$ with cobaltocene in toluene at 130°C, following the procedure already described.[13] The XPS analyses were performed with a Surface Science Instruments spectrometer (model 301) using focused monochromated Al K_α radiation (1486.6 eV). The diameter of the irradiated area was 300 µm. The spectrometer was calibrated by using the photoemission lines of Au (Au $4f_{7/2}$: 83.9 eV) and Cu (Cu $2p_{3/2}$: 932,5 eV). The peaks were recorded with a constant pass energy of 50 eV.The powder samples were pressed onto sample holders in a glove box (O_2 and H_2O levels below 2 and 6 ppm, respectively) directly attached to the introduction chamber. Charging effects were minimized with a low-energy flood gun. The calibration of the spectra was done with the C_{1s} line (284.6 eV) from the carbon contamination layer. The XPS signals were analysed by using a peak synthesis program in which the fitting peaks of the experimental curve are defined thanks to a combination of gaussian and lorenzian distributions (L/G < 20%). Magnetic measurements have been carried out on powdered samples of typical weight 30 mg using a Quantum Design SQUID magnetometer.

RESULTS

Elemental analysis confirmed the formulation $NiPS_3(CoCp_2)_{0.37}$ previouly given. The X-ray powder diffraction pattern of 1 exhibits sharp reflections, previously indexed using the monoclinic cell of $NiPS_3$ elongated along the c direction [13].

The Ni XPS spectra of the samples investigated consist of spin-orbit doublets $2p_{3/2}$ and $2p_{1/2}$, each component of the doublet showing a satellite feature. The best fit of the experimental spectra are shown in Figure 1 and the parameter values derived are listed in Table I. Comparison of $NiPS_3$ and of 1 shows that insertion of cobaltocene results in a significant shift towards lower energy (1.2 eV) of the Ni peaks and considerably weakens the intensity of the satellites.

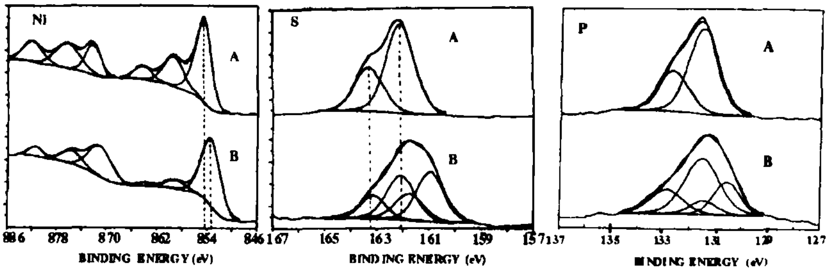

FIGURE 1 Ni, S and P XPS spectra in (A) $NiPS_3$ and (B) $NiPS_3(CoCp_2)_{0.37}$

The sulfur XPS spectrum in $NiPS_3$ (Figure 1) shows the two resolved components of the $2p_{3/2}$-$2p_{1/2}$ doublet, in contrast to previous data[14, 15]. The spectrum of Intercalate **1** appears broad, but the fit allows decomposition of the peak into two doublets of similar intensity, one of them unchanged with respect to $NiPS_3$, the other one shifted towards lower binding energy (Table I).

TABLE I : Binding energy (eV) in $NiPS_3$ and in $NiPS_3(CoCp_2)_{0.37}$.

	$NiPS_3$	$NiPS_3\ (CoCp_2)_{0.37}$
$Ni\,2p_{3/2}$ - $2p_{1/2}$	854.8 - 872.4	853.6 - 871.2
	859.6* - 876.5*	859.2* - 875.8*
* (satellite)	864.5* - 882.2*	864.0* - 881.6*
$S\,2p_{3/2}$ - $2p_{1/2}$	162.1 - 163.3	162.1 - 163.3 [47%]
		160.9 - 161.9 [53%]
$P\,2p_{3/2}$ - $2p_{1/2}$	131.5 - 132.6	131.5 - 132.7 [70%]
		130.6 - 131.6 [30%]

The phosphorus XPS spectrum of pristine $NiPS_3$ (Figure 1) also shows the two resolved components of the $2p_{3/2}$-$2p_{1/2}$ doublet. Analysis of the phosphorus spectrum of Intercalate **1** shows that the broad peak can be decomposed into two doublets, one of them unchanged with respect to $NiPS_3$, the other one significantly shifted towards lower binding energy (Table I). However the relative intensity of these P doublets (70% / 30%) is different from that of the sulfur doublets mentioned above (47% / 53%).

The Co XPS spectrum of Intercalate 1 shows the $2p_{3/2}$ - $2p_{1/2}$ doublet at 780.9 eV and 796.1 eV, respectively. Comparison with the spectrum of neutral cobaltocene shows that the Co doublet in Intercalate 1 is shifted towards higher energies by 1.9 eV with respect to neutral solid cobaltocene.

The temperature dependance of the magnetization of Intercalate 1 in a low field and in zero field is shown in Figure 2. The field-cooled magnetization (FCM) curve obtained by cooling in a field of 30 G shows a rapid increase of M below 70K. Switching off the field at 10 K and warming reveals the existence of a remnant magnetization (Re) that vanishes at T_C. The zero field cooled magnetization (ZFCM), obtained upon warming under 30 Oe a sample previously cooled to 10 K in zero field, progressively increases until it vanishes when the temperature reaches T_C. These results give evidence for the occurrence of magnetic ordering taking place in two steps below 70 K.

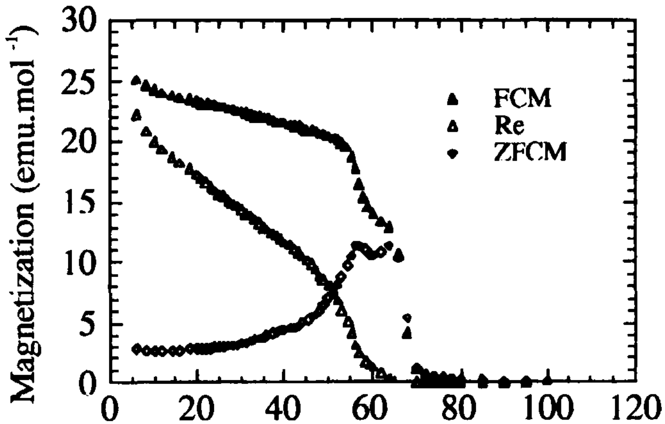

FIGURE 2 : Magnetization of $NiPS_3 (CoCp_2)_{0.37}$ versus temperature

The field dependance of the magnetization of Intercalate 1 at 20 K is shown in Figure 3. The M(H) curve is very steep at low fields, then reaches a saturation plateau (≈ 900 emu per mole of Ni).

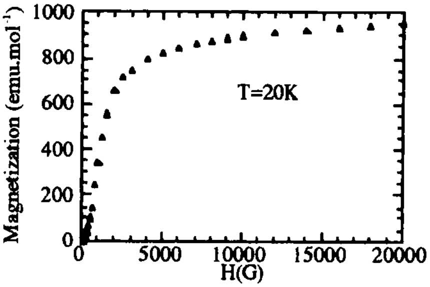

FIGURE 3: Magnetization vs magnetic field for $NiPS_3(CoCp_2)_{0.37}$ at 20K

DISCUSSION.

The whole body of XPS results clearly show that electrons are donated from cobaltocene to $NiPS_3$ upon intercalation. Increase of the electron density on the host lattice is demonstrated by the shift towards lower energy of the 2p levels of Ni, P, S, whereas oxydation of the cobaltocene is evidenced by an opposite shift of the 2p level of cobalt. Therefore it is worth comparing the XPS data of $NiPS_3(CoCp_2)_{0.37}$ to those of the well documented lithium intercalates Li_xNiPS_3.[6,16]

On going from $NiPS_3$ to $Li_{1.55}NiPS_3$, the 2p levels of Ni and S shift towards lower energy by 1.6 eV and 0.8 eV respectively, whereas the 2p level of P shifts towards higher energy by 0.7 eV[14]. Only one type of S and P atoms has been evidenced in $Li_{1.55}NiPS_3$. In the case of the cobaltocene Intercalate **1**, the smaller shift of the Ni 2p level (1.2 eV) indicates a lower extent of nickel reduction. However two types of P and S atoms are present in this intercalate, one type unchanged with respect to pristine $NiPS_3$, the second type significantly reduced (shifts towards lower energy by 1.4 eV and 1.0 eV for S and P, respectively). The $NiPS_3$ host lattice therefore appears to be more perturbed by cobaltocene intercalation than by lithium insertion, an effect which may be related to the much larger size of the cobaltocene guest species.

The most dramatic difference between the two intercalates is that the cobaltocene intercalate acquires a spontaneaous magnetization below 70 K, whereas both Li_xNiPS_3 and pristine $NiPS_3$ are antiferromagnets[6]. The saturated magnetization of Intercalate **1** is only 8% of the theoretical value ($N_{Av}g\beta S$ per mole of Ni) corresponding to all spins being aligned. This behavior closely resembles that of the $MnPS_3$ and $FePS_3$ intercalates[4,5], and it demonstrates that either ferrimagnetism or weak ferromagnetism are present, but not ferromagnetism. The similarity of the magnetic behavior of $NiPS_3(CoCp_2)_{0.37}$ is all the more puzzling since the intercalation of cobaltocene into $NiPS_3$ involves a (redox) mechanism which should not create intralayer vacancies (responsible for the magnetization of the $MnPS_3$ intercalates). The reduction of Ni^{2+} in the lithium intercalates has been shown to result in the formation of diamagnetic Ni° atoms. If such diamagnetic atoms are also formed in the cobaltocene intercalate, then they may play the same role as the vacancies in the $MnPS_3$ intercalates. The originality of $NiPS_3(CoCp_2)_{0.37}$ with respect to Li_xNiPS_3 could then be related to an ordering phenomenon of the diamagnetic Ni° sites.

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