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Dramatic Modification of the Magnetic Properties of Lamellar $MnPS_3$ upon Intercalation

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Transition-metal hexathiohypodiphosphates MPS_3, where M is a divalent metal cation, form a class of lamellar materials which belong to the structural family of the transition-metal dichalcogenides $M'X_2$.[2] Their structure is related to that of $CdCl_2$, with metal ions and P–P pairs occupying the cadmium positions and sulfur atoms occupying the chloride positions.[3] Optical and electrical measurements have shown that MPS_3 behave as broad band semiconductors.[4] Interest for these materials has grown because of their ability to intercalate lithium reversibly, either chemically or electrochemically: $NiPS_3$ has thus led to interesting high-density batteries.[5,6] Recently, one of us has shown[7,8] that a number of MPS_3 compounds could also intercalate organometallic species such as cobaltocene or bis(benzene)chromium. Infrared and Raman spectra of these new transparent intercalates have been studied in detail:[9] they show that the intercalated species are cationic, no matter how the intercalation reaction has been carried out, i.e., by using a neutral organometallic species or its cation. The general purpose of our present work is to examine the influence of large guest cations on the magnetic properties of the MPS_3 lamellar hosts. Very few related studies have been published so far; among them, the magnetic properties of Li_xNiPS_3 have been reported[4,10] to be identical with those of pure $NiPS_3$ for $x < 0.5$. This note deals with results obtained for $MnPS_3$ and some intercalates. The susceptibility of $MnPS_3$ has been previously measured down to 77 K,[11] and it has been suggested that this phase behaves as a two-dimensional (2-D) antiferromagnet. The results of measurements extended to 4.2 K are presented here, and a quantitative interpretation is given in terms of an isotropic 2-D spin–spin interaction. Furthermore, susceptibility measurements on various intercalates reveal drastic modifications in the magnetic behavior of $MnPS_3$ upon intercalation.

Experimental Section

Pure $MnPS_3$ was synthesized according to the procedure described in ref 2, by heating stoichiometric amounts of manganese, red phosphorus, and sulfur in a sealed quartz tube; purity of the reagents was about 99.9%. Identification was obtained from X-ray diffraction and chemical analysis. The organometallic intercalation compounds were prepared as described in ref 7.

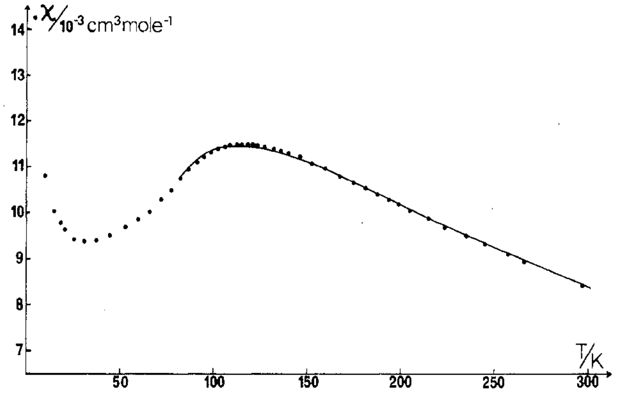

Figure 1. Experimental (···) and fitted (—) temperature dependence of the molar magnetic susceptibility for $MnPS_3$.

(i) Reaction of $MnPS_3$ with neutral cobaltocene in toluene for 3 days at 120 °C gave $MnPS_3[Co(\eta\text{-}C_5H_5)_2]_{0.33}$, denoted hereafter I. Anal. Calcd for I: Mn, 22.5; P, 12.7; S, 39.3; Co, 7.96; C, 16.2; H, 1.35. Found: Mn, 22.8; P, 12.0; S, 38.5; Co, 7.5; C, 16.2; H, 1.6.

(ii) Reaction of $MnPS_3$ with an aqueous solution of cobaltocenium iodide for 1 day at room temperature led to an intercalate formulated as $Mn_{1-x}PS_3[Co(\eta\text{-}C_5H_5)_2]_{2x}$ where $x \approx 0.16$ (II). Anal. Calcd for II: Mn, 19.7; P, 13.2; S, 41.1; Co, 8.2; C, 16.4; H, 1.4. Found: Mn, 19.2; P, 12.8; S, 39.2; Co, 8.0; C, 16.4; H, 1.7. This formulation for II slightly differs from the one proposed in ref 7 on the basis of an erroneous manganese analysis. The intercalation route leading to II proceeds through the creation of Mn^{2+} intralayer vacancies, accompanied by a corresponding interlayer uptake of $Co(\eta\text{-}C_5H_5)_2^+$ cations. Details about this new intercalation route will appear elsewhere.[12] Similarly, reaction of $MnPS_3$ with bis(benzene)chromium iodide led to $Mn_{1-x}PS_3[Cr(\eta\text{-}C_6H_6)_2]_{2x}$ where $x \approx 0.14$ (III). Anal. Calcd for III: Mn, 20.3; P, 13.3; S, 41.3; Cr, 6.3; C, 17.3; H, 1.4. Found: Mn, 19.7; P, 12.7; S, 39.6; Cr, 6.0; C, 16.2; H, 1.7. The analytical values found for II and III are systematically low (except for H) because of the presence of ~3% water which is not considered in their formula. Because of the similar magnetic properties observed in the above described intercalates (see below), it appeared interesting to compare I, II, and III to an intercalate containing another kind of guest species. As it is known that amines react,[13] $MnPS_3$ was soaked in allylamine for 1 day at room temperature, leading to an intercalate IV which has not yet been fully characterized: an approximate formulation of IV is $MnPS_3(\text{allylamine})_{0.28}$, but part of the guest allylamine is likely to be protonated and associated with water.

X-ray powder patterns all showed sharp 00*l* reflections. The interplanar (basal) spacings calculated from these reflections were 6.5 Å for pure $MnPS_3$, 11.82 Å for I and II, 12.26 Å for III, and 10.5 Å for IV.

Magnetic susceptibility measurements were made on powdered samples of about 5 mg using the Faraday method. The magnetic field intensity was about 10^3 G. The molar susceptibilities of $MnPS_3$ and its intercalates were corrected for diamagnetism by using the measured susceptibility of $CdPS_3$ (-92×10^{-6} cm³·mol⁻¹) and Pascal constants.

Results and Discussion

$MnPS_3$. The molar susceptibility of powdered $MnPS_3$ between 4.2 and 300 K is shown in Figure 1; the broad maximum around 110–120 K is typical of low-dimensional antiferromagnetism. The exchange interaction between Mn^{2+} ions (fundamental $^6A_{1g}$) is expected to be properly described by an isotropic Heisenberg Hamiltonian.[14] The Mn^{2+} ions are located at the corners of a two-dimensional honeycomb lattice. For any 2-D lattice, if the nearest-neighbor interaction is

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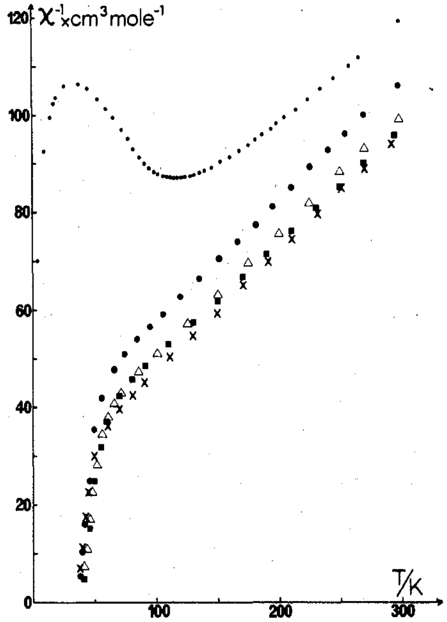

Figure 2. Experimental inverse susceptibility (per mole of manganese) vs. temperature for (•) $MnPS_3$, (●) $MnPS_3[Co(\eta\text{-}C_5H_5)_2]_{0.33}$ (I), (△) $Mn_{1-x}PS_3[Co(\eta\text{-}C_5H_5)_2]_{2x}$ ($x \approx 0.16$, II), (■) $Mn_{1-x}PS_3[Cr(\eta\text{-}C_6H_6)_2]_{2x}$ ($x \approx 0.14$, III), and (×) $MnPS_3(\text{allylamine})_{0.28}$ (IV).

written $-J\hat{S}_i\hat{S}_j$, only limited expansions of the susceptibility are known: for $MnPS_3$, the expansion given by Rushbrooke and Wood[15] for the $S = {}^5/_2$ honeycomb lattice has been used, i.e.

$$\chi = \frac{Ng^2\beta^2S(S+1)}{3kT}\,\frac{1}{1+\sum\limits_{i=1}^{6} b_i(J/T)^i} \qquad (1)$$

in which J is expressed in cm⁻¹; the coefficients b_i have the values $b_1 = -12.5960$, $b_2 = 57.4192$, $b_3 = -113.4000$, $b_4 = -266.2017$, $b_5 = 1686.5311$, and $b_6 = 36761.4104$. Such an expression only holds in the high-temperature range, and it is important to know how far the limited expansion is valid at low temperature. To answer this question, two fittings have been made, one down to 170 K and the other one down to 82 K, treating g and J as adjustable parameters.

(i) Over the temperature range 170–298 K, where expression 1 is certainly valid, an excellent agreement is obtained with $J = -11.9$ cm⁻¹ and $g = 1.915$ ($\sum(\chi_e - \chi_c)^2/\sum\chi_e^2 = 0.15 \times 10^{-5}$).

(ii) Over the temperature range 82–298 K, expression 1 still provides a good fitting with similar values, $J = -12.1$ cm⁻¹ and $g = 1.926$ ($\sum(\chi_e - \chi_c)^2/\sum\chi_e^2 = 0.16 \times 10^{-4}$).

Therefore, $MnPS_3$ behaves as a bidimensional isotropic antiferromagnet at least down to 82 K with expression 1 correctly describing the susceptibility up to $J/kT = 0.21$; considering the experimental accuracy, the value $J = -12.1$ cm⁻¹ was retained. The g value seems to be slightly low for the Mn^{2+} ions; however, g is known to be very sensitive to experimental uncertainties. The increase of the susceptibility below 30 K is ascribed to noncoupled paramagnetic centers, such as impurities or layer edges. Finally, a tentative fitting with a limited expansion,[16] based on the assumption of a classical spin for the Mn^{2+} ions, gave a good agreement only down to 130 K.

$MnPS_3$ Intercalates. The magnetic susceptibility per mole of Mn of a number of intercalates is presented in Figure 2 as $\chi_M^{-1} = f(T)$. Inspection of the curves clearly shows that the magnetic properties of $MnPS_3$ (recalled in Figure 2 for comparison) are strongly modified upon intercalation and that all the studied intercalates exhibit the same basic features, namely: (i) they still show antiferromagnetic interactions above ~70 K, but the coupling is much weaker than in pure $MnPS_3$; (ii) when the intercalates are cooled from 60 to 40 K, their susceptibility sharply increases and eventually becomes field dependent. As the Faraday method was not suitable for studying the field dependence, the related magnetization studies will be published later. However, comparison of these magnetic transitions with the magnetic transitions encountered in the organic intercalated tetrachloromanganate layered salts[17] strongly suggests that weak ferromagnetism appears in the $MnPS_3$ intercalates below ~40 K.

Since all the studied intercalates show a similar behavior, any interpretation should not depend on the details of a particular intercalation mechanism: with comparison, for instance, of I and II, the existence of Mn^{2+} vacancies in the layers of II is not an essential factor, as there are no Mn^{2+} vacancies in I.

Let us first consider the intralayer antiferromagnetic coupling, much weaker in the intercalates than in pure $MnPS_3$. Exchange interaction is known to be very sensitive to small geometry changes such as modification of the Mn–S–Mn angles, because of the dependence of orbital overlap on these factors. In the absence of any structure determination of the intercalates, we do not know exactly to what extent the layers are affected by intercalation. However, X-ray powder patterns show that the *hk*0 reflections exhibited by $MnPS_3$ persist at the same diffraction angles in the intercalates, indicating that the interatomic distances within a layer are almost unchanged. A more satisfactory explanation for the weakening of the exchange interaction comes from the cationic character of the guest species, an important feature common to I, II, III, and probably IV. A model is thus proposed where the electrostatic field created by the guest cations modifies the shapes of the sulfur orbitals, making them point less toward the manganese ions so that these orbitals are less effective in transmitting exchange energy between the manganese spins (less available for overlap with the appropriate manganese orbitals). Further experimental work is in progress to check the validity of such an electrostatic approach. Efforts are also directed at synthesizing monocrystalline intercalates, which would allow more detailed structural analyses.

One must turn now to the low-temperature transitions, ascribed to the appearance of weak ferromagnetism. This phenomenon results from spin canting in the antiferromagnetic layers, leading to a noncompensated macroscopic magnetic moment. The main factor responsible for the occurrence of weak ferromagnetism is generally considered to be an antisymmetric exchange term in the 2-D Hamiltonian.[18] We suggest that this anisotropic term already exists in pure $MnPS_3$, but only as a minor factor with respect to the exchange interaction. As the latter is considerably reduced in the intercalates, anisotropy becomes relatively more important and leads to an enhancement of the magnetization of the low-temperature phase. Further work is intended to determine whether the transition temperature depends on the nature of the guest species. Finally, it is relevant to note that the magnetic properties of $FePS_3$ are affected in a similar way as those of $MnPS_3$ upon intercalation of cobaltocenium cations: weak ferromagnetism also appears, but at a higher temperature (75 K). This observation gives strength to the above suggested analogy between the intercalated $MnPS_3$ and the tetra-

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chloromanganate systems, since the tetrachloroferrate salts are known to undergo transitions similar to the tetrachloromanganates, but at higher temperature (87 K).

Conclusion

This work has shown that $MnPS_3$ behaves as a two-dimensional antiferromagnet. Intercalation reduces the intralayer coupling because of the cationic character of the guest species. Anisotropy in the 2-D Hamiltonian is thus revealed, with the occurrence of weak ferromagnetism as a consequence.

Registry No. $MnPS_3$, 43000-56-2; I, 74346-92-2; II, 74346-93-3; III, 74346-94-4; IV, 74346-95-5.

Correspondence

Ferrocene as an Internal Standard for Electrochemical Measurements

Sir:

Electrochemistry is an increasingly popular technique for the characterization of new compounds. The basic thermodynamic quantity that is assigned to an electrode process is the standard or formal reduction potential ($E°$ or E^f). In aqueous solution the measurement of reduction potentials is facilitated by the use of reliable and universally accepted reference electrodes such as the normal hydrogen electrode (NHE) or the saturated calomel electrode (SCE).[1] In many instances electrochemical measurements in water are impossible due to insolubility or instability of the compound. Unfortunately, no universal reference electrode exists for nonaqueous solvents.[2,3]

Since a variety of reference electrode systems have been employed, the literature contains numerous reduction potentials which cannot be related to each other and which are, occasionally, difficult to reproduce. For example, two common methods for reporting nonaqueous potentials are vs. the SCE which inevitably includes unknown liquid junction potentials[2] and vs. pseudo reference electrodes such as a silver wire. We believe that the situation described above need not exist, and on the basis of concepts and data already in the literature, we suggest a simple method for reporting reduction potentials in nonaqueous solvents.

Internal Standard. During the course of our studies of copper–macrocyclic ligand complexes we have found that a practical approach to this problem is the use of the potential of the oxidation of ferrocene as an internal standard.[4-10] After the electrochemistry attributed to the compound of interest has been identified, ferrocene is added to the working compartment of the cell. The electrochemical experiment is repeated, and the position of the waves can be directly compared to the potential of the ferrocenium/ferrocene (Fc^+/Fc) couple. Figure 1a illustrates this method by showing a cyclic voltammogram of tris(acetylacetonato)ruthenium(III) in CH_3CN.

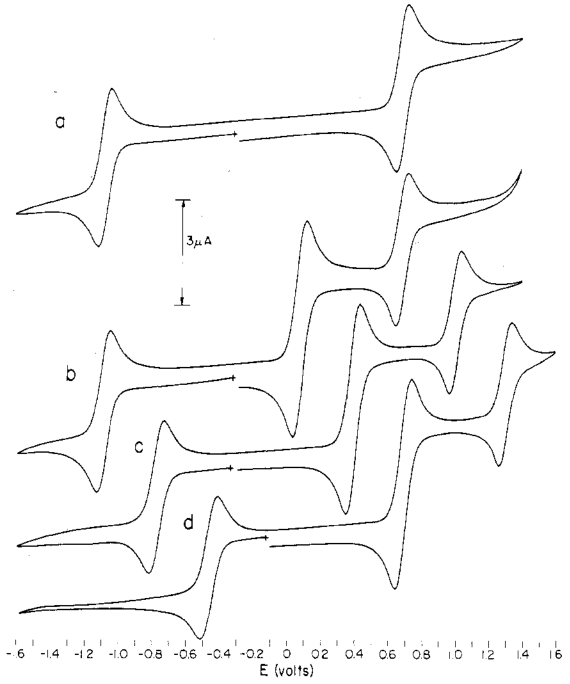

Figure 1. Platinum button cyclic voltammetry at 50 mV/s of 0.005 M $Ru(acac)_3$ in CH_3CN with 0.1 M tetrabutylammonium perchlorate: b, c, and d, ferrocene added; a and b, vs. $Ag/AgNO_3$ (0.01 M), TBAP (0.1 M), CH_3CN; c, vs. SCE; d, vs. Cu wire.

Figure 1b shows the same voltammogram after addition of a similar amount of ferrocene. Use of the formula $E^f = (E_{p(anodic)} + E_{p(cathodic)})/2$ allows calculation of formal potentials for the processes in Figure 1 of 0.602 and −1.157 V vs. $E^f(Fc^+/Fc)$. An important advantage of this method is that choice of the reference electrode used to satisfy the three-electrode potentiostat (a Ag/Ag^+ electrode in Figure 1a,b) is reduced to a matter of experimental convenience. Parts c and d of Figure 1 were recorded under conditions identical with those for Figure 1b except that an SCE was used as a reference electrode for Figure 1c, while a copper wire was used for Figure 1d. From the values on the potential axis the waves appear to be shifted, but formal potentials relative to $E^f(Fc^+/Fc)$ remain unchanged. Formal potentials obtained in the manner described above should be reproducible because variables such as type of reference electrode, liquid junction potentials, and reference electrode degradation are eliminated.[11]

The Fc^+/Fc couple ($E° = 0.400$ V vs. NHE)[12] may be

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