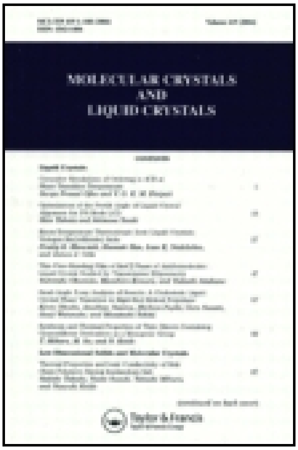

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Electron Paramagnetic Resonance Study of Magnetic Ordering in $MnPS_3$, $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$ and $Mn_{0.84}PS_3(1,10\text{-Phen})_{0.64}$ Compounds

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We report Electron Paramagnetic Resonance (EPR) studies on intercalation ferromagnets $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$ and $Mn_{0.84}PS_3(1,10\text{-phen})_{0.64}$ and their antiferromagnetic host $MnPS_3$, in the temperature range 300 – 15 K. The nature of the organic guest cation appears to have a strong influence on the magnetic behaviour of this inorganic-organic hybrid system. The continued appearance of the exchange-narrowed sharp line, characteristic of the paramagnetic phase, even at 15 K suggests that the bulk of the intercalate ferromagnets in this system do not attain a completely ordered state.

Keywords: Electron paramagnetic resonance; intercalate ferromagnets

INTRODUCTION

The antiferromagnetic transition metal phosphorous trichalcogenides MPS_3 (M = Mn^{2+}, Co^{2+} and Fe^{2+}), where M is in high spin state, crystallize in layered structures (monoclinic, space group *C2/m*) and exhibit a unique non-redox intercalation chemistry. In them, the van der Waals forces hold the layers together, into which large organic cations from a solution can get intercalated as cationic guests, discharging intralamellar M^{2+} cations back into solution to maintain charge balance. The intralayer M^{2+}-vacancies can lead to a dramatic modification of the magnetic behaviour of the host compounds, making them excellent candidates for designing new molecular magnets[1]. Intercalation of 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen), for instance, expands the interlayer spacing and transforms a quasi-2D antiferromagnet $MnPS_3$ (T_N = 78K) into molecular ferromagnets $Mn_{0.86}PS_3(2,2'\text{-bipy})_{0.56}$ and $Mn_{0.84}PS_3(\text{phen})_{0.64}$, which exhibit spontaneous magnetization below 40K. Similarly, intercalation of 4,4'-bipyridine in $MnPS_3$ or $FePS_3$ (T_N = 120K) transforms them into

$Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$ and $Fe_{0.76}PS_3(4,4'\text{-bipy})_{0.48}$ which exhibit ferromagnetic behaviour below 35K and 60K, respectively. In the recent past, we have made extensive use of EPR to obtain valuable insights into the nature of the magnetic behaviour in molecular magnets[2-5]. In particular, we have reported the appearance of a ferromagnetic resonance signal in the range of temperature 40 - 25K, at the expense of the exchange-narrowed paramagnetic line for $Mn_{0.86}PS_3(2,2'\text{-bipy})_{0.56}$ as well as the existence of two different Mn sites in this compound[6]. Our present EPR studies on the ferromagnets $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$, $Mn_{0.84}PS_3(\text{phen})_{0.64}$ and their host $MnPS_3$, indicate a profound influence of the nature of the intercalated organic guest on the magnetic behaviour of the $MnPS_3$ - intercalates.

EXPERIMENTAL

The details of synthesis of these $MnPS_3$ - intercalates have been published elsewhere[1]. Briefly, the host compound $MnPS_3$ was prepared first and characterized using X-ray powder diffraction to be single phase (monoclinic, space group *C2/m*; a = 6.094 Å, b = 10.589 Å, c = 6.817 Å, and β = 107.23°). The two intercalate samples were obtained by slow reaction of $MnPS_3$ with 4,4'-bipyridine or 1,10-phenanthroline in a vacuum-sealed ampoule. The product was characterized using elemental analysis, I.R., TGA and X-ray powder diffraction. All the X-ray reflections could be indexed in the space group *C2/m* with a, b and β values being almost identical with those of the host $MnPS_3$. The c axis and the lattice spacing showed a large expansion for $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$ and $Mn_{0.84}PS_3(\text{phen})_{0.64}$ as expected. SQUID magnetometric measurements showed these two samples to be bulk ferromagnets below 35 and 40 K, respectively. EPR data was taken on a Bruker ESP-300 EPR spectrometer operating in X-band. The second derivative spectra were also recorded for improved resolution. A closed-cycle He refrigerator (Air Products, Inc.) and a Lake Shore temperature controller were used to control the temperature of the sample (~2x3x1 mm^3) between 15-300K.

RESULTS and DISCUSSION

The spectra for the pure $MnPS_3$ showed a broad line located at g = 2.004, concomitantly with a sharp and intense line at g = 2.002. Whereas the sharp resonance peak did not show any temperature dependence, the broad line reduced in intensity upon cooling the sample and disappeared close to its Neel temperature (Fig. 1). The sharp line has the features of an exchange-narrowed component of a paramagnet. Interestingly, an unresolved doublet, corresponding to $g = 2.053$ and $g = 2.029$ appeared below T_N. However, no zero field signal was observed upon cooling down to 14 K, unlike in some the case of some other compounds, pointing possibly to the absence of glassy boundaries[7].

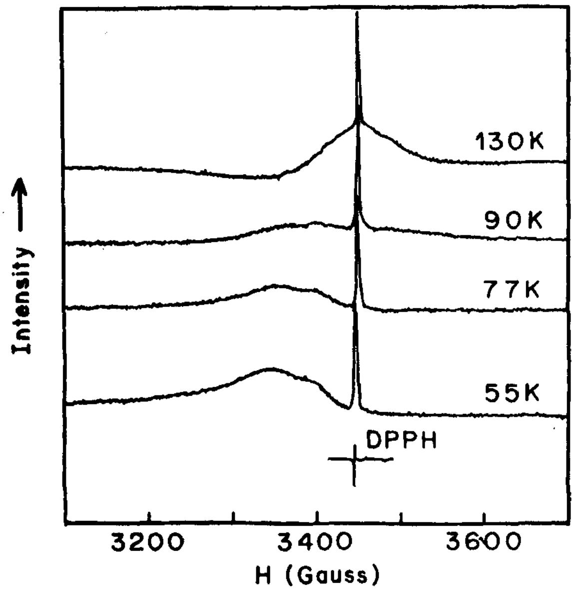

FIGURE 1 Second derivative plots for $MnPS_3$ at different temperatures.

Fig. 2 shows the first derivative EPR spectra for the sample $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$ at different temperatures in the range 300 -15 K. In the high temperature paramagnetic region the spectra consist of a rather broad and symmetric line at $g = 2.003$. The sharp kink is the g-marker signal from DPPH loaded in the second resonator of the dual cavity. The first derivative spectra (Fig. 2) become quite asymmetric as one cools the sample, producing almost a step-like feature on the high-field shoulder. This suggests that it should be comprising of a very broad line, superposed by at least one sharp line.

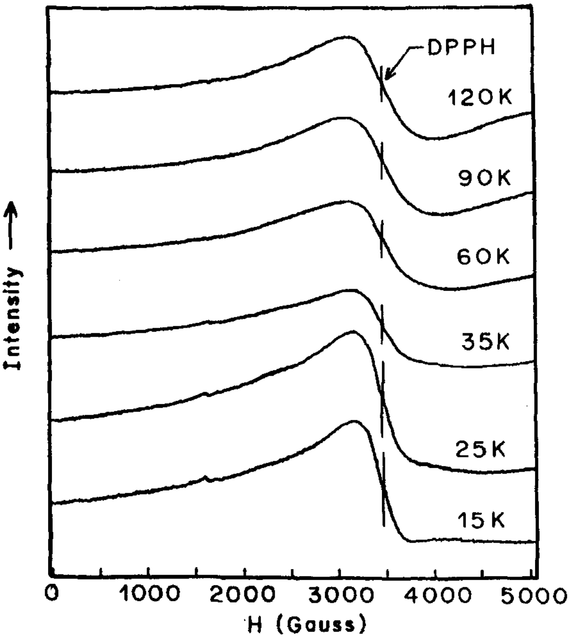

FIGURE 2 First derivative EPR spectra for $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$.

These features become apparent only at and below the Curie temperature (T_c = 35 K), and are reflected (deconvoluted) clearly in the second derivative plots. The broad EPR feature in Fig. 2 is characteristic of the dipolar broadened paramagnetic line, and contributes only to the baseline of the second derivative plots (Fig. 3). The second derivative plot at room temperature consists of just an exchange-narrowed sharp line, but two additional broad features emerge in it upon cooling (Fig. 3). For instance, at 15 K we have an exchange-narrowed sharp line P1 at g = 2.003, a broad feature P2 at g = 2.003 and, another broad feature FM at g = 2.04 which appears only below 35K. The broader component P2 has its peak position coinciding with the exchange narrowed paramagnetic line P1. This implies that they both belong to paramagnetic phase except that P2 is dipolar broadened and not yet entered the exchange-narrowed regime and might, in fact, be intermediate between the broad feature of Fig. 2 and exchange-narrowed component P1. This points to the existence of a magnetic inhomogeneity which made it possible for paramagnetic and ferromagnetic signatures

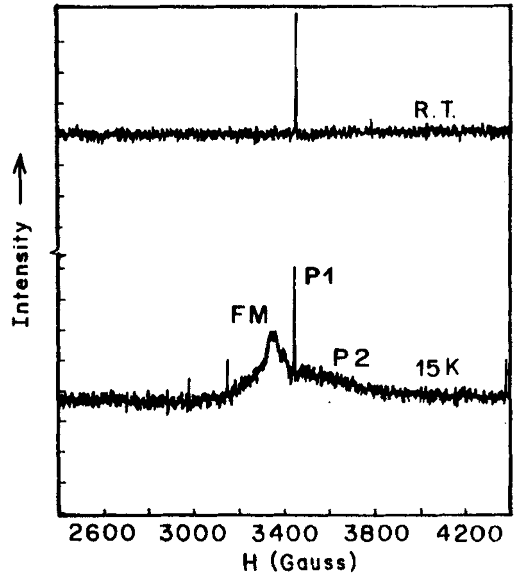

FIGURE 3 Second derivative plots for $Mn_{0.79}PS_3(4,4'\text{-bipy})_{0.42}$ at room temperature and at 15 K.

observable in the same sample. The line FM is due to the ferromagnetic resonance shifted to lower fields due to demagnetization and/or internal fields. The continued appearance of the exchange-narrowed sharp line, characteristic of the paramagnetic phase, even at 15 K suggests that the bulk of this compound has not attained a completely ordered state. This experimental evidence for the coexistence of paramagnetic and ferromagnetic states over a wide temperature range suggests one or both of the following: (i) the compound is inhomogeneous, particularly with regard to the 'bipy' content, with a spatial fluctuation of magnetically ordered and disordered states; and/or (ii) the compound is homogeneous but there is a temporal fluctuation between the ordered and disordered states, the correlation times, as estimated from the g-values, being $\geq 0.5 \times 10^{-8}$ sec. It is informative to point out that similar EPR features were observed for the compound $Mn_{0.86}PS_3(2,2'\text{-bipy})_{0.56}$ too, though to a much smaller extent [6].

The room temperature EPR spectrum of $Mn_{0.84}PS_3(\text{phen})_{0.64}$ consisted of a broad feature at g = 2.004 and a sharp feature at g = 2.002, which did not show any temperature dependence upon cooling down to 14 K. A zero field line, however, appeared prominently below the Curie temperature (T_c = 40 K), a feature attributable to the presence of regions of frustrations.

In conclusion, our studies show that the ferromagnets obtained by intercalating 'bipy' or 'phen' in between the layers of the antiferromagnet $MnPS_3$ are inhomogeneous with spatial fluctuations in regard to the organic guest cation and/or temporal fluctuation between the ordered and disordered states.

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