Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., Vol. 348, pp. 295-300
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Electron magnetic resonance (EMR) studies of intercalation ferromagnet 2,2′-bipyridine-$MnPS_3$ (T_c = 40 K) in the temperature range 300 – 14 K have revealed many interesting features across the (magnetic) order ← → disorder transition. The exchange narrowed line in the paramagnetic phase exhibited sudden reduction in its intensity concomitant with a g-shift to lower values (line shifted to higher fields) and increased line width. These changes took place in the 40–25 K range. In the 25–22K range of temperature, the paramagnetic line disappeared and the FMR signal appeared at lower fields. It is significant that two closely lying FMR signals appeared in the magnetically ordered regime, suggesting the possibility of existence of two different Mn-sites having different g-values, in this state. This may be responsible for the reported magnetic moments values of less than 5.98 BM from bulk magnetisation studies.

Keywords: Electron magnetic resonance; intercalation ferromagnet

INTRODUCTION

High spin transition metal phosphorous trichalcogenides (hexathiohypodiphosphate) MPS_3, ($M = Mn^{2+}$, Co^{2+} and Fe^{3+}) with unique non-redox intercalation chemistry, are excellent candidates for designing a new class of molecular magnets[1]. The interesting behaviour of these intercalation compounds is primarily due to their ability to take up cations from the solution with great ease albeit at

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the expense of the host cation. These compounds, with layer planes held together by van der Waals forces, can incorporate large organic cations, resulting in dramatic changes in the bulk magnetic properties of the host. Intercalation of 2,2′-bipyridine, for instance, transforms a quasi-two dimensional antiferromagnet $MnPS_3$ ($T_N = 78K$) into $Mn_{0.86}PS_3(bipy)_{0.56}$, a molecular ferromagnet exhibiting spontaneous magnetization below 40K. Electron magnetic resonance (EMR) is a useful technique which, under suitable conditions, gives valuable insights into the changes that occur during the magnetic order $\longleftrightarrow$ disorder transition[2]. In this paper, we describe the results of EMR studies which encompasses both the electron paramagnetic resonance (EPR) and ferromagnetic resonance (FMR) using a convenional EPR spectrometer, on $Mn_{0.86}PS_3(bipy)_{0.56}$. Our investigations give clear evidence for: (i) the presence of magnetic frustration around 70 K, which is close to the Neel temperature of the parent compound $MnPS_3$; (ii) existence of fluctuations in the temperature region 40–25K, as evidenced by a large linewidth; and, (iii) the possibility of existence of Mn in two different states, with different g-values, caused by site and/or electronic structure differences. The last observation might imply the existence of a structural phase transition along with the magnetic phase transition.

EXPERIMENTAL

The details of the synthesis of the compound $Mn_{0.86}PS_3(bipy)_{0.56}$, used in this study have been published elsewhere[1]. Briefly, the host compound $MnPS_3$ was prepared first and charaterized using X-ray powder diffraction to be single phase, with monoclinic structure (space group *C2/m*; $a = 6.094$ Å, $b = 10.589$ Å, $c = 6.817$ Å, and $\beta = 107.23°$). The $Mn_{0.86}PS_3(bipy)_{0.56}$ was obtained by the slow reaction of $MnPS_3$ with 2,2′-bipyridine in a vacuum-sealed ampoule, in the presence of acetonitrile. 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 pure host $MnPS_3$. The c axis and the lattice spacing, however, showed a large expansion. The lamellar distance increased by *ca.* 9.27 Å, for the intercalate, which agrees well with the dimension of $Mn(bipy)_3^{2+}$ cation. SQUID magnetometric measurements showed that the material exhibited bulk ferromagnetism below 40 K.

EMR Measurements were conducted on a Bruker ESP-300 EPR spectrometer operating at X-band. The spectra were recorded in the second derivative mode for obtaining improved resolution. A closed-cycle He refrigerator (Air Products,

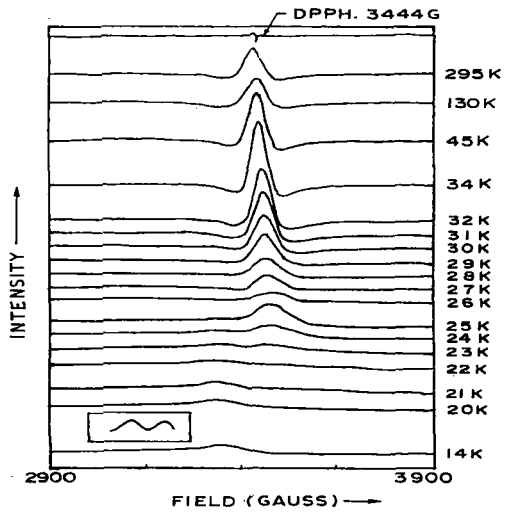

FIGURE 1 Second derivative EMR Spectra of $Mn_{0.86}PS_3(bipy)_{0.56}$ in 300–15 K temperature range. Spectrum below 22 K consists of two closely-spaced lines, as shown schematically in the inset

Inc.) in conjunction with a Lake Shore temperature controller was used to control the temperature of the sample between 15–300K while recording the spectra. The sample was in the form of a pellet 2×3×1 mm^3.

RESULTS AND DISCUSSION

Fig. 1 shows the second derivative EMR spectra of the sample $Mn_{0.86}PS_3(bipy)_{0.56}$ at different temperatures in the range 300 –15 K. No striking changes were seen in the shape or intensity of the EPR line observed around g = 2.00, as the sample was cooled from 300 K to 35 K. The sharp kink is a pick up signal from DPPH loaded in the second resonator of the dual cavity and it could be used conveniently as a g-marker. The line intensity got significantly reduced, however, as the sample was cooled from 34 K to 25 K, despite a concomitant increase in the line width. The main line disappeared completely at about 22 K. Below 22 K, two new lines, placed closely, appeared in the lower field region. Interestingly, a coexistence of the spectra belonging to the disordered and ordered states could be seen in the narrow range of temperature, 25 – 21 K. These features are shown in Figures 2 and 3. In addition to these features, a relatively weak, but definite, out-of-phase signal was observed at zero field in the temperature region 68–70 K, which lies close to the T_N value of the parent host

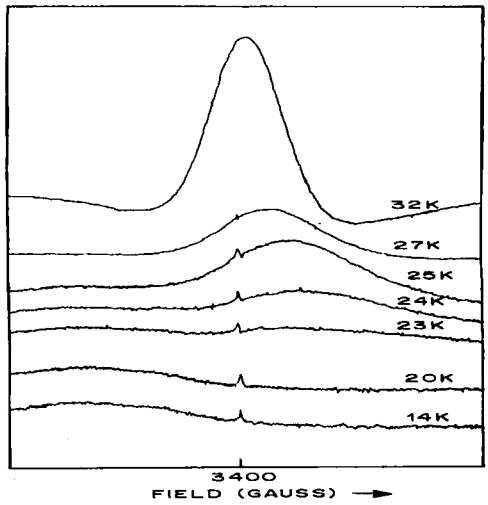

FIGURE 2 Temperature variation of spectra in the close vicinity of T_c. Unusual broadening of higher temperature lines and coexistence of low and high temperature phases can be seen

$MnPS_3$. This signal shown in Fig. 4, is symptomatic of magnetic frustration or a spin glass behaviour [3].

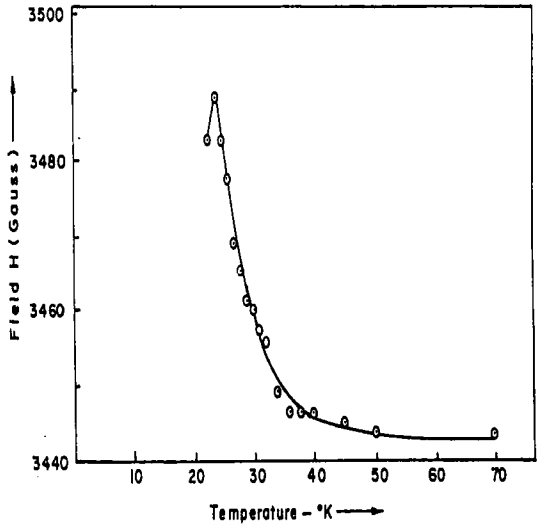

FIGURE 3 Temperature dependence of resonance line position in 30–20 K temperature range

The above observations suggest the following. Firstly, the indication of a spin glass behaviour at 70 K indicates that the incorporation of bipyridine group into the lattice brings in ferromagnetic correlations in competition with those of the antiferromagnetic order even at a temperature as high as 70 K. The obvious conclusion that the antiferromagnetic order is destroyed and a ferromagnetic order appears at 40 K, consequent upon the intercalation of 2,2′-bipyridine in $MnPS_3$, is still valid with the possible exception that both the types of magnetic order coexist and compete with each other even at 70 K, at least in some parts of the sample, where the respective correlation times are roughly of the same magnitude.

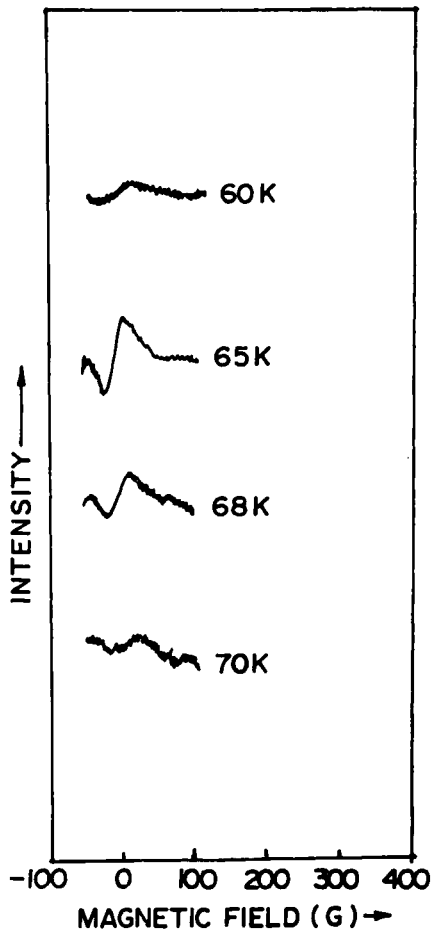

FIGURE 4 Appearance of out-of-phase signal at zero field around 68–70 K temperature range

The most noteworthy change that occurred in the spectra, however, when the sample was cooled below 40 K (T_c) was the gradual disappearance of the prominent signal present in the paramagnetic phase, and the appearance of two new lines in the low field region at temperatures where the sample is supposed to be ferromagnetically ordered. The observation of a large increase in the line width as the sample is cooled between 30 K to 20 K, is a clear indication of the existence of fluctuations. The appearance of two new lines, with g-values of 2.036 and 2.054, below 20 K indicates that there are two inequivalent sites for Mn, definitely observable in the ferromagnetic state. Such a situation may arise either due to a structural inequivalence and/or due to an inequivalence in the electronic structure brought about by the electron withdrawing ability of bipyridine groups. The latter may result in the occurrence of Mn in more than one valence states, most likely in the Mn^{2+} and Mn^{4+} in the present context. This could also be the reason for the lower magnetic moment value reported[1]for the compound under the present study than 5.98 BM expected for Mn^{2+} in the ferromagnetic state.

Preliminary experiments conducted on the effect of light (copper vapour laser, $\lambda = 510.5$ and 578.2 nm, overlapping with Mn^{2+} absorption) gave evidence for decoupling of spin correlations, the illumination of the sample resulting in an enhancement of the paramagnetic signal.

In conclusion, EMR investigations for the ferromagnetic compound $Mn_{0.86}PS_3(bipy)_{0.56}$ gave evidence of the changes that occur in the magnetic behaviour of $MnPS_3$ consequent upon intercalation of the bipyridine cations in the lattice. These include the presence of regions of magnetic frustration at 70 K, just below the antiferromagnetic ordering temperature of the parent phase $MnPS_3$; fluctuations in the region 35–20 K, which is just below the Curie temperature of the intercalate; and, the existence of two inequivalent sites of Mn in the ferromagnetic state.

Acknowledgements

J. V. Y. is thankful to the Indo-French Centre (I.F.C.P.A.R.) New Delhi for support under the project # 1308–4.

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