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: 04 Oct 2006

To cite this article: R. M. Kadam, M. D. Sastry, S. A. Chavan, J. V. Yakhmi & O. Kahn (1997): Coexistence of Spin Fluctuations and Magnetic Order in $(Nbu_4)_2Mn_2$ $[Cu(Opba)]_3$: An Epr Evidence, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 219-225

To link to this article: http://dx.doi.org/10.1080/10587259708044569

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 219–225
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COEXISTENCE OF SPIN FLUCTUATIONS AND MAGNETIC ORDER IN $(NBu_4)_2Mn_2[Cu(opba)]_3$: AN EPR EVIDENCE

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Abstract EPR investigations have been carried out both in the first and second harmonic modes on the organic ferromagnet $(NBu_4)_2Mn_2[Cu(opba)]_3$ with T_c = 22 K. The data was collected in the temperature range 300 - 15 K. At temperatures much higher than T_c ($T \geq$ 100 K), the spectrum consists of a single line at g = 2.00 exhibiting Curie behaviour. Upon cooling below 100 K, the line shows strong temperature dependent g - shift in resonance field to higher value by 50 G at 15 K . This is taken as evidence for the onset of uncompensated antiferromagnetic spin correlations well above T_c. Evidence was also obtained for spin fluctuations which got slowed down with lowering of temperature. The correlation time at 15 K is greater that 10^{-10} sec.

INTRODUCTION

The discovery of spontaneous magnetization in molecular organic materials has triggered many investigations directed towards understanding the complexities of their magnetic behaviour[1-3]. Among different methods adopted to synthesize organic ferromagnets, a popular approach has been to use bimetallic quasi-one-dimensional chains (sub-units) comprising antiparallel alignment of alternate uncompensated spins as building blocks[4]. When these ferrimagnetic chains are assembled appropriately in a three dimensional lattice, interchain interactions may, under suitable conditions, lead to ferromagnetic order, as happens in the case of $Mn^{II}Cu^{II}(obbz).1H_2O$ (T_c = 14 K)[5,6], where obbz = oxamido bis benzoato. An interesting development in this area is the ability to raise the Curie temperature (T_c) by attempting to strengthen the interchain interactions by increasing the dimensionality of the bimetallic sub-units. For instance, the use of a two dimensional $Mn_2^{II}Cu_3^{II}$ network, yields ferromagnetism at 15 K in $(NBu_4)_2Mn_2[Cu(opba)]_3.6DMSO.1H_2O$ and at 22.5 K in its desolvated analogue $(NBu_4)_2Mn_2[Cu(opba)]_3$[7-10],

where opba stands for o-phenylenebis(oxamato).

In this paper, we report the results of detailed studies on $(NBu_4)_2Mn_2[Cu(opba)]_3$ using electron paramagnetic resonance (EPR) technique which offers interesting possibilities to investigate the transition between localized moments to itinerant ferromagnetism and/or delocalistion of spins by exchange interaction with lowering of temperature. The potential of this technique in this emerging area was demonstrated for the soft molecular ferromagnet $[TDAE]C_{60}$[11-13]. In the compound under present investigation, Mn^{II} ($3d^5$, ^6S) and Cu^{II} ($3d^9$,t_{2g}^6, e^3, $^2B_{1g}$) are two sites with localized spins. For high spin Mn^{II}, the g value is 2.00 and for Cu^{2+}, g_{iso} is always greater than 2 and is in the region of 2.1 to 2.2, most of the times[14] . Any exchange of spins between these two sites would reflect in the g values of the resonance and one can infer the time scale of spin exchange. EPR studies on a number of $Mn^{II}Cu^{II}$ bimetallic organic ferromagnets including the title compound were briefly reported by Stumpf et al[7,8]. Mathoniere et al[15] have estimated the values of the zero-field splitting parameters within the S = 2 state of $Mn^{II}Cu^{II}$ pairs belonging to some other $Mn^{II}Cu^{II}$ compounds using X-band EPR. We have observed, during the present EPR study, a strong temperature dependent g shift, well above T_C, for $(NBu_4)_2Mn_2[Cu(opba)]_3$, albeit towards g < 2. In the second harmonic mode of detection, we report clear evidence for possible dynamic spin fluctuations upon cooling below 100 K which slowed down below T_C. Unlike in the case of $[TDAE]C_{60}$, our results seem to suggest that the g shift is not due to spin exchange between two sites, but is due to antiferromagnetic spin correlations.

EXPERIMENTAL

The sample of $(NBu_4)_2Mn_2[Cu(opba)]_3$ was synthesized following the procedure given by Stumpf et al[7]. AC susceptibility measurements made using Air Products Ltd (APD) susceptometer and dc magnetization (ZFC and FC) measurements by using an E.G. & G. Princeton Applied Research model 4500 vibrating sample magnetometer confirmed its Curie temperature to be 22 K[9-10]. EPR measurements were made on the sample in pellet form using Bruker ESP - 300 spectrometer operating at X- band frequency. An APD Cryogenics closed cycle helium refrigerator was used to vary the sample temperature between 13K and 300K.

RESULTS AND DISCUSSION

Figure 1 shows the EPR spectra obtained at different temperatures in the paramagnetic phase and Figure 2 shows that obtained in the vicinity of T_C (=22 K). We report in

these two figures the EPR spectra recorded in second harmonic mode only because we obtained greater resolution in this mode. At higher temperatures, the spectrum consisted of a single symmetric line at g = 2.00, the position of which showed slight temperature dependence with lowering of temperature down to 100 K. Below 100 K, however, the line showed a steep shift towards higher fields, as depicted in Figure 3. Interestingly, the line also split below 100K into two parts alongwith a third component in the middle. The intensity of this central component decreased upon cooling below T_c, resulting eventually in an EPR spectrum with partially resolved double peak at lower temperatures (<15K).

In case there are non-interacting localized moments on Mn^{2+} and Cu^{2+}, the EPR spectra would have contained two lines one at g = 2.000 and another in the region of g = 2.1 - 2.2. These would have been easily resolvable at X - band frequency. The presence of a single isotropic line at higher temperatures at g = 2.000, therefore, suggests that the EPR lines of Mn and Cu are averaged due to exchange interaction. The nearly temperature independent linewidth further suggests that the interaction between Mn and Cu is predominantly non dipolar.

A significant g-shift below 100 K indicates that the factors responsible for magnetic ordering have become operative in this range of temperature itself, in EPR time scale. This g-shift could come either due to onset of an anisotropic internal field with spin correlation time greater than 10^{-10} sec and/or due to spin delocalization onto an orbital with g less than 2.000. The shift of the resonance line to higher fields upon cooling right down to 15K might be due to one of the following reasons:

(i) Exchange of spins between Mn and Cu sites, analogous to the mechanism suggested by Gotchy[13] for $(TDAE)^{+}C_{60}^{-}$. This would not, however, lead to a g-shift to lower values unless Mn is in 4^{+} state. This possibility is therefore rejected.

(ii) The observed g-shift to lower values might be due both to short range effects and selective population of opposite spins of Mn^{II} and Cu^{II} with lowering of the temperature[16]. Continuance of the same trend in g(T) below T_c suggests that the same mechanism would have been operative throughout the temperature range 100 - 15 K.

The presence of two lines with an averaged central peak below 90 K continued right down to 18 K. One possible cause for the occurrence of these two lines can be the anisotropy of the internal field[12], with both parallel and perpendicular components showing up for the powdered sample. The other possibility, and which appears more likely, is that the equivalence of copper sites is gradually lost upon cooling below 100 K and the exchange interaction is different at these two sites. *This would be*

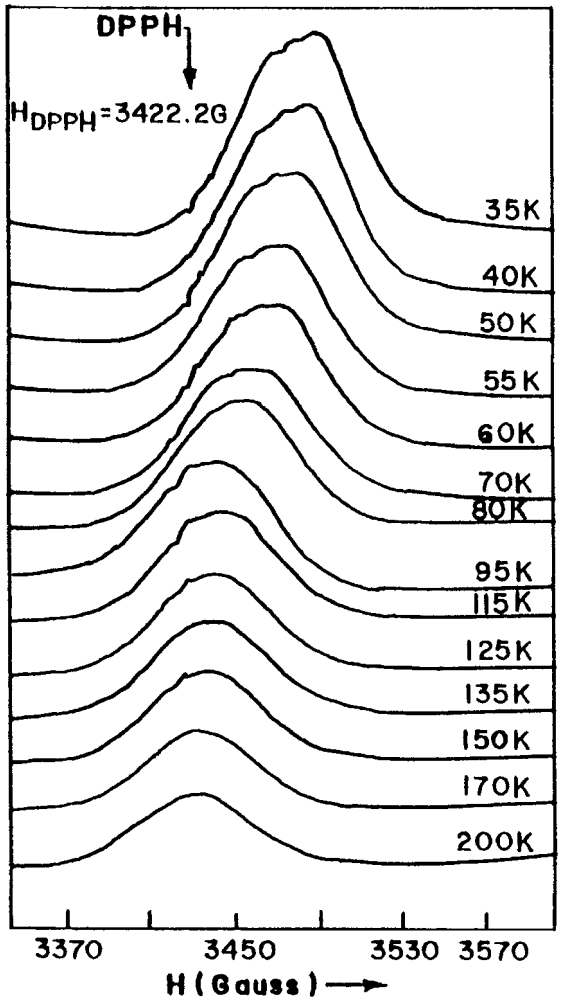

FIGURE 1 Second harmonic presentation of EPR spectra at different temperatures in the paramgnetic phase

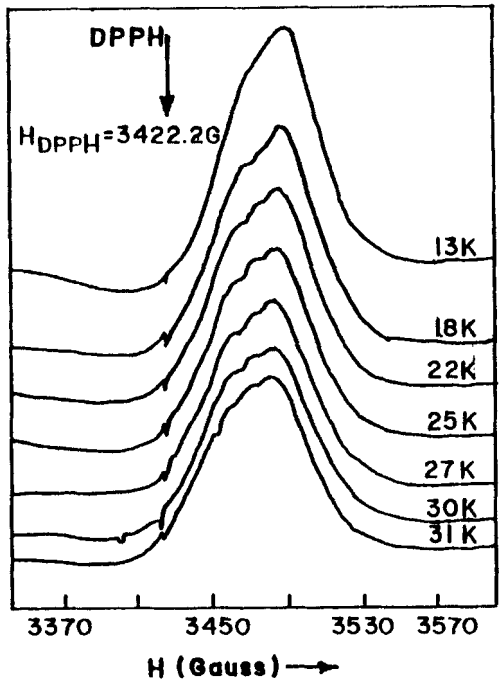

FIGURE 2 Second harmonic presentation of EPR spectra in the close vicinity of T_c. It may be noted that the intensity of the central component reduced with lowering of temperature

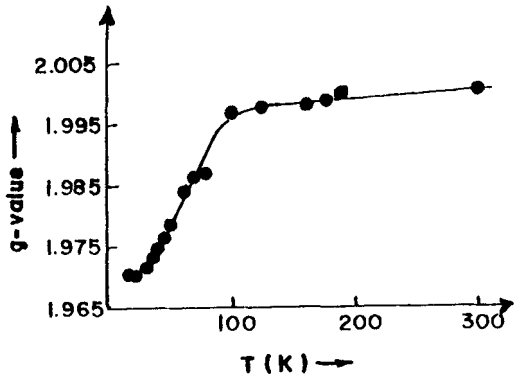

FIGURE 3 Temperature dependence of g - factor

a typical case of dynamic to static distortion. The inequivalence of Mn^{II} sites is ruled out as it would not result in two lines due to relative insensitivities of its g-value to site symmetry.

The spin fluctuations are occurring at a time longer than 10^{-10} sec. Therefore the spin exchange /correlation time in 100 - 15 K region is greater than 10^{-10}sec. Some evidence for spin fluctuations in $Mn^{II}Cu^{II}$ compounds far above T_c has been obtained by muon spin relaxation technique[17].

In summary, our EPR investigations show evidence for antiferromagnetic correlation in the title compound at temperatures as high as 100 K. The spin correlation time is greater than 10^{-10}sec. Evidence is also obtained for possible existence of dynamic inequivalence of copper sites which get slowed down resulting in static inequivalence at 15 K.

ACKNOWLEDGEMENTS

O.K. and J.V.Y. thank I.F.C.P.A.R. for Project Grant #1308-4 under which the work reported was carried out. S.A.C. would like to thank D.A.E. (India) for a Senior Research Fellowship.

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