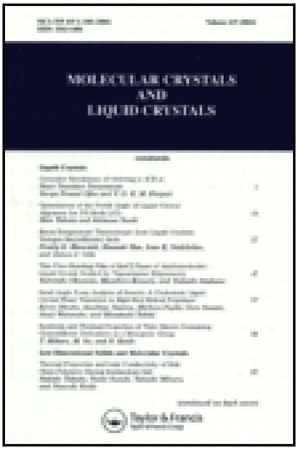

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Spin Flop Transition in the Substituted Mn-Porphyrin Magnet $[Mn(OC_{12}H_{25})_4TPP][TCNE]^{*}2PhMe$

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Spin Flop Transition in the Substituted Mn-Porphyrin Magnet $[Mn(OC_{12}H_{25})_4TPP][TCNE]*2PhMe$

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The modificated Mn-porphyrin magnet $[Mn(OC_{12}H_{25})_4TPP][TCNE]*$ solvent orders ferromagnetically at $T_c = 22$ K. Close to T_c transition to the spin glass-like state occurs. The coercive field H_c at $T = 2.3$ K equals 21 kOe but decreases quickly with temperature. In the paper the low temperature magnetization curves are investigated. The observed field induced magnetization jump we identify as the spin flop which is the transition from the longitudinal to the transverse spin glass state. The transition may come from the sign change of the anisotropy constant. The critical field for the transition decreases with temperature and equals zero for $T > 7.5$ K. Above 7.5 K magnetic uniaxial anisotropy is lost and a single ion anisotropy favours the ferromagnetic ordering of spins.

Keywords: Mn-porphyrin magnet; spin flop; magnetic anisotropy; spin glass

INTRODUCTION

Between the more intensely studied molecular magnets are the charge transfer salts based on Mn-porphyrin, like $[Mn^{III}(TPP)][TCNE]*$solvent, where TPP-tetraphenyloporphyrin, TCNE-tetracyanoethylene[1,2]. This compound is built of one-dimensional ferrimagnetic chains with alternating Mn-donor ($S = 2$) and TCNE-acceptor ($s = 1/2$) units, where S and s are appropriate spins. The ferromagnetic ordering temperature T_c is equal 18 K. Structure modifications, consisting in use of a different spinless solvent or a different acceptor and/or substitution of functional groups at the periphery of the porphyrin disc may change T_c and the other properties[3,4,5]. Solvent molecules usually incorporated into the structure give rise to random anisotropy and are the origin of the spin glass-like behaviour[6].

The subject of our investigation is [MnR$_4$TPP][TCNE]*2PhMe, where PhMe is toluene and R = $OC_{12}H_{25}$. Characterization of a magnetic ordering has been done[7,8] by means of AC susceptibility and DC magnetization measurements performed for polycrystalline samples. A sharp AC susceptibility peak at T_c = 22 K and a remarkable hysteresis loop with a coercive field H_c = 5 kOe at T = 4.2 K (compared to 375 Oe at T = 5 K for a nonsubstituted compound[2]) have been observed[7,8]. Of the special interest was a magnetization jump at the virgin curve identified as the spin flop. On the other hand, it was also found that H_c decreases quickly with temperature what would imply a strong change of a magnetization process with temperature, as well. At the end, the frequency dependence of AC susceptibility and an irreversibility of ZFC-FC magnetization *vs* T behaviour showed that we are dealing with the reentrant spin glass-like system. In the light of the facts above, it seemed interesting to investigate more carefully the low temperature magnetization process in order to understand the origin of the observed magnetization jump (i.e. spin flop) and to evaluate the role of the anisotropy.

EXPERIMENTAL

Synthesis of the sample is described in Ref.[5]. Magnetization measurements in the field up to ± 56 kOe were performed for zero field-cooled (ZFC) sample by means of the 7225 Lake Shore instrument using the extraction technique. The runs at temperatures below 4.2 K were perfomed with a helium vapour pump-out with an auxiliary vacuum pump. Time dependence of the isothermal magnetization was registered for the step-like increase of the magnetic field.

RESULTS

Figure 1 presents magnetization hysteresis loops at T = 2.3 K and T = 4.2 K for the investigated [Mn(R)$_4$TPP][TCNE]*2PhMe (R = $OC_{12}H_{25}$) sample together with the T = 4.2 K loop for R = CH_3 sample, shown for comparison. One can see that the magnetization process for the R = CH_3 sample is practically reversible, coercivity field H_c = 60 Oe is not visible in the used figure scale. Magnetization at H = 50 kOe is close to approaching the saturation value M_{sat} = 16800 cm^{3}G/mol = 3 μ_B/mol. For the compound substituted with R = $OC_{12}H_{25}$ one gets the high coercivity loop of the shape characteristic for the system with uniaxial anisotropy. At T = 2.3 K H_c = 21 kOe and the remanence M_r = 5900 cm^{3}G/mol what is less than 0.5*M_{sat}. At T = 4.2 K H_c = 5 kOe and M_r = 2900 cm^{3}G/mol.

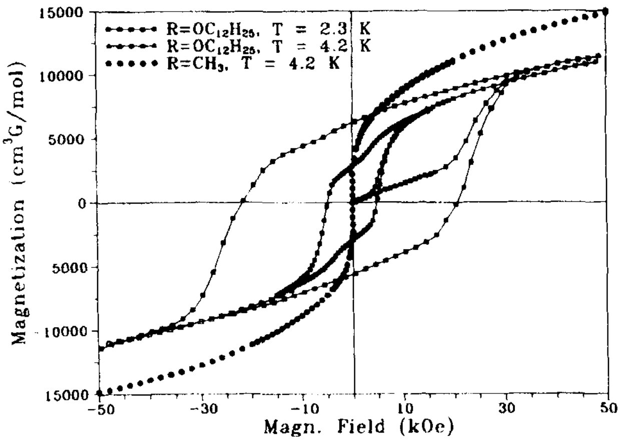

FIGURE 1 Magnetic hysteresis loops for R = $OC_{12}H_{25}$ at 2.3 K and 4.2 K. The loop for R = CH_3 at 4.2 K is shown for comparison.

It appeared that the remanence and coercivity decrease quickly with temperature. Figure 2 shows the determined temperature dependence of the hysteresis half width (i.e. coercive force). At first approach it is an exponential decay.

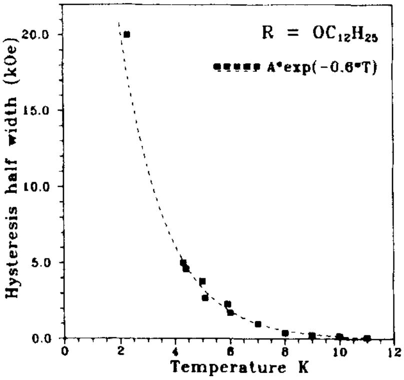

FIGURE 2 Temperature dependence of the hysteresis half width (= H_c).

In the case of our powder sample the virgin magnetization curves are smeared but it is doubtless that they differ from the S-shape curves observed for cannonical spin glasses. The magnetization jump, i.e. a rapid increase, starts at the critical field H_j. At the T = 2.3 K curve (Fig.1) one can distinguish three regions: (1) the first, linear part for $H < H_j \approx 19$ kOe where susceptibility is small and equals 0.15 cm^3/mol; (2) for $H \geq H_j$, where strong magnetization increase is observed; (3) for H > 30 kOe, the last part with slow, nonlinear increase, still far from saturation.

Figure 3a and Figure 3b show the change of the magnetization process with temperature. The initial susceptibility hardly changes with T but the critical field H_j falls down. This decrease is adequate to the H_c decrease. At T = 7.5 K the critical field for the jump equals zero, magnetization increase with the field starts with a high susceptibility but then shows some complexity which may be caused by the fact that in the system more than two sublattices are present.

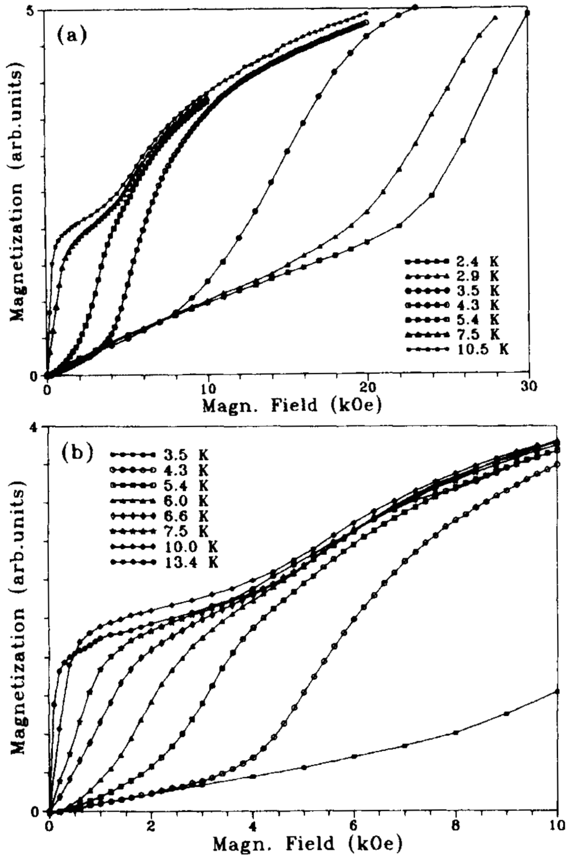

FIGURE 3 ZFC magnetization curves at the temperatures shown for the applied field (a) H up to 30 kOe, (b) H up to 10 kOe.

We have also registered the time dependence of isothermal magnetization after the step-like increase of the magnetic field. Figure 4 shows relaxation of the magnetization at 4.2 K for a given H sequence. The interesting fact was observed: for H = 4 kOe after the time t_c equal to about 2000 s the relaxation rate increased ca. 2.5 times. We have checked that such a double stage relaxation occured also for other temperatures (5 K, 6 K) and that t_c was dependent on T and on the field step.

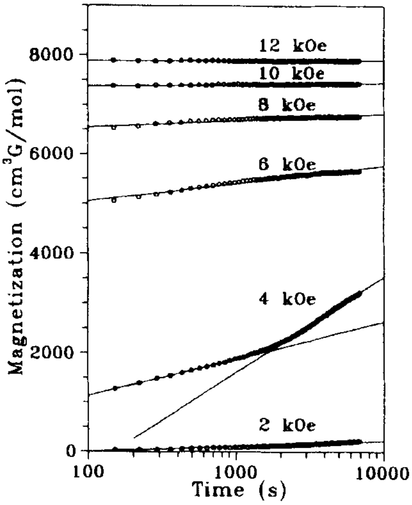

FIGURE 4 Time dependence of the magnetization at T = 4.2 K for the given field sequence.

DISCUSSION

The observed by us at low T field induced magnetization jump recalls the behaviour of metamagnets: for strong magnetocrystalline anisotropy, which prevents the spins from rotating away from the easy axis, at the threshold field a sharp magnetization jump up to M_{sat} with the spin reverse (spin flip) takes place; when the anisotropy is weaker, the transition proceeds through the change of the magnetization axis to the direction perpendicular to the filed (spin flop) and then by rotation of spins. There are examples of a metamagnetic (AFM → FM) spin flip transition observed for other chain based molecular magnets: among the others, for $[FeMe_5C_5)_2][TCNQ]$ metamagnet[9] (T_c = 2.55 K) and for [MnOEP][HCBD] antiferromagnet[10] (T_N = 22 K). Such a behaviour takes an origin in the antiferromagnetic interactions between the chains. However, our compound is ferromagnetic: it has high coercivity and the intensity of the AC susceptibility peak at T_c is the same as for other ferromagnets from the family. The two details of the hysteresis loop: M_r less than $0.5*M_{sat}$ and difficulty in obtaining saturation, may be natural for an amorphous magnet. Thus, we will have to take into consideration the relative magnitudes of all the interactions in our low-dimensional system not forgetting about the spin glass like properties.

The occurrence of a critical field for the magnetization jump points to the presence of the relatively strong anisotropy. In the Mn-porphyrin based magnets the interaction responsible for interchain magnetic coupling is, most probably[11], of the dipolar origin. This interaction is anisotropic and weak (T_c is determined both by inter- and intrachain coupling). The resulting spin configuration will depend on the interplay of: (a) interchain coupling energy (given by J), (b) random anisotropy due to the solvent, (c) single ion anisotropy, probably enhanced in our compound because of the increased intercolumnar distances[7], and of (d) the Zeeman term. It is most probable that at T = 0 the local environment of the Mn^{III} ion and the chain structure result in strong uniaxial anisotropy (along the chain axis) given by D, but this may change with temperature. We expect that in the investigated compound the change of the sign of anisotropy constant (from positive to negative) takes place with increasing temperature and this fact is crucial for spin configuration[11]: for $0\ K < T < 7.5\ K$ uniaxial anisotropy along the chain axis (D positive) favours the antiparallel spin configuration (state I), while for $T > 7.5\ K$ the uniaxial anisotropy is lost and the parallel spin alignment perpendicular to the chain axis is preferable (state II). The reason for such a strong anisotropy change *vs* temperature could be the changes in distribution of solvent molecules in the space between the chains which, in turn, may affect the interatomic distances. Applying strong enough magnetic field H_j transforms the spin system from state I to state II. H_j is strongly temperature dependent: falls down with T and for $T \geq 7.5\ K$ $H_j = 0$.

The influence of the uniaxial anisotropy on the resulting spin configuration has been considered also in the frames of the spin glass behaviour. It is known that single-ion uniaxial anisotropy also in spin glasses leads to a preferred "easy" axis of magnetization. It has been predicted by Cragg and Sherrington[11] that, depending on the D/J^* ratio, where J^* denotes the width of the exchange distribution, the longitudinal (L), transverse (T) or intermediate (L + T) spin glass order occurs. The limiting cases are: (i) $D \rightarrow + \infty$ (Ising), (ii) $D \rightarrow - \infty$ (planar XY) and (iii) $D = 0$ (Heisenberg) models. Magnetic susceptibility in the longitudinal spin glass (LSG) should be much weaker than for the transverse spin glass (TSG) or the Heisenberg type one. The slow magnetization increase at $T = 2.3$ K (Fig.1) for $H < H_j$ shows that for this field region we deal with LSG. For $H > H_j$ transition to TSG takes place followed by easier rotation of spins towards the field direction. The time dependence of isothermal magnetization at the critical field (see Figure 4) illustrates two stages of the transition: for time up to 2000 s a change from easy axis to easy plane anisoptropy takes plane and then is followed by spin rotation which occurs with a larger relaxation rate.

In summary, we conclude that observed at low temperatures for $[Mn(OC_{12}H_{25})_4TPP][TCNE]{\bullet}2PhMe$ the field induced magnetization jump comes from the spin flop which is the transition from the longitudinal to the transverse spin glass state. The transition probably comes from the sign change of the anisotropy constant with temperature and is due to the subtle interplay of the weak magnetic dipolar interaction and the anisotropies involved. The critical field for the transition decreases with temperature and for $T > 7.5$ K $H_j = 0$. Above 7.5 K magnetic uniaxial anisotropy is lost and a single ion anisotropy favours the ferromagnetic ordering of spins.

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