Low-energy excitations in electron-doped metal phthalocyanines

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Abstract

Magnetization and NMR relaxation measurements in $Li_x(Mn, Zn)Pc$ were performed in order to study the evolution of the electronic properties of metal phthalocyanines upon electron doping. For $x = 2$ the doubly degenerate lowest unoccupied molecular orbital (LUMO) is half filled and the electrons are coupled in a singlet state owing to the Jahn–Teller distortions. The effects of the Jahn–Teller distortions on the spin excitations are discussed in the light of NMR relaxation measurements.

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Recently alkali doped metal phthalocyanines (A_xMPcs) have been proposed as strongly correlated metals and some similarities with fullerides have been evidenced [1]. In particular, a transition to a metallic state and, possibly, to a superconducting one are expected as the condition of half filling of the doubly degenerate lowest unoccupied molecular orbital (LUMO) is approached, for $x = 2$. Although some experimental evidences of a metallic behaviour have been already observed in thin films [2], the investigation of bulk materials is still at a preliminary stage [3]. Hereafter we present an experimental study of β-Li_xMnPc and β-Li_xZnPc powders by means of magnetization and NMR relaxation measurements.

In the pristine compound MnPc the Mn^{2+} ions are in the intermediate $S = \frac{3}{2}$ spin ground state and the molecules are ferromagnetically coupled along the b axis, forming chains. At low temperature the magnetization slowly relaxes due to a sizeable Ising anisotropy [3]. By lightly doping with Li, for $x = 0.5$, the magnetic properties seem to be almost unchanged. For $T > 30$ K the susceptibility data can be fit by a Curie–Weiss law with a Curie constant $C = 2.342 \pm 0.001$ emu K/mol and $\Theta = 7.5 \pm 0.1$ K, indicating that the

coupling is still ferromagnetic. From the value of C, assuming a Landé factor close to 2, one estimates a spin per molecule larger than $\frac{3}{2}$. This increase has been suitably described as due to a disordered ensemble of fragmented chains [4]. The majority of segments is still in the pristine state with $S = \frac{3}{2}$, while in some segments two lithium ions per molecule allocate to reach the more stable configuration of Li_2MnPc. Accordingly, a local spin crossover to a high-spin state is expected.

The evolution of the spin state with doping can be further verified by directly measuring the magnetic susceptibility of Li_2MnPc. Results are shown in Fig. 1. The temperature dependent susceptibility follows a Fisher law [5], which is found for high-spin antiferromagnetic (AF) chains. From the fit with Fisher's law one effectively obtains $S = 2.07 \pm 0.01$ and $\Theta = -11.32 \pm 0.05$ K. The evolution from $S = \frac{3}{2}$ to $S \to \frac{5}{2}$ for $x = 2$ involves a modification in the energy levels. On one hand, each lithium injects an electron in the $2e_g$ LUMO and, on the other hand, the presence of the dopants deeply modifies the symmetry of the crystal field. In principle, several spin configurations should be considered. If Jahn–Teller (JT) coupling is lower than Hund coupling, the two electrons can form a triplet $S = 1$ state on the doubly degenerate LUMO without affecting the other levels. This aspect can be clarified by studying Li_xZnPcs, in which the magnetic

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properties are entirely determined by the filling of the LUMO, as the pristine ZnPc is diamagnetic. The magnetization measurements were performed on two samples with $x = 1.5$ and 1.8, both showing approximately Curie–Weiss behaviour (Fig. 1) with a number of effective Bohr magnetons per molecule vanishing for $x = 2$, as $p_{eff} \simeq (2 - x)\mu_B$. This clearly evidences that no triplet state is formed in the LUMO, but rather a formation of a localized $S = 0$ state or a delocalization of unpaired electron spins occurs. We can borrow this information to interpret Li_2MnPc spin configuration. If the electrons in the LUMO form an $S = 0$ state, in order to explain an $S \rightarrow \frac{5}{2}$ per molecule, at least one electron has to be promoted to the b_{1g} $d(x^2 - y^2)$ orbital lowered by the crystal field (Fig. 1). This would indicate that JT distortions remove the degeneracy of the LUMO and overcome Hund coupling, favouring the $S = 0$ state, a scenario which encourages the intriguing perspective of strongly correlated singlet superconductivity in A_xMPcs [1]. Further support to an $S = 0$ state in the LUMO is provided by NMR spin–lattice relaxation rate $(1/T_1)$ measurements presented in the following. In $Li_{0.5}MnPc$ one can distinguish two different spin dynamics [4]. In Li-depleted $S = \frac{3}{2}$ segments we found peaks in ^1H $1/T_1$ at low temperature due to the freezing of Mn spins, induced by the Ising anisotropy. On the contrary, in Li-rich segments both ^1H and ^7Li $1/T_1$ probe an activated electron hopping along the chains. This can be now verified in the more homogeneous compound Li_2MnPc. Recovery laws are characterized by a fast and a slow component. Fast relaxation is dominant for ^1H, while slow relaxation is dominant for ^7Li. This two relaxation rates are reported in Fig. 2. ^1H $1/T_1$ at high temperature is an order of magnitude larger than in $Li_{0.5}MnPc$. This cannot be simply ascribed to an increase of the hyperfine coupling since the powder NMR linewidths both of ^1H and ^7Li are comparable in the two compounds. On the contrary, this could be related to an enhancement of the low-frequency spectral density in Li_2MnPc. Low temperature peaks are not observed in $1/T_1$, confirming a modification in the crystal field at Mn^{2+} and a reduction of the Ising anisotropy. Quantitative estimates show that $1/T_1$ is much larger than the one expected for Mn^{2+} AF correlated dynamics. Furthermore, for $T < \Theta$ $1/T_1$ does not grow as one would expect in an $S = \frac{5}{2}$ AF chain [6] but rather decreases on cooling below $T \sim 50$ K, following an
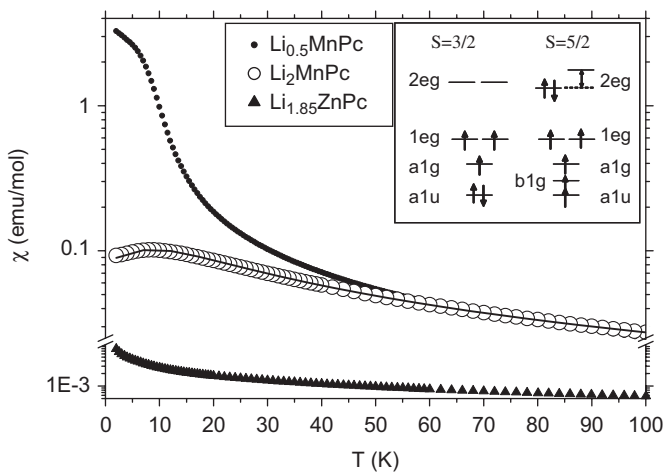

Fig. 1. Susceptibility of $Li_{0.5}MnPc$ and $Li_{1.85}ZnPc$ powders for $H = 1000$ Gauss and of Li_2MnPc powders, defined as the slope of $M(H)$, for $H = 4$ Tesla. Data were obtained with a SQUID Magnetometer. The solid line is a fit. The inset shows the electronic spin configurations of the ground states $S = \frac{3}{2}$ in MnPc and $S = \frac{5}{2}$ in Li_2MnPc (see text).

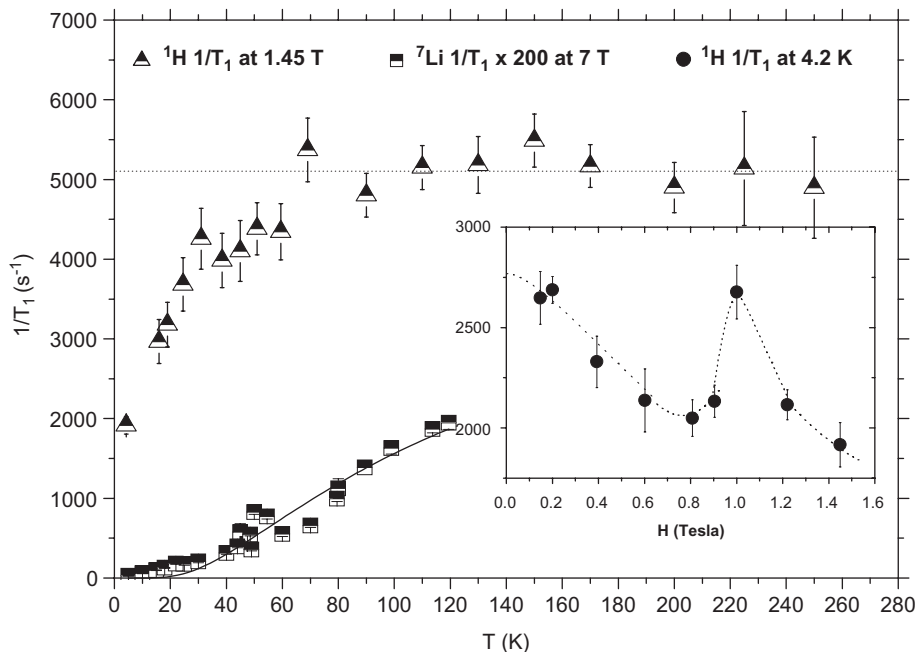Fig. 2. ^1H and ^7Li (multiplied by a factor of 200) $1/T_1(T)$ in Li_2MnPc. The inset shows ^1H $1/T_1$ vs. H at 4.2 K. The solid line is the best fit of ^7Li $1/T_1$. The dashed lines are guides to the eye.

activated behaviour (Fig. 2). We suggest that ^{7}Li $1/T_1$ probes mainly the spin fluctuations associated with an activated hopping determined by the gap $\triangle \simeq 100\,\mathrm{K}$ between the localized $S = 0$ and 1 states related to the JT and Hund couplings [7], in agreement with the interpretation of the susceptibility data. From ^{1}H $1/T_1$ one still observes a decrease for $T < 50\,\mathrm{K}$ and a plateau at high temperature, analogous to the one observed in K_4C_{60}[7]. This T-independent behaviour, characteristic of a paramagnet for $T \gg J$, the exchange coupling along the chain, can be associated with the fluctuations of the $S = 1$ spins in the LUMO, at a frequency $\omega_e = (Jk_B/\hbar)\sqrt{4S(S+1)/3}$ of the same order of magnitude of $\Delta k_B/\hbar$. Finally, besides a diffusive behaviour associated with the spin dynamics at low fields, $1/T_1$ vs. H at fixed temperature shows also a resonant peak around 1 Tesla whose origin still has to be clarified (inset of Fig. 2).

In conclusion, magnetization and NMR relaxation measurements in Li_2MnPc have clarified the spin configuration of the molecule in the presence of LUMO half filling. The comparison between Li_xMnPc and Li_xZnPc suggests that an $S = 0$ state associated with Jahn–Teller distortions is present in the $2e_g$ LUMO. By means of NMR $1/T_1$ it is possible to probe either the low-frequency excitations associated with the electron hopping or the correlated dynamics for the electrons in the $S = 1$ state.

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