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FERROMAGNETIC COUPLING IN THE LITHIUM PHTHALOCYANINE NEUTRAL \(\pi\)-RADICAL

Ph. Turek, M. Moussavi, J.-J. André and G. Fillion

Institut Charles Sadron (CNRS-ULP), 6 rue Boussingault, 67083 Strasbourg, France

Abstract. – Residual molecular dioxygen is shown to be responsible of a net ferromagnetic alignment of the neighbouring lithium phthalocyanine \(\pi\)-radicals. The consecutive localization of the spin system is characterized by a drastic broadening of the EPR absorption line.

The lithium phthalocyanine LiPc neutral \(\pi\)-radical has been shown previously to be an intrinsic semiconducting molecular compound [1]. An extremely narrow EPR absorption line has been evidenced and it has been attributed to very efficient spin exchange narrowing processes [2]. Whereas the conducting properties are not affected by the air exposure the magnetic properties are strongly dependent upon the presence of air [2].

The present contribution reports on magnetization measurements performed on different air-evacuated samples of LiPc at low temperature (2-10 K) in the 1-40 kOe field range with the help of SQUID susceptometers and on EPR studies performed in the 10-300 K temperature range. The differences between the samples (hereafter denoted by I, II and III) result either from their different crystallinity or from different electrosynthesis routes [3]. The efficiency of the vacuum will be shown to differ from sample to sample. Sample I has been grown in acetone and is a powder. Sample II has been grown in acetonitrile and consists in well defined crystalline materials whose structure is isotypic with that previously reported [4, 5]. Sample III was grown in the same conditions as sample II but it consists in different batches (powder and crystals).

The magnetization curves are represented in figure 1 for all samples. A saturation behaviour is clearly seen and the whole results are well fitted by the Brillouin function \(B_J(x)\) for \(J = 3\):

\[
M = M_S B_J(x),
\]

where \(x = g_J \mu_B J H/k_B T\), \(M_S = N g_J \mu_B J\), and \(J = L + S\) as given in standard notations. The data are normalized to the respective extrapolated saturation magnetizations \(M_S\) reported in table I. The deviation observed for \(T = 1.85\) K in the high \(H/T\) range may be related to the great inhomogeneity of sample III and may be indicative of an evolution towards superparamagnetism. As usual for \(\pi\)-electrons the role of the orbital moment \(L\) is neglected, i.e. \(J = S = 3\). Such a high spin multiplicity in an organic \(\pi\)-radical compound is exceptional because it involves a ferromagnetic coupling between the 1/2-spin \(\pi\)-radicals. The way to stabilize ferromagnetic interactions in organic

1Laboratoire Louis Néel, C.N.R.S., BP 166 X, 38042 Grenoble Cedex, France.
compounds is of current interest and the study of precursors has been recently reported [6-8].

The variation of the EPR peak-to-peak linewidth $\Delta H_{pp}$ with the temperature is represented in figure 2 for an air-evacuated crystal of sample II. The observed behaviour is similar to that previously reported on polycrystalline samples [2]. A large broadening of $\Delta H_{pp}$ is observed below c.a. 50 K which is the approximate range of validity of a Curie-Weiss law for this material [9]. The linewidth at room temperature under vacuum is considerably smaller (16 mOe) than that observed in a powdered compound (100 mOe). Owing to the crystalline structure (Fig. 3), molecular oxygen may easily diffuse through the free channels between the stacking of the macrocycles. The observation of the reversibility and of the rapidity of successive absorption/desorption processes favors our proposal for the diffusion pathes of $O_2$ in LiPc.

Dioxygen is a paramagnetic species with spin $S_1 = 1$. The septet state evidenced by the magnetization curves is therefore attributed to the magnetic interactions of $S_1$ with the $\tau$-spins ($S_2 = 1/2$) and may result either from an antiferromagnetic coupling ($8S_2 - S_1$) or from a ferromagnetic coupling ($4S_2 + S_1$). The net LiPc-LiPc interaction is locally ferromagnetic in both cases. It is responsible of the broadening of the EPR line either at low temperature or when the samples are exposed to air. Note in table I the different $O_2$ concentrations derived from this analysis. The efficiency of the vacuum depends strongly upon the crystallinity of the materials. The search for bulk ferromagnetism in the fully $O_2$ exposed system is currently under progress.

Fig. 3. – Schematic view of the inclusion sites/diffusion pathes of $O_2$ in the crystalline structure of LiPc (courtesy of J. Fisher et al. [4]). The indicated Van der Waals contours define the diffusion channel surrounding the $O_2$ molecules.

[9] Turek, P. et al., to be published.