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To cite this version:

P. Petit, J.-J. André. LOW DIMENSIONAL MOLECULAR SEMICONDUCTORS: CRYSTALS OF LUTETIUM BISPHTHALOCYANINE RADICAL. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-833-C8-834. <10.1051/jphyscol:19888375>. <jpa-00228559>

HAL Id: jpa-00228559
https://hal.archives-ouvertes.fr/jpa-00228559
Submitted on 1 Jan 1988

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LOW DIMENSIONAL MOLECULAR SEMICONDUCTORS: CRYSTALS OF LUTETIUM BISPHALOCYANINE RADICAL

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Abstract. – The lutetium bisphthalocyanine π-radicals are available in two different crystalline structures which are clearly related to different low-dimensional spin diffusions. On the opposite, the conductivity of these molecular semiconductors appears to be isotropic.

The lutetium bisphthalocyanine PcLu is a sandwich type molecule composed of two staggered phthalocyanines coordinated to a Lu³⁺ central ion [1]. This molecule has been shown to be a π-radical: P₃⁻Lu³⁺ [2, 4].

From this molecule, two different crystalline structures are available (Fig. 1). In the first one, the PcLu molecules are regularly stacked and parallel in the c direction (long axis of the crystals) and the material is solvated (PcLu.CH₂Cl₂) [1]. The second one shows an arrangement of parallel molecules in the (ac) planes (perpendicular to the long axis of the crystals), and the material is unsolvated (PcLu) [5].

These two materials are spin localized systems [3, 6, 7], and, in view of their crystalline structures, an anisotropy of the magnetic interactions between π-electrons belonging to successive molecules is expected. The analysis of the anisotropy of the E.S.R. linewidth has been performed in order to determine the dimensionality of spin diffusion in these systems. The results obtained on PcLu.CH₂Cl₂ [6] are shown in figure 2a and are very well fitted by:

$$\Delta H_{1/2} = 0.08 \left| 3 \cos^2 \theta - 1 \right|^{4/3} + 0.57$$

where $\theta$ is the angle between the applied magnetic field and the c axis of the crystal: it characterizes a one-dimensional spin diffusion [8, 9]. Figure 2b shows the anisotropy of the E.S.R. linewidth of the unsolvated material PcLu [7] and the experimental values are in this case fitted by:

$$\Delta H_{1/2} = 0.113 \left( 3 \cos^2 \theta - 1 \right)^2 + 1.254$$

where $\theta$ is the angle between the applied magnetic field and the b axis; it characterizes a two-dimensional spin diffusion [8, 9]. It must be noted that only secular terms appear in these fits indicating a strong intrachain (intraplane) spin interaction compared to the interchain (interplane) one in the solvated (unsolvated) system. However, no experimental data allow us to evaluate the ratio of these interactions.

The analysis of the lineshapes of PcLu has been carried out [7] and shows a Lorentzian shape on more than 10 peak-to-peak linewidths for the 55° orientation while a deviation from the Lorentzian shape is observed after 4 linewidths for the 0° orientation, confirming the low dimensional nature of spin diffusion [8, 9]. The ESR experiments, to-

Fig. 1. – Schematic view of the stacking of the PcLu molecules: (a) in the solvated crystals; (b) in the unsolvated crystals.
Fig. 2. – Anisotropy of the half linewidth at half maximum as a function of the orientation in the magnetic field of: (a) the solvated system; (b) the unsolvated system.

gether with the crystalline structures, lead to interpret these results in terms of one-dimensional spin diffusion in Pc2Lu·CH2Cl2 and of a two-dimensional one in Pc2Lu. RMN studies of the spin lattice relaxation time as a function of frequency on these systems and other phthalocyanine derivatives (yttrium bisphthalocyanine for example) are under progress and confirm the ESR studies. Clear dimensionality effects on RMN spectra on such π-radicals available in two drastically different stackings is exceptional.

Conductivity measurements on crystals of Pc2Lu·CH2Cl2 have shown this system to be an intrinsic semiconductor [3, 4, 6]. The room temperature conductivity of this material is σRT = 6 × 10^{-6} Ω^{-1} cm^{-1} and its activation energy is of ΔE_{act} = 0.32 eV (σ = σ0 exp − ΔE_{act}/kT). Crystals of Pc2Lu, on the contrary, are extrinsic semiconductors [3, 7] with σRT = 5.3 × 10^{-8} Ω^{-1} cm^{-1} and ΔE_{act} = 0.13 eV. From these studies, it is not possible to compare the electrical behaviour of these two materials, and therefore, no conclusion may be drawn concerning the role of the packing of the molecules on the macroscopic electrical conductivities. However, the electrical properties of crystals of Pc2Lu·CH2Cl2 are very closed to those of thin films of evaporated Pc2Lu [10] (same room temperature conductivity, same activation energy, very small frequency dependence of σRT), which tend to demonstrate that the conduction process is insensitive on the detail of the molecular packing and suggest that these materials are isotropic semiconductors.