LOW DIMENSIONAL MOLECULAR SEMICONDUCTORS: CRYSTALS OF LUTETIUM BISPHTHALOCYANINE RADICAL

P. Petit, J.-J. André

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

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
LOW DIMENSIONAL MOLECULAR SEMICONDUCTORS: CRYSTALS OF LUTETIUM BISPHTHALOCYANINE RADICAL

P. Petit and J.-J. André
Institut C. Sadron, CNRS, 6 rue Boussingault, 67083 Strasbourg Cedex, France

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 \( \text{Pc}_2\text{Lu} \) is a sandwich type molecule composed of two staggered phthalocyanines coordinated to a \( \text{Lu}^{3+} \) central ion [1]. This molecule has been shown to be a π-radical: \( \text{Pc}_2^\ominus\text{Lu}^{3+} \) [2, 4].

From this molecule, two different crystalline structures are available (Fig. 1). In the first one, the \( \text{Pc}_2\text{Lu} \) molecules are regularly stacked and parallel in the \( c \) direction (long axis of the crystals) and the material is solvated (\( \text{Pc}_2\text{Lu} \cdot \text{CH}_2\text{Cl}_2 \)) [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 (\( \text{Pc}_2\text{Lu} \)) [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 \( \text{Pc}_2\text{Lu} \cdot \text{CH}_2\text{Cl}_2 \) [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 \( \text{Pc}_2\text{Lu} \) [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 \( \text{Pc}_2\text{Lu} \) 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. 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.

together with the crystalline structures, lead to interpret these results in terms of one-dimensional spin diffusion in P$_2$Lu·CH$_2$Cl$_2$ and of a two-dimensional one in P$_2$Lu. 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 ESR spectra on such π-radicals available in two drastically different stackings is exceptional.

Conductivity measurements on crystals of P$_2$Lu·CH$_2$Cl$_2$ have shown this system to be an intrinsic semiconductor [3, 4, 6]. The room temperature conductivity of this material is $\sigma_{RT} = 6 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and its activation energy is of $\Delta E_{\text{act}} = 0.32$ eV ($\sigma = \sigma_0 \exp(-\Delta E_{\text{act}}/kT)$). Crystals of P$_2$Lu, on the contrary, are extrinsic semiconductors [3, 7] with $\sigma_{RT} = 5.3 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ and $\Delta E_{\text{act}} = 0.13$ 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 P$_2$Lu·CH$_2$Cl$_2$ are very closed to those of thin films of evaporated P$_2$Lu [10] (same room temperature conductivity, same activation energy, very small frequency dependence of $\sigma_{RT}$), 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.