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Low dimensional molecular semiconductor.  
II. the two-dimensional radicalar bisphthalocyaninato lutetium Pc2Lu (*)

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Résumé. — Nous présentons dans cet article des résultats concernant le magnétisme et les propriétés de conduction des cristaux de bisphthalocyanine de lutécium non solvatés, Pc2Lu. La structure cristalline et l'étude par RPE de ce système révèlent une diffusion de spins bidimensionnelle. Les mesures de conductivité montrent que les cristaux de Pc2Lu sont des semiconducteurs moléculaires extrinsèques.

Abstract. — This paper deals with the magnetic and electrical properties of the unsolvated crystals of bisphthalocyaninato lutetium, Pc2Lu. The crystalline structure and the magnetic properties determined by ESR reveal a bidimensional spin diffusion in this system. The conductivity measurements show that Pc2Lu crystals are extrinsic molecular semiconductors.

1. Introduction.
Radicalar phthalocyanine derivatives have been shown to form a new class of semiconductors: the molecular semiconductors [2]. Two different examples have been studied in details. The first one is a narrow band semiconductor: the bisphthalocyaninato lutetium Pc2Lu [2], the other one is a broad band narrow gap semiconductor: the lithium monophthalocyanine PClLi [4]. In the former case, the intrinsic nature of the electrical properties has been unambiguously established [3, 5-9]. The π-nature of the unpaired electron of this system has been proved [3, 8].

Reported results only concern the solvated system, Pc2Lu.CH2Cl2 which behaves as a Heisenberg paramagnet exhibiting a one-dimensional spin diffusion [1] and as a three-dimensional semiconductor [7, 8]. The one-dimensional spin diffusion has been deduced from its crystalline structure and its magnetic behaviour. The very close electrical properties of thin films of evaporated Pc2Lu and crystals of Pc2Lu.CH2Cl2 (similar electronic structure, similar activation energy and very small frequency dependence of the room temperature conductivity) show the weak sensitivity of conduction process on the detail of molecular packing.

This independence between electrical and magnetic properties is also revealed on the Pc2Lu.CH2Cl2 system by the reversible oxygen effect observed on the ESR linewidth whereas the presence of this impurity does not affect the conductivity [3, 1], contrary to the insulating similar systems for which oxygen acts as an electron acceptor dopant, as revealed by a strong increased conductivity and modified characteristics of metallophthalocyanine-based Schottky contacts [10-13].

It is then tempting to extend the study to Pc2Lu in an other available type of packing: single crystals of unsolvated bisphthalocyaninato lutetium, referred as Pc2Lu. Crystals of bisphthalocyaninato lutetium being obtained by recrystallisation, a polymorphism is however observed, depending on the experimental conditions. This paper deals with the magnetic and electrical properties of the unsolvated Pc2Lu, which crystalline structure differs from the solvated material [14, 15].

The Pc2Lu molecule is a sandwich type molecule, composed of two staggered phthalocyanines coordinated to a lutetium atom (Lu\textsuperscript{III}) [14] (Fig. 1). The pure (unsolvated) material, referred as Pc2Lu, is obtained by precipitation of the molecules in chloroform [15]. Its crystalline form has been de-
scribed by A. N. Darouskikh et al. [16] and shows an arrangement of parallel molecules in the (ac) planes [17] (Fig. 2). This crystalline structure should induce very weak interactions between π-electrons of molecules belonging to successive planes, compared to the intraplane interactions.

Fig. 2. — Schematic crystal packing in Pc₂Lu structure (ac plane), after [16, 17]: \( a = 10.553 \, \text{Å} \); \( c = 8.959 \, \text{Å} \).

2. Magnetic properties of Pc₂Lu.

In solid state, the ESR signal is composed of a single unresolved line near the free electron. Its intensity corresponds to the presence of one spin 1/2 per Pc₂Lu molecule, as found in solution [3], indicating that the overlap between two adjacent molecules is weak as compared to the Coulomb repulsion of two electrons on the same molecule. Thus this system can be described within a Hubbard model in the atomic limit.

All the reported ESR experiments were performed on single crystals at low power and modulation amplitude in order to avoid saturation and distortion effects, on a Brucker ER420 X-band spectrometer. The temperature dependence of the unpaired π-electron magnetic susceptibility determined by integration of the ESR signal follows a Curie-Weiss law on the whole temperature range (20-300 K). The lineshape of this signal is nearly Lorentzian indicating strong spin exchange interactions in this material. This system will then be assimilated to a Heisenberg paramagnet. Contrary to the solvated one, no notable effect related to the presence of oxygen is observed on these single crystals: the linewidth increase is less than 0.03 Gauss when the vacuum sealed samples are exposed to air. This different oxygen effect on the two systems (solvated and unsolvated) is probably due to the difference in the specific area of the materials which is very high in the case of solvated crystals [1].

In view of the stacking of molecules in this system, an anisotropy of the magnetic interactions is expected. In such low dimensional magnetic systems, both ESR lineshape and linewidth will depend on the spectral density \( \Gamma(\omega) \) of correlation functions involving four spin operators [18]. These correlation functions are governed by spin diffusion at long time [19] and vary as \( |t|^{-d/2} \) as \( t \to \infty \), introducing a divergence of the spectral density for low dimensional systems. This behaviour leads to particular dependence of both linewidth and lineshape with the sample orientation in the magnetic field.

In the case of a 2D system, the linewidth is given by [20, 21]:

\[
\Delta H = \omega_{\alpha}^2 [F_{\alpha}^0 \Gamma(0) + 10 F_{\alpha}^2 \Gamma(\omega_0) + F_{\alpha}^2 \Gamma(2 \omega_0)]
\]

where \( \omega_{\alpha} \) and \( F_{\alpha} \) are the characteristic frequency and the geometrical coefficients associated with the dipolar couplings respectively. This expression can be rewritten as:

\[
\Delta H = \alpha (3 \cos^2 \theta - 1)^2 +
\]

\[+ \beta \cos^2 \theta \sin^2 \theta + \gamma \sin^4 \theta + \delta \]

where \( \theta \) is the angle between the magnetic field and the normal of the magnetic planes and \( \alpha, \beta, \gamma, \) and \( \delta \) are constants.

The lineshape of a 2D system is Lorentzian at the magic angle (55°) and deviates from a Lorentzian for the other orientations. In particular, at 0°, the lineshape is given by the Fourier transform of a logarithmic expression.

The anisotropy of the linewidth of Pc₂Lu with the orientation of the sample in the magnetic field is shown in figure 3, where \( \theta \) is the angle between the magnetic field and the long axis of the crystal which is normal to the magnetic planes (b axis). Experimental data are well fitted by:

\[
\Delta H = 0.113 (3 \cos^2 \theta - 1)^2 + 1.254 \text{ gauss} .
\]

It should be noted that only the secular term appears in this fit. The relative importance of the constant term is probably due to the important delocalization of the electronic spin on each molecule which
Fig. 3. — Variation of the half linewidth at half height, \( \Delta H_{1/2} \), expressed in Gauss as a function of the orientation between the normal to the magnetic planes (ac) and the magnetic field at room temperature.

\[
\Delta H_{1/2} = 0.11 (3 \cos^2 \theta - 1)^2 + 1.25 \quad \text{(full line : 2D)}
\]
\[
\Delta H_{1/2} = 0.19 |3 \cos^2 \theta - 1|^{1/3} + 1.20 \quad \text{(dotted line : 1D)}
\]

prevent vanishing of the dipolar term at the magic angle [22]. The dotted line represents the best fit obtained with an expression corresponding to the angular dependence of the linewidth for a system in which spin diffusion is one-dimensional.

Figure 4 shows the angular dependence of the square of the \( g \)-factor associated with the observed anisotropy of \( \Delta H \). This anisotropy of \( g^2 \) is fitted by:

\[
g^2 = g_{xx}^2 \cos^2 \theta + g_{yy}^2 \cos \theta \sin \theta + g_{zz}^2 \sin^2 \theta
\]

with

\[
g_{xx}^2 = 4.0083 \quad g_{yy}^2 = 0.0001 \quad g_{zz}^2 = 4.0064
\]

The long axis of the crystals (b axis) is a principal axis of the \( g \)-tensor; \( g_{xx} \) is non degenerated and \( g_{zz} \) is twice degenerated [23]. This result demonstrates the correct orientation of the samples in the magnetic field, i.e. the crystals long axis is normal to the magnetic planes.

The anisotropy of the linewidth as a function of the azimuthal angle \( \varphi \), i.e. in the magnetic planes, shows a very weak variation of \( \Delta H \) of total amplitude less than 0.04 gauss, confirming the two dimensional nature of the system [20].

In such localized spin systems, the low-dimensional character of the spin diffusion is unambiguously demonstrated by the deviation of the ESR lineshape from the classical 3D lorentzian line; this shape should only be observed at the magic angle. The analysis of the lineshapes for two orientations \(( \theta = 55^\circ \) and \( \theta = 0^\circ \)) are shown in figure 5. The derivative of the ESR absorption time the magnetic field at a power 3 is plotted as a function of the magnetic field [24]. In the case of a lorentzian shape, i.e. for the 55\(^{\circ}\) orientation, a constant is obtained, whereas for the 0\(^{\circ}\) orientation a deviation from a lorentzian is observed after four linewidths confirming the low-dimensional nature of the spin diffusion in this system.

Fig. 4. — Variation of the square \( g \)-factor as a function of the orientation between the normal to the magnetic planes and the magnetic field at room temperature. Full line : fit discussed in the text.

Fig. 5. — \((H - H_0)^3 \times Y'(H)\) versus \((H - H_0)/\Delta H_{pp}\) at room temperature : a) for the 55\(^{\circ}\) orientation ; b) for the 0\(^{\circ}\) orientation (see Fig. 3).
The linewidth anisotropy for several temperatures between 300 and 100 K is given in figure 6. We observe a significant increase of $\Delta H$ for $\theta = 0^\circ$ and $\theta = 90^\circ$, whereas its value is constant for the $55^\circ$ orientation. This evolution of the linewidth anisotropy is attributed to an anisotropic lattice contraction. However, it should be noted that the ratio $\Delta H(0^\circ)/\Delta H(90^\circ)$ is constant on this temperature range, as reported for rigid lattices [20].

![Figure 6](image)

Fig. 6. — Variation of $\Delta H_{\theta \parallel}$ as a function of the orientation between the normal to the magnetic planes and the magnetic field for several temperatures (300, 250, 200, 150, 100 K).

3. Electrical properties.

Electrical conductivity measurements on single crystals (typical size: $1 \times 0.08 \times 0.05$ mm$^3$) were performed by two methods: d.c. measurements with two contacts realized with silver paint and 5 µ diameter gold threads and a.c. measurements (10 GHz) [25] on an apparatus built in the laboratory. The variation of the d.c. conductivity as a function of the temperature is shown in figure 7. A room temperature d.c. conductivity of $5.3 \times 10^{-5}$ Ω$^{-1}$ cm$^{-1}$ is measured and, assuming that the conductivity follows an exponential law:

$$\sigma = \sigma_0 \exp\left(-\frac{E_{\text{act}}}{kT}\right)$$

where $k$ is the Boltzman's constant, an activation energy of 0.13 eV is found. However, these values depend on the electric field intensity and are not intrinsic characteristics of the materials. This fact is corroborated by the frequency dependence of the conductivity, an a.c. value of the room temperature conductivity of $2 \times 10^{-3}$ Ω$^{-1}$. cm$^{-1}$ being measured.

4. Discussion.

The ESR studies of the unsolvated bisphthalocyaninato lutetium, $\text{Pc}_2\text{Lu}$, have shown that this system is comparable to a Heisenberg paramagnet. We have shown that, according to the crystalline structure, the ESR linewidth follows a variation with the orientation of the crystal in the applied magnetic field characteristic of a two dimensional spin diffusion system. This result is confirmed by the lineshapes analysis which shows a deviation from the lorentzian for the $0^\circ$ orientation, characteristic of low dimensional spin diffusion. In this system, the intraplane spin exchange interaction $J$ is very large as compared to the interplane interaction $J'$. However, no experimental data allow us to determine the ratio $J/J'$. To our knowledge, this system and the corresponding solvated one [1] are the first examples of pure molecular π-systems exhibiting such dimensionality effects; reciprocally, these studies show the extensibility of the theories developed for d-electrons systems. Such low dimensional features have also been recently observed in cation radical salts [26]. Concerning the electrical properties of $\text{Pc}_2\text{Lu}$, we have shown that these crystals are extrinsic molecular semiconductors; the presence of impurities and structural disorder being revealed by the dependence of the conductivity on the intensity and the frequency of the applied electrical field. Therefore, it is not possible to compare the electrical behaviour of these 2D single crystals to the 1D solvated $\text{Pc}_2\text{Lu}$ crystals; no conclusion can be drawn concerning the role of the packing on the macroscopic electrical properties.

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