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# EPR study of the x, $\alpha$ and $\beta$ structures of lithium phthalocyanine

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The magnetic properties of the lithium phthalocyanine radical are investigated for the x, $\alpha$ and $\beta$ crystal structures *via* electron paramagnetic resonance (EPR). Different magnetic behaviours (susceptibility, line shape) are evidenced in PcLi powders and interpreted in terms of the molecular packing. A Curie–Weiss susceptibility is observed for the $\alpha$-phase with a mean-field temperature, $T_{CW}$ of *ca.* $4.5 \pm 1$ K, whereas a two-component susceptibility must be considered for the x-phase (powders grown in acetonitrile) involving a Curie–Weiss contribution ($T_{CW}$ *ca.* $-3 \pm 1$ K) and a thermally activated contribution with an activation energy $E_a$ of *ca.* 0.04 eV. For the PcLi $\beta$ structure two temperature domains can be distinguished: for $T > 50$ K a Curie–Weiss susceptibility with a mean-field temperature $T_{CW}$ of *ca.* $-60 \pm 5$ K is observed while for $T < 20$ K a Curie–Weiss-like susceptibility with $T_{CW}$ *ca.* $-7 \pm 1$ K dominates. The overall magnetic properties of the PcLi polymorphs are discussed in terms of McConnell's mechanism for ferromagnetism and antiferromagnetism in solid free radicals. The magnetic properties of $\beta$-PcLi needles (magnetic susceptibility, anisotropy of spin diffusion) have been investigated. Adsorbed oxygen is shown to alter strongly the line shape, the linewidth and the $g$-factor anisotropy in $\beta$-PcLi crystallites and powders at temperatures below 55 K.

Among the unsubstituted and undoped phthalocyanines, lithium phthalocyanine (PcLi) shows both exceptional magnetic and electrical properties.[1] It is a stable neutral radical and one of the few intrinsic molecular semiconductors. The optical, magnetic and structural properties have been extensively studied in solution[2] and in the solid state for the tetragonal x structure in powders and single crystals.[3–5] In particular EPR studies have shown that the extremely narrow EPR linewidth of the x structure powders under vacuum is broadened with increasing dioxygen pressure. Recent work[6,7] has paid attention to the peculiar polymorphism of PcLi in thin films and powders which affects among other properties its sensitivity to the presence of $O_2$. At least two structures were evidenced in powders and thin films: (i) the PcLi x polymorph which shows a tetragonal unit cell with parameters $a = b = 1.385$ nm, $c = 0.65$ nm and space group $P4/mcc$[8a,b] and (ii) the $\alpha$ structure of PcLi which shows a monoclinic unit cell with parameters $a = 2.57$ nm, $b = 0.381$ nm, $c = 2.36$ nm, $\beta = 91°$ and space group $C2/c$.[9] Beside these two structures, the monoclinic $\beta$ form of PcLi has been reported in powders by Homborg *et al.* (unit cell parameters are $a = 1.94$ nm, $b = 0.49$ nm, $c = 1.46$ nm and $\beta = 120.36°$ and space group $P2_1/c$).[10] As a consequence, PcLi appears as the only unsusbtituted and undoped phthalocyanine occurring in all the three structures x, $\alpha$ and $\beta$ since the $\alpha$ and $\beta$ structures are observed in the undoped compounds and the tetragonal structure in the only doped compounds.[11,12] The oxygen sensitivities of the x and $\alpha$ structures have also been investigated for thin films and powders and it appeared that (i) the oxygen diffusion is possible in the tetragonal x structure owing to the presence of diffusion channels, (ii) this diffusion is ruled out in the case of the $\alpha$ structure owing to the molecular packing.[6,13] Detailed EPR studies on PcLi thin films grown on glass or mica substrate[6,9] evidenced the low dimensionality of spin diffusion as well as the important role of the demagnetizing field on the temperature dependence of the $g$-factor and line shape.[14]

The aim of the present work is to highlight the magnetostructural correlations in PcLi (x, $\alpha$ and $\beta$ structures) and especially to see how the various stacking modes of PcLi molecules affect the magnetic properties (see Fig. 1). We also present a detailed study of the magnetic properties of $\beta$ PcLi needles. The EPR signal anisotropy as well as the effect of oxygen at $T < 55$ K are investigated.

## Sample preparation and experimental procedure

### Synthesis

The x and $\alpha$ PcLi powders were obtained by two different electrochemical procedures. The first was to synthesise PcLi by electrochemical oxidation of $PcLi_2$ in acetonitrile as previously described.[7] In the present case, we used tetraethylammonium perchlorate as the conducting salt. The second type of PcLi powder was obtained by electrochemical reduction of phthalodinitrile in ethanol as described by Petit *et al.*[15] The latter synthesis route leads to the $\alpha$ structure of PcLi. As reported in our previous work, elemental analysis gives satisfactory results for the x structure while for the $\alpha$ structure, some traces of unreacted phthalodinitrile and/or LiCl are observed.[6] However, the presence of the latter substances does not affect the magnetic properties of the $\alpha$ structure observed *via* EPR.

The x-form powders grown in acetonitrile show needle shaped microcrystallites of typical length 100–200 µm whereas those of the $\alpha$ powder are in general much smaller (10–20 µm).

The $\beta$ form of PcLi (powders and needles) was obtained *via* annealing under vacuum ($P < 10^{-5}$ Torr) of x-form powders in a molybdenum crucible kept at *ca.* 400 °C (sublimation temperature of PcLi). The heat-treated powders were abundantly rinsed with acetone such as to remove traces of $PcLi_2$ resulting from the prolonged heating of PcLi powders. The elemental analysis of the powders gives satisfactory results concerning carbon, nitrogen and hydrogen, only a small lithium excess is observed (Found: C = 74.12; H = 3.07; N = 21.24; Li = 1.54. Calc.: C = 73.30; H = 3.08; N = 21.58; Li = 1.38%) indicating the presence of trace of residual $PcLi_2$. After a prolonged heat-

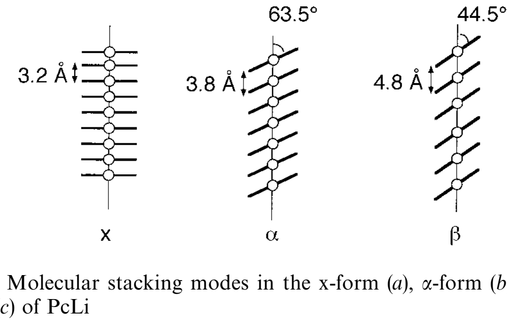

**Fig. 1** Molecular stacking modes in the x-form (*a*), $\alpha$-form (*b*) and $\beta$-form (*c*) of PcLi

treatment, small and flat needle shaped crystallites of size up to 1 mm × 0.08 mm × 0.08 mm are formed within the crucible. The small size of the crystallites did not allow for a complete structural study. Nevertheless, their structure was checked by X-ray diffraction ($2\theta$ powder diffractometer) for a selected batch of crystallites. The X-ray diagram has been simulated using the $\beta$ structure proposed by Brown[16] and the unit cell parameters given by Homborg.[10] The comparison between both diagrams indicates that the $\beta$ structure of PcLi is isostructural to other metallophthalocyanines PcM (Co, Cu, Ni, Zn, Pt).[17] Moreover, the X-ray analysis of the $\beta$-form needles indicates that the *b* axis (molecular stacking axis) coincides with the long axis of the needles[14] and the flat surface of the crystallites is assumed to be the (*a*,*b*) plane as reported for other metallophthalocyanines. Concerning the powders, only one diffraction peak of very small intensity corresponding to the (200) diffracting planes of the $\alpha$ structure is observed in $\beta$-form powders. The latter peak is due to some traces of isolated $\alpha$ crystallites also formed during thermal treatment of the x-form powders. Nevertheless, the larger crystallites are always in the $\beta$ form owing to size effects and no single crystals of the $\alpha$ form of PcLi have been reported.[18] Thus we exclude the presence of any polymorphism in the $\beta$-PcLi crystallites which is further supported by the EPR study at 300 K showing no signal of the x or $\alpha$ structure.

### Electron paramagnetic resonance

EPR spectroscopy was performed using a Bruker ER300 spectrometer equipped with a $TE_{102}$ cavity and an Oxford ESP300 cryostat. Data acquisition was achieved using a HP9000–360 computer. For the x and the $\beta$ form of PcLi, the powdered samples or the needles were kept under vacuum in a sealed quartz tube ($P < 10^{-3}$ Torr) such as to avoid any contacts with residual traces of $O_2$. A thermocouple [AuFe (0.3%)–chromel] was held in the vicinity of the quartz tube close to the sample. In the case of the $O_2$ insensitive $\alpha$-form powders and in order to check the oxygen effect at $T < 55$ K on PcLi $\beta$-form needles, the samples were held in the continuous helium flow within the cryostat. The *g*-factor was obtained from the direct measurements of the magnetic field at resonance by using a NMR gaussmeter and by measuring the microwave frequency (X band) by using an HP5053B frequency counter. The magnet field homogeneity and stability is higher than 30 mG leading to a *g*-factor uncertainty of less than $5 \times 10^{-5}$.

In the case of $\beta$-PcLi needles, the small and flat shaped crystallites were mounted on an EPR silent cubic Teflon holder with the flat surface of the crystallite [(*a*,*b*) plane] parallel to one of the cube faces (see Fig. 11). The direction perpendicular to the (*a*,*b*) plane is referred to as the ***c**** axis. Nevertheless it is not possible to ascertain the single-crystal nature of the crystallites since structural defects such as twinning along the stacking axis of phthalocyanine crystals are commonly observed.[19] The anisotropy of the EPR signal is studied in three perpendicular planes by changing the orientation of the cubic sample holder (see Fig. 11). The rotation angles are defined as follows: $\theta$ is the angle within the (*a*,*b*) plane located between the Zeeman field and the *b* axis (the $\theta = 0°$ direction is obtained when the needle axis ***b*** is parallel to the applied Zeeman field $B_0$), $\varphi$ and $\psi$ are the angles within the (*a*,*c**) and the (*b*,*c**) planes respectively (the $\varphi = 0°$ and $\psi = 0°$ orientations are obtained when the ***c**** direction is parallel to the $B_o$ field as shown in Fig. 11). The temperature dependences of the susceptibility were recorded for three orthogonal directions of the sample in the $B_0$ field namely ***a***, ***b*** and ***c****. The errors in the orientation of the crystallites within the EPR cavity are less than 10°.

## Results and Discussion

### Powders

**EPR line shape variation.** The various polymorphs of PcLi exhibit very different magnetic behaviours (Table 1). First, the line shapes at room temperature and at 4 K are different for the three polymorphs (Fig. 2). At room temperature and under vacuum, a narrow asymmetric signal with a half-width at half-maximum $\Delta H_{1/2}$ between 5.5 and 7.0 μT is observed for the x structure whereas the $\alpha$ and $\beta$ structures of PcLi exhibit both a Lorentzian-like signal of linewidth 130 μT and 80 μT, respectively. Even though the EPR signals of the $\alpha$ and $\beta$ structures are broader as compared to the x structure, the Lorentzian EPR lines are also exchange narrowed since a solution of purely isolated PcLi molecules in $\alpha$-chloronaphthalene exhibits a Gaussian line characterised by a linewidth of *ca.* 6 G at 395 K.[2] Exchange narrowing is the most efficient in the x structure because of strong $\pi$ molecular orbitals overlaps between successive molecules in the stacks along the *c* axis. The molecular orbital overlaps are quite important in the x structure. The molecules are stacked in a face-to-face configuration such as the C···C distance between successive molecules in a column is shorter than the C···C Van der Waals distance (Fig. 1) (3.21 *vs.* 3.45 Å respectively). As opposed to this, in the $\alpha$ and $\beta$ structures, the molecules are tilted against the stacking axis which results in larger intermolecular interatomic distances and smaller orbital overlaps (Table 2).

The three structures of PcLi show also different apparent spin 1/2 concentrations ($N_s$) at 300 K. As reported previously,[2,3] for the x structure, $N_s$ is estimated in the range 0.1–0.05 (spin per molecule) while $N_s$ is *ca.* 0.8 and 0.7 for the $\alpha$ and $\beta$ structures, respectively. The $N_s$ value observed in $\alpha$-PcLi powders is slightly larger than for $\alpha$-PcLi thin films deposited at a substrate temperature $T_s$ *ca.* 200 °C on glass or mica substrate ($N_s$ *ca.* 0.5).[6] This difference is ascribed to the coexistence of the x and the $\alpha$ polymorphs in thin films. As shown in Fig. 3(*a*), the temperature dependences of the linewidths are also very different for the three polymorphs. These latter will be discussed successively.

For x-form powders, the line shape of the EPR signal changes significantly with temperature. There is a continuous increase of the linewidth $\Delta H_{1/2}$ from 5.5 μT at 300 K up to 126 μT at 4 K (see Fig. 2 and 3). The asymmetry of the EPR signal at 300 K has been previously discussed in terms of a powder signal with anisotropic *g*-factor and linewidth.[6] Nevertheless, this assumption was not sufficient to account for the asymmetric line shape, since the EPR signal of one single crystallite was also clearly asymmetrical and the possibility of two overlapping components with slightly different *g*-factors was postulated. The *g*-factor and linewidth anisotropies which are observed in x-structure single crystals at room temperature may account for the difference in linewidth between single crystals (2 μT) and powder (5.5 μT). The change of the asymmetry of the EPR signal with temperature may point to possible competition between two components of the EPR signal. The analysis of the EPR signal asymmetry in terms of two overlapping components is further supported by the presence of two contributions to the magnetic susceptibility as discussed later. Even though the occurrence of two components is supported by the line shape observed at *ca.* 45 K where two shoulders appear on either side of the dominant component, the fitting of the EPR signal with two Lorentzian lines did not lead to any satisfactory results since the two possible signals are never clearly separated. The latter observation points at the possible occurrence of two strongly exchange coupled magnetic subsystems, *i.e.* localised and itinerant $\pi$ electrons as reported by Ogawa *et al.* in the case of metallic CuPcI.[20,21]

The weak temperature dependence of the *g*-factor of the x-form powders is within the experimental accuracy, *i.e.* affecting the fifth decimal between 4 and 300 K.

For $\alpha$-form powders, the EPR line shape changes drastically with temperature as shown in Fig. 4. As for x powders, the linewidth continuously increases from 0.13 mT at 300 K up to *ca.* 1.3 mT at 4 K [Fig. 3(*b*)]. This linewidth increase is accompanied by a strong line shape modification: the line

**Table 1** EPR data of the x, α and β structures of PcLi

| structure | half-width at half-maximum $\Delta H_{1/2}/\mu T$ (at 300 K under vacuum) | apparent spin 1/2 concentration at 300 K (spin 1/2 per molecule) | EPR susceptibility |
|---|---|---|---|
| x | powder: 5.5–8.0<br>single crystal:[2] 2.0[a] | 0.05–0.1 | $\frac{c_1}{T}\exp(-\Delta E/k_B T)+\frac{c_2}{T-T_{CW}}$<br>powder: $\Delta E=0.04$ eV, $T_{CW}=-2\pm1$ K and $c_1/c_2\approx40$<br>single crystals: $\Delta E=0.051$ eV, $T_{CW}=4\pm1$ K and $c_1/c_2\approx180$[2] |
| α | 130 | powder: 0.8<br>thin films:[6] 0.5 | $\frac{c_1}{T-T_{CW}}$<br>$T_{CW}=4.5\pm1$ K |
| β | powder: 70–80<br>needles: 130–160[a] | 0.7 | $\frac{c_1}{T-T_{CW}}$<br>$T>50$ K: powder: $T_{CW}=-60\pm5$ K<br>needles: $T_{CW}=-37\pm3$ K<br>$T<50$ K: $-7\text{ K}<T_{CW}<-3$ K |

[a] Minimum linewidth at the magic angle (θ *ca.* 55°).

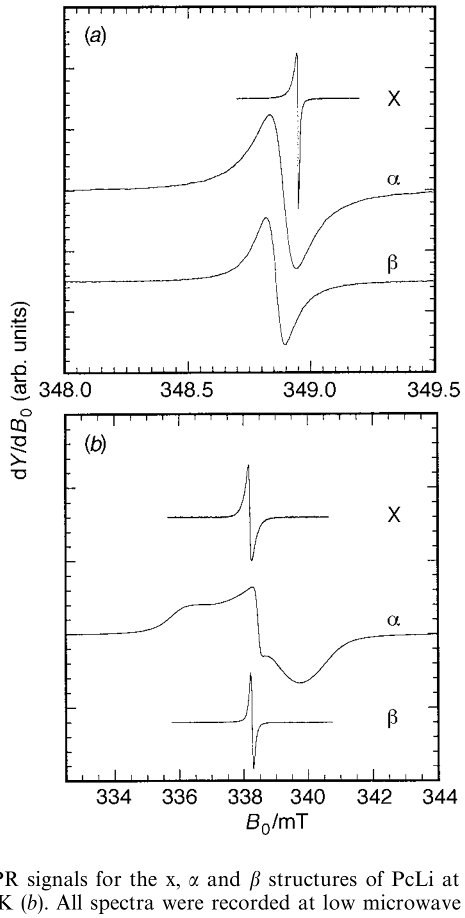

**Fig. 2** EPR signals for the x, α and β structures of PcLi at 300 K (*a*) and at 4 K (*b*). All spectra were recorded at low microwave power to avoid saturation effects.

shape is clearly non-Lorentzian for $T<10$ K. For $T<20$ K, the EPR signal consists in two components with similar *g*-factors, a broad asymmetrical signal ($\Delta H_{1/2}$ *ca.* 0.6 mT and *g ca.* 2.00217 at 10 K) and a narrow one ($\Delta H_{1/2}$ *ca.* 0.09 mT and *g ca.* 2.00219 at 10 K). The linewidth of the narrow signal is similar to that reported for x- and β-form powders at 4 K. As a consequence, we attribute the narrow signal to the presence of some traces of x or β structure in the α-form powder. This observation is not surprising since polymorphism is a general feature observed for all metallophthalocyanines. The line shape of the broad component attributed to the α-form is quite different from a Lorentzian line at 4 K and the corresponding adjustments with two or three Lorentzians did not give any satisfactory result. The line shape is most probably inhomogeneous (Fig. 4). Such a line shape with similar linewidth has been observed in oriented α-PcLi thin films on glass substrate.[14] In these thin films, the modifications of the line shape with temperature were interpreted in the framework of the demagnetizing field effect.[22,23] We may account for the asymmetrical signal by following a similar analysis as for thin films. Indeed, the demagnetizing field $H_m$ in a given crystallite will depend on its orientation in the Zeeman field $B_0$ as well as on its shape. Accordingly, each crystallite of given orientation (θ, φ) in $B_0$ will probe a different local field and the resonance frequency or equivalently the *g*-factor will depend on the θ and φ angles. The resulting EPR signal will be the sum of all the components arising at different *g*-factors from crystallites with different orientations and different shapes. The present situation is quite similar to that of a powder spectrum with an anisotropic *g*-factor. The main difference with a conventional powder spectrum is that the $g_\parallel$ and $g_\perp$ values are temperature dependent because of the demagnetizing field effect.

**Table 2** Distances between closest atoms of neighbouring molecules in the x, α and β structures of PcLi[a]

| structure | $d_{CC}$/Å | $d_{NN}$/Å | $d_{CN}$/Å |
|---|---|---|---|
| x | 3.17 (2) | 3.22 (2) | 3.27 (4) |
| α | 3.54 (2) | 3.60 (2) | 3.47 (2) |
| β | 3.57 (2) | 3.46 (2) | 3.37 (4) |

[a] The x structure has been proposed by Sugimoto *et al.*[8b] and the structures of the α and β polymorphs are identical to those defined by Brown.[16] The numbers in parenthesis are the numbers of atomic pairs corresponding to the shortest interatomic intermolecular distances between molecules within the stacks of each structure.

The overall variations of the linewidth of β-form powders is much weaker than that observed for x- and α-form powders. The linewidth first decreases between 77 μT at 300 K and 58 μT at 15 K and then increases up to 80 μT at 4 K [see Fig. 3(*c*)]. The linewidth variation shows two anomalies. The

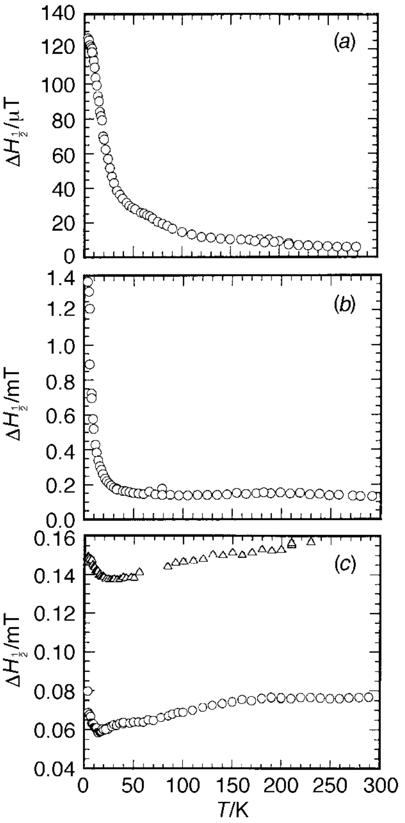

**Fig. 3** Temperature dependence of the linewidth $\Delta H_{1/2}$ for the x (*a*), $\alpha$ (*b*) and $\beta$ (*c*) polymorphs of PcLi. In the case of the $\beta$ structure of PcLi, the temperature dependences are shown for a powder (circles) and a needle (triangles). x and $\beta$ powders were kept under vacuum to avoid oxygen effects.

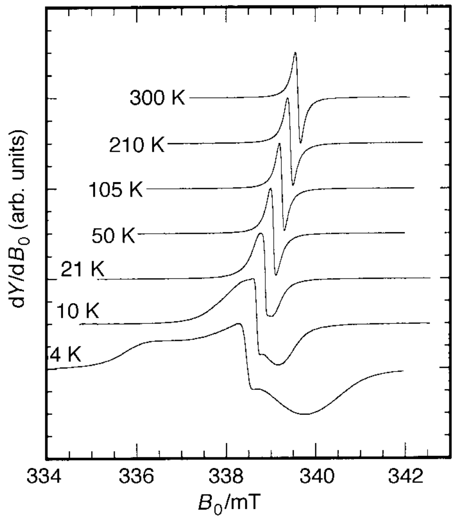

**Fig. 4** Temperature dependence of the EPR line shape between 4 and 300 K for the $\alpha$ form of PcLi. The spectra were shifted along the $B_0$ field axis for the sake of clarity.

first occurs at *ca.* 50 K and might be correlated to that observed for the susceptibility (see following section), while the second is observed near *T ca.* 15 K. The overall linewidth behaviour is quite similar to that reported in the organic semiconductor 3,3′-diethyl-2,2′-selenacyanine-[TCNQ]$_2$ (DESeCN-TCNQ) radical salt.[24] The line shape of the signal remains close to a single Lorentzian line over the whole temperature range 4–300 K.

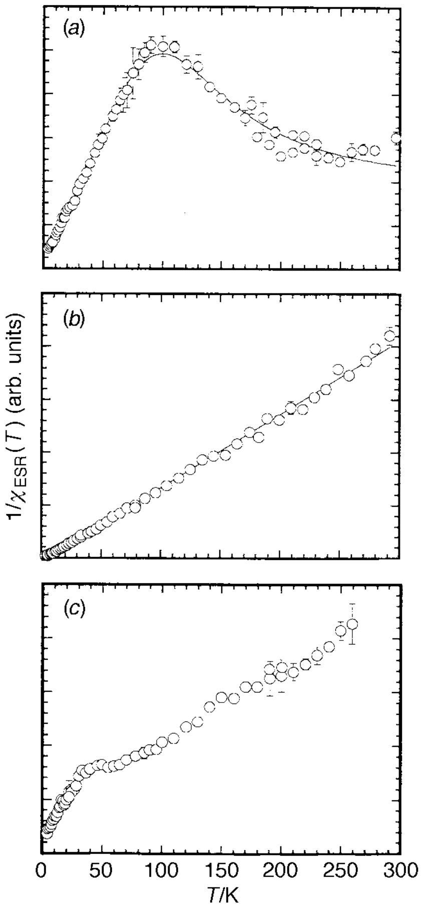

**Fig. 5** Temperature dependence of the reciprocal EPR susceptibility in PcLi powders deduced by double integration of the EPR signal: (*a*) x form, (*b*) $\alpha$ form and (*c*) $\beta$ form. The susceptibility for the x and $\beta$ forms was recorded under vacuum to avoid any oxygen effects. In the case of the x structure, the full line corresponds to a fit using eqn. (1) (see text).

**Magnetic susceptibility.** The x, $\alpha$ and $\beta$ forms of PcLi exhibit very different temperature variations of the magnetic susceptibilities as shown in Fig. 5 (inverse of the EPR susceptibility). The overall characteristics of the x, $\alpha$ and $\beta$ structures are collected in Table 1.

The apparent spin number per molecule ($N_s$) at room temperature for x-form powders lies in the range 0.1–0.05 spin molecule$^{-1}$. Such a small $N_s$ value hints at strong antiferromagnetic couplings:[2,3] only a small fraction of the PcLi molecules are visible *via* EPR. Previous studies have suggested a two component susceptibility involving two-independent spin populations[14] for the fitting of the susceptibility in PcLi x powders and single crystals. These two contributions consist in an activated paramagnetic term $\chi_{ac}(T)$ and a Curie–Weiss term $\chi_{CW}(T)$ as given in eqn. (1)

$$\chi(T)=\chi_{ac}(T)+\chi_{CW}(T) \qquad (1)$$

with

$$\chi_{ac}(T)=\frac{c_1}{T}\exp(-\Delta E/k_B T)$$

and

$$\chi_{CW}(T)=\frac{C_2}{T-T_{CW}}$$

This model leads to satisfactory results as can be seen from Fig. 5(*a*). At low temperatures ($T<50$ K) the susceptibility is dominated by the Curie–Weiss contribution characterised by a mean field temperature $T_{CW}$ *ca.* $-3\pm1$ K whereas for

$T > 100$ K the activated contribution dominates. The activated component is characterised by an activation energy $\Delta E$ of *ca.* 0.042 eV. This value is quite close to that observed in single crystals.[25,26] However it is smaller than the activation energy reported for the electrical dc conductivity which is in the range 0.1–0.2 eV.[27] Similar behaviours of the susceptibility are reported for several charge-transfer compounds such as TEA(TCNQ)$_2$ and hint at a decoupling of spin and charge carrier excitations.[28]

The origin of the two spin populations giving rise to the activated and the Curie–Weiss contribution to the susceptibility has been previously discussed.[25,27,29] The spin population characterised by the narrow EPR line and the activated behaviour of the susceptibility is assigned to the conduction electrons whereas the Curie–Weiss term of the susceptibility is attributed to localised states. Localised states in the x structure of PcLi may have various origins such as: (i) the presence of residual oxygen in the crystallites, (ii) the presence of chemical impurities, (iii) the presence of structural defects and (iv) the occurrence of surface states.

The origin of the Curie–Weiss contribution to the total susceptibility has first been discussed in terms of localised states owing to residual traces of oxygen in the samples.[29] Oxygen molecules can diffuse inside the channels of the x-form crystals and act as trapping centres for the spins diffusing along the *c* axis. The trapping of the spins results in a broadening of the EPR linewidth which is proportional to the oxygen amount inside the structure. The presence of residual oxygen in the samples studied by Turek *et al.*[29] was supported by the occurrence of an $S = 3$ spin population. The $S = 3$ spin states were believed to originate from the antiferromagnetic coupling of one spin $S = 1$ of molecular oxygen and the eight surrounding $S = 1/2$ spins of PcLi. Nevertheless, the present knowledge of the polymorphism of PcLi shows that the studied samples were most likely polymorphic.[29] More precisely, the EPR signals given in ref. 29 show clearly two contributions: a narrow line associated to the x structure and a large oxygen insensitive line which shows exactly the same temperature dependence as that observed for the $\alpha$ structure of PcLi. The probable presence of the PcLi $\alpha$ structure in the samples studied by Turek may also explain the reported positive Curie–Weiss temperature ($T_{CW}$ *ca.* +2 K) as compared to the negative one observed in our case [$T_{CW}$ *ca.* $-3 \pm 1$ K]. If oxygen is supposed to be at the origin of the localised states in the x structure, the $c_1/c_2$ ratio as well as the susceptibility at 300 K should be dependent on the amount of oxygen present in the crystallites. This is not the case, the susceptibility between 20 and 300 K is independent on the presence of oxygen. Accordingly, the presence of residual oxygen in the crystallites cannot be considered as the major source for spin localisation in the x structure.

Chemical impurities can be introduced in the PcLi x structure during electrochemical synthesis. It is quite possible that some non-oxidised PcLi$_2$ molecules are trapped in the structure during the crystal growth. Moreover PcLi$_2$ solutions in acetone show a strong protonation when exposed to humidity and lead to the formation of PcH$_2$.[30] Accordingly, PcLi$_2$ and PcH$_2$ can be considered as two potential chemical impurities in PcLi x powders.

The presence of structural defects is quite possible in our samples since polymorphism is commonly observed in phthalocyanines, especially in thin films.[1] In PcLi thin films obtained by vacuum deposition onto glass substrates, we have shown that the contribution of the Curie–Weiss term to the susceptibility increases with increasing substrate temperature in the range 25–200 °C, *i.e.* as the $\alpha$ *vs.* x structure amount increases.[14] It also appears that the proportion of localised states is much more important in x-like films grown at room temperature than for x-form powders ($c_1/c_2$ *ca.* 2–3 in thin films grown at 300 K on glass substrate *vs.* $c_1/c_2$ *ca.* 40 for x powders). Moreover, films grown at room temperature show many structural defects, the ordering of the molecules in columns is maintained but the relative packing of the columns is much more random.[19] The comparison between the characteristics of the susceptibility in powders and thin films indicates that structural defects and more generally disorder may be considered as the major origin for the localised states in the PcLi x structure. The $c_1/c_2$ ratio is then an indicator of the presence of structural defects interrupting the molecular stacks in the x structure. The structural nature of the defects might be derived from the Curie–Weiss temperature. Indeed, the $\alpha$ and $\beta$ polymorphs show ferromagnetic and antiferromagnetic couplings respectively (see below). Accordingly we attribute the Curie–Weiss contribution of the susceptibility in x-form powders to structural defects consisting either in $\alpha$-form domains ($T_{CW} > 0$) or $\beta$-form domains ($T_{CW} < 0$). Nevertheless, the present study does not allow to distinguish between bulk and surface defects.

Other models have been proposed to fit the susceptibility in the PcLi x structure.[26] In the case of x-form single crystals and thin films grown onto mica substrate, instead of the activated contribution to the susceptibility, Wachtel *et al.*[26] proposed an activated Fisher-Bonner[31] component for an infinite chain with antiferromagnetic intrastack couplings. The latter component is justified by the small $N_s$ value as well as the one-dimensional arrangement of the molecules into well separated columns. Nevertheless, in the present case, the strong uncertainty affecting the activation energy $E_a$ and the coupling constant $J_{FB}$ obtained after the fitting of the experimental data did not allow for any relevant interpretation as previously discussed for thin films.[14]

For $\alpha$-PcLi powders, the magnetic susceptibility obtained *via* EPR spectra can be fitted by a simple Curie–Weiss law with $T_{CW}$ *ca.* $4.5 \pm 1$ K [Fig. 5(*b*)]. The static susceptibility of a powder sample of the $\alpha$ form has also been recorded as a function of the temperature with the help of a SQUID susceptometer and weak ferromagnetic coupling was ascertained. The presence of ferromagnetic impurities in the sample did not allow either a detailed analysis or a direct comparison with the EPR experiments. However, no transition towards a ferromagnetic ordering is observed down to 2 K. The lack of the observation of a ferromagnetic ordering below $T_{CW}$ must be related to the low-dimensional molecular packing within the structure of the $\alpha$ polymorph. The one-dimensional packing of the PcLi molecules into well separated stacks leads to stronger molecular overlaps between molecules within the stacks as compared to those between molecules of neighbouring stacks. We thus expect the intrastack coupling constant $|J_\parallel|$ to be much more important than the interstack coupling constant $|J_\perp|$. Accordingly the corresponding Curie–Weiss mean-field temperature $T_{CW} \propto S(S+1)\,(J_\parallel J_\perp)^{\frac{1}{2}}$ can be quite important but three-dimensional ordering of the spins will only be observed for $T < |J_\perp|/k_B$ and not for $T < T_{CW}$.[32]

Concerning the $\beta$-form of PcLi, we must consider two temperature domains since there is a clear change in the slope of the inverse susceptibility curve around 50 K [Fig. 5(*c*)]. For $T > 50$ K a Curie–Weiss-like susceptibility with a strong antiferromagnetic coupling characterised by $T_{CW} = -60 \pm 5$ K is observed. Below $T_{CW}$, an obvious change in the EPR susceptibility is observed, the latter shows a Curie–Weiss behaviour with $T_{CW}$ *ca.* $-7 \pm 1$ K. A similar behaviour is observed for the temperature dependence of the static susceptibility recorded with the help of a SQUID susceptometer as shown in Fig. 6.

A tentative analysis of the susceptibility in terms of two contributions as for the x structure does not give any relevant result. In particular, the activation energy of the thermally activated contribution to the susceptibility is quite small ($\Delta E/k_B$ *ca.* 75 K). In several organic systems like $\alpha,\alpha'$-diphenylpicrylhydrazyl (DPPH) a transition of the susceptibility towards a purely paramagnetic behaviour is observed at low temperatures

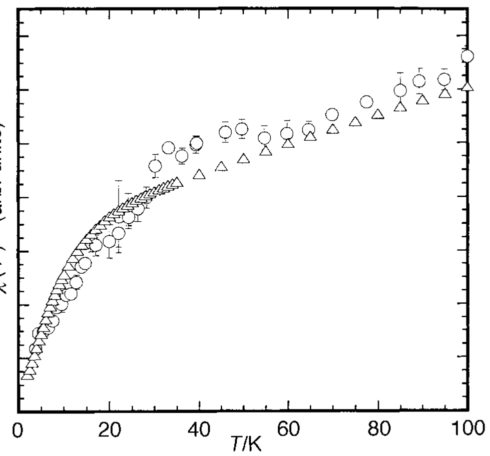

**Fig. 6** Temperature dependence of the reciprocal susceptibility of PcLi powders of the $\beta$-form: (i) dc susceptibility (SQUID magnetometer) (triangles), and (ii) EPR susceptibility (circles). In both experiments, the samples were handled in an oxygen free atmosphere.

arising from the presence of some residual paramagnetic impurities.[28,33] In the case of $\beta$-form powders of PcLi, we obtain a value of the ratio $r$ between the Curie constant observed for $T < 50$ K and the Curie–Weiss constant derived for $T > 50$ K of the order of 0.3. The latter high value of $r$ does not allow attribution of the low temperature behaviour of the susceptibility to residual paramagnetic impurities. Another alternative to fit the magnetic susceptibility observed in $\beta$-form PcLi involves two independent spin populations: (i) a spin population at the origin of the high temperature behaviour of the susceptibility with high antiferromagnetic couplings and (ii) a second spin population characterised by a Bleaney–Bowers behaviour of the susceptibility, *i.e.* corresponding to dimers.[34] Nevertheless, an analysis of the results obtained from the fitting procedure indicates that the values of the Curie–Weiss temperature ($T_{CW}$ *ca.* $-100$ K) and the coupling constants $J_{BB}$ ($J_{BB}$ *ca.* $-12.5$ K) are not relevant. The latter values are in particular very different from the temperature corresponding to the change in the susceptibility behaviour.

As seen from the EPR study of the PcLi $\beta$-form needles (below), the temperature corresponding to the change in the behaviour of the susceptibility is closely related to the Curie–Weiss temperature $T_{CW}$ deduced from the susceptibility above $T_{CW}$. Moreover, since it is not possible to observe clearly two different contributions to the EPR signal below $T_{CW}$, it is quite probable that the change of the susceptibility below $T_{CW}$ is not due to a contribution from a second spin population but rather to a change in the magnetic behaviour of the spin population observed for $T > 50$ K.[28] Another possible modelling of the susceptibility is suggested on the basis of the results obtained by Fisher and Bonner (F–B) in the case of short segments of antiferromagnetically coupled spins.[31] In particular, the overall behaviour of the susceptibility obtained for spin segments with an odd number of sites close to five is very similar to that observed for the $\beta$ structure of PcLi for $T < 50$ K. The application of the F–B model to the $\beta$ form of PcLi implies that: (i) the molecules are assembled into well defined segments, (ii) the inter-segment magnetic couplings are negligible as compared to the intra-segment coupling. However, it appears that (i) as shown from the single crystal study, no low dimensional behaviour is evidenced, and (ii) from a structural standpoint, there is no obvious reason for the preferential packing of molecules into segments of five molecules.

### *β* form PcLi needles

**Temperature dependence of the line shape.** As compared to powders, needles of $\beta$-form PcLi exhibit an anisotropic linewidth $\Delta H_{1/2}$ which reaches a maximum value of *ca.* 0.27 mT at 300 K when the crystal axis is parallel to the $B_0$ field. The difference in linewidth observed between needles and powders may be due to different impurity or defect concentrations owing to the different preparation methods. Indeed, PcLi $\beta$-form crystallites are obtained after a prolonged heating under vacuum of x powders at a temperature near the sublimation temperature at which a marked chemical transformation into PcLi$_2$ is observed. This implies that PcLi needles may contain a high amount of PcLi$_2$ impurities. As for $\beta$-PcLi powders, the line shape of the EPR signal of the crystallites held under vacuum remains nearly unchanged over the whole temperature range, one single line is observed in absence of oxygen. The overall temperature dependence of the linewidth recorded for a crystal oriented close to the magic angle ($\theta$ *ca.* 55°) in the Zeeman field $B_0$ is quite similar to that observed in powders [Fig. 3(*c*)]. The linewidth decreases from 0.170 mG at 300 K to 0.135 mG at 15 K and increases at $T < 15$ K. This behaviour is in line with the AF behaviour of the susceptibility (see below). Indeed, in low-dimensional antiferromagnets, the linewidth is expected to decrease with decreasing temperature.[35]

The temperature variations of the $g$-factor are within experimental accuracy in the temperature range 4–300 K.

**Magnetic susceptibility.** The magnetic susceptibility of the $\beta$-form crystallite has been recorded for the three orientations ***a***, ***b*** and ***c**** of the needle axis in the Zeeman field B$_0$ (see Fig. 7). Differences in the susceptibility measured along the ***a***, ***b*** and ***c**** directions are of the order of 10–15%, *i.e.* within the error bars. Thus, as opposed to MnPc[36] which shows clearly an anisotropic susceptibility, the EPR susceptibility of the $\beta$ form of PcLi is isotropic. The overall temperature dependence of the susceptibility in $\beta$-form needles is similar to that observed in powders. Regardless of the sample orientation in the Zeeman field, the experimental data can be fitted by a single Curie–Weiss susceptibility at temperatures $T > 12$ K. The $T_{CW}$ temperatures derived for the various orientations of the sample in the Zeeman field are identical and close to $-37 \pm 2$ K. This temperature is smaller in absolute value than that observed in $\beta$-form powders ($T_{CW} = -60 \pm 5$ K). Different defect and/or chemical impurity concentrations may account for these differences. PcLi $\beta$-form needles show also a similar behaviour of the susceptibility at $T < 50$ K as reported for powders: a transition towards a Curie–Weiss susceptibility with $T_{CW}$ in

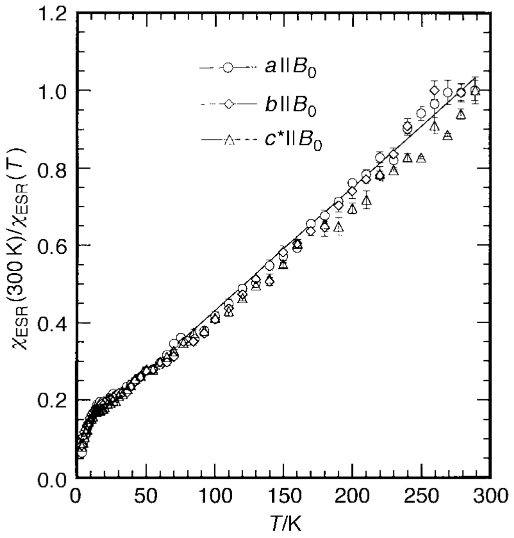

**Fig. 7** Temperature variation of the reciprocal EPR susceptibility of a PcLi $\beta$-form needle under vacuum recorded along the three orientations ***a***, ***b*** and ***c**** of the crystallite in the Zeeman field (see Fig. 11). The susceptibility is normalised to its value at room temperature. The full line represents a Curie–Weiss behaviour for $T > 40$ K.

the range $-3$ to $-7$ K is observed. The large uncertainty for the later $T_{CW}$ value is ascribed to the reduced temperature range for the fitting procedure. As for powders, no AF ordering is observed below $T_{CW}$.

**Oxygen effect at low temperature.** The major role of oxygen on the magnetic properties of the PcLi x structure is well established.[4,29,37] Oxygen can diffuse inside the x structure of PcLi through diffusion channels along the *c* axis. Magnetic interactions between the spins of the PcLi molecules and the $S=1$ spins of oxygen molecules result in a broadening of the EPR line. Bulk diffusion of oxygen in the denser $\alpha$ and $\beta$ structures seems improbable. In the particular case of the $\alpha$ structure, no oxygen effect is observed either in powders or in thin films. In $\beta$-form powders and needles, no oxygen effect is observed at room temperature but the situation at low temperature is different, in particular below the boiling point of oxygen (55 K). Fig. 8 shows the lineshapes at 4 K for two orientations of the sample in the $B_0$ field for two situations: (i) the sample is heated at 310 K under a flow of helium such as to remove any traces of adsorbed oxygen before the temperature is lowered and (ii) direct cooling of the sample. The differences in the EPR signal are obvious and consist mainly in a strong line shape modification with the appearance of one or several broad components when oxygen is present in the sample. The characteristics of these broad signals are not reproducible from one experiment to the other. Similar effects have also been observed in x powders but not for $\alpha$ powders. Since oxygen is the only paramagnetic species present in the ambient atmosphere, the EPR signal modifications are ascribed to the presence of adsorbed oxygen on the surface of the crystallites. The fact that a simple heating of the sample at 310 K under a flow of helium is sufficient to prevent the magnetic properties from being altered means that the interactions between the phthalocyanine and the oxygen molecules are characteristic of physisorption. In the special case of the PcLi x structure, it has been shown that the PcLi radicals and the oxygen molecules interact *via* reversible magnetic interactions between the spins of both species.[29] A similar interaction between the PcLi radicals and the $S=1$ spins of $O_2$ is very likely to occur in the $\beta$ form of PcLi. The possibility of chemisorption and charge transfer between PcLi and $O_2$ molecules which is observed for metallophthalocyanines[38] can be discarded.

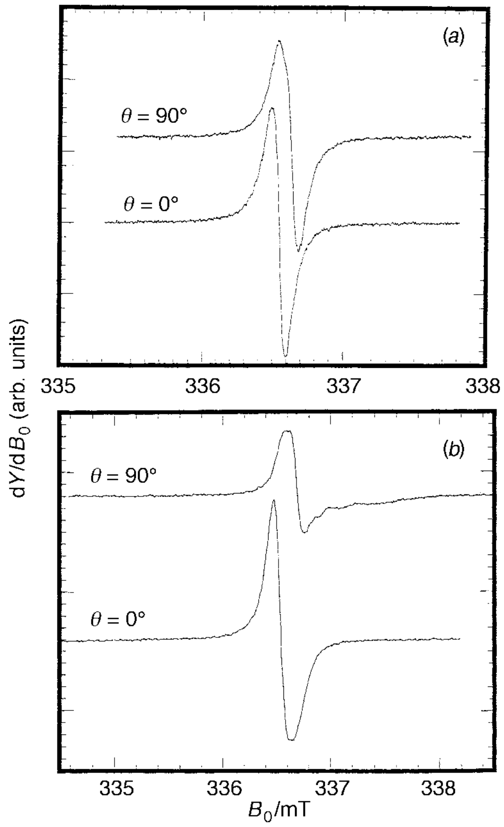

**Fig. 8** Effect of adsorbed oxygen on the ESR spectra of a PcLi $\beta$-form crystal. The spectra were recorded at 4 K along the *b*-axis ($\theta=0°$) and the *c**-axis ($\theta=90°$): (*a*) the sample is heated at 310 K under helium flow prior to temperature lowering, and (*b*) the sample is directly cooled to 4 K.

Not only is the line shape strongly altered by adsorbed oxygen but also the linewidth anisotropy recorded in the (*a,b*) plane as shown in Fig. 9. The linewidth maximum in the absence of $O_2$ is observed for $\theta=0°$ (needle parallel to $B_0$), while $\theta=90°$ in presence of adsorbed $O_2$. In a similar way, the *g*-factor anisotropy is strongly affected by the presence of adsorbed $O_2$. As can be seen from Fig. 10, the extrema of the *g*-factors are shifted by 20° and the anisotropy is much larger ($1.998<g<2.0027$).

Oxygen has been shown to alter strongly the properties of several charge-transfer salts such as TTF-TCNQ and ($\phi_4$DTP)-TCNQ.[39] In the latter two compounds, the influence of oxygen has been observed to result in a steep increase of the susceptibility near 48 K. Partial pressures as low as 0.005 Torr ($P_{tot}$ *ca.* 1 Torr He) were reported to alter the susceptibility. Susceptibility modifications were ascribed to physisorbed or chemisorbed oxygen on the surface of the crystals. For PcLi, the presence of adsorbed oxygen at the surface of the $\beta$-form needles results in a negligible effect on the susceptibility.

In the case of the $\beta$ structure of PcLi, a similar analysis might be considered as for the previously mentioned TCNQ charge-transfer salts. Modifications of the linewidth indicate whether the magnetic dipolar interactions or the diffusive motion of the spins are altered by the presence of oxygen. The linewidth anisotropy of x-form single crystals has been shown to be strongly affected by the presence of $O_2$ in the bulk of the crystallites. More precisely, a change from a 1D linewidth anisotropy in absence of oxygen to a 3D isotropic situation in presence of oxygen is observed in x-PcLi single crystals.[25] For the $\alpha$ and $\beta$ structures, the situation should be quite different since the denser packing of molecules should not allow for a bulk diffusion of molecular oxygen. In the $\beta$ structure, the magnetic properties may only be altered *via* surface or

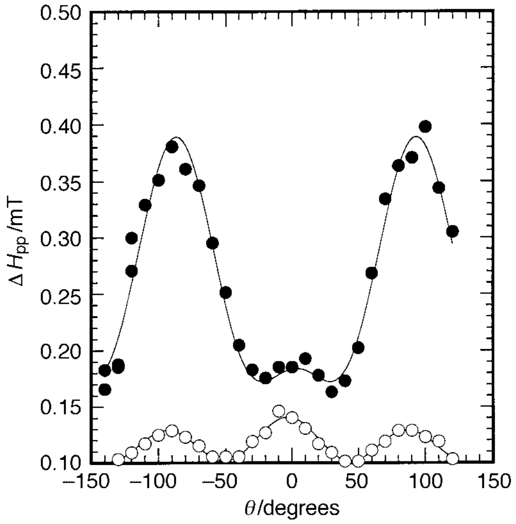

**Fig. 9** Oxygen effect on the peak-to-peak linewidth anisotropy of the EPR signal at 4 K of a $\beta$-form PcLi needle: (i) the sample is held under vacuum ($10^{-5}$ Torr) in a sealed quartz tube (open circles), and (ii) the sample is flushed by the helium flow within the cryostat (filled circles). The data have been fitted using eqn. (2) (see text).

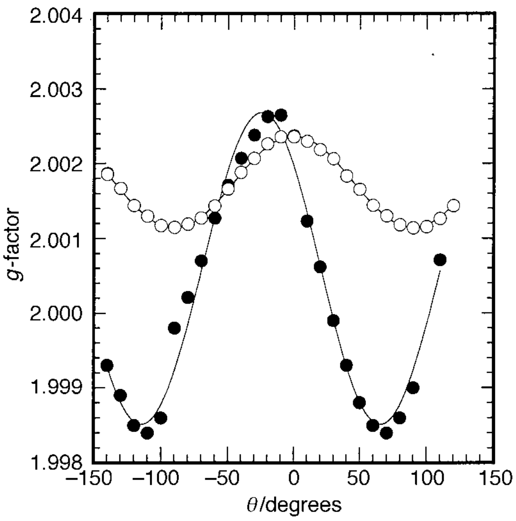

**Fig. 10** Oxygen effect on the g-factor anisotropy of the EPR signal at 4 K of a β-PcLi needle: (i) the sample is held under vacuum ($10^{-5}$ Torr) in a sealed quartz tube (open circles), and (ii) the sample is flushed by the helium flow within the cryostat (filled circles). The full lines corresponds to the fitting of the experimental data using the general expression for the g-factor angular dependence $g^2(\theta)=g_\parallel{}^2\cos^2(\theta)+g_\perp{}^2\sin^2(\theta)$ ($g_\parallel$ and $g_\perp$ are the g-factor values when the b axis of the crystallite is parallel and orthogonal to the Zeeman field respectively).

structural defects such as gaps enabling the diffusion of $O_2$ molecules into the bulk of the material.

**Linewidth anisotropy.** The linewidth anisotropy has been measured in three orthogonal planes at 293 K and the resulting curves are shown in Fig. 11. In the (*a,b*) plane as well as in the (*b,c**) plane, the maximum of the linewidth is observed when the crystal long axis (*b* axis) is parallel to the $B_0$ field. Thus the *b* axis may be considered as the magnetic axis of a 1D or 2D system since the maximum of the linewidth corresponds to the direction along which the magnetic dipolar interactions are the most important, *i.e.* the direction where the distances between successive molecules are the shortest. A closer insight into the β structure of PcLi indicates that the *b* axis is indeed the axis of closest molecular packing. Moreover, an obvious anisotropy of the linewidth is observed in the (*a,c**) plane. Anisotropy of the magnetic properties has also clearly been noted in the (*a,c**) plane of MnPc.[36,40] The study of the structure shows that the shortest interatomic distances between molecules of neighbouring columns are of C···N type along the *a* axis ($d_{CN}$ *ca.* 3.34 Å) whereas the shortest distance between carbon and nitrogen atoms belonging to columns along the *c* axis is much larger. This situation is quite different from that observed in PcLi x-form single crystals. In the tetragonal x structure, molecules are stacked along the *c* axis, and no anisotropy of the linewidth is observed in the (*a,b*) plane perpendicular to this direction.[25]

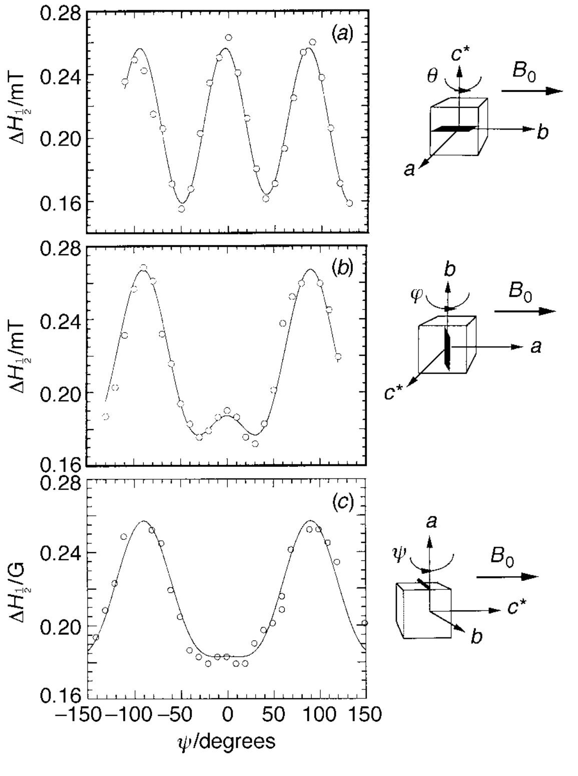

**Fig. 11** Angular dependence of the halfwidth at half-maximum ($\Delta H_{1/2}$) of the EPR absorption spectra of a β-PcLi crystallite recorded at 300 K within: (*a*) the (*a, b*) plane, (*b*) the (*a, c**) plane, and (*c*) the (*b, c**) plane. The data have been fitted using eqn. (2) (see text).

The temperature dependence of the linewidth anisotropy has been recorded in the (*a,b*) plane as well as in the (*a,c**) plane (Fig. 12). The angular variations of the linewidth have been fitted using the following expression:

$$\Delta H_{1/2}(\theta)=aF_0{}^2(\theta)+10bF_1{}^2(\theta)+cF_2{}^2(\theta) \qquad (2)$$

with the dipolar secular contributions $F_0(\theta)=3\cos^2(\theta)-1$ and the non-secular terms $F_1(\theta)=\sin(\theta)\cos(\theta)$ and $F_2(\theta)=\sin^2(\theta)$.

A different expression for $\Delta H_{1/2}(\theta)$ has been used for PcLi x-form single crystals[25] and thin films on mica and glass substrates.[9,14] 1D spin diffusion was assumed in the latter cases

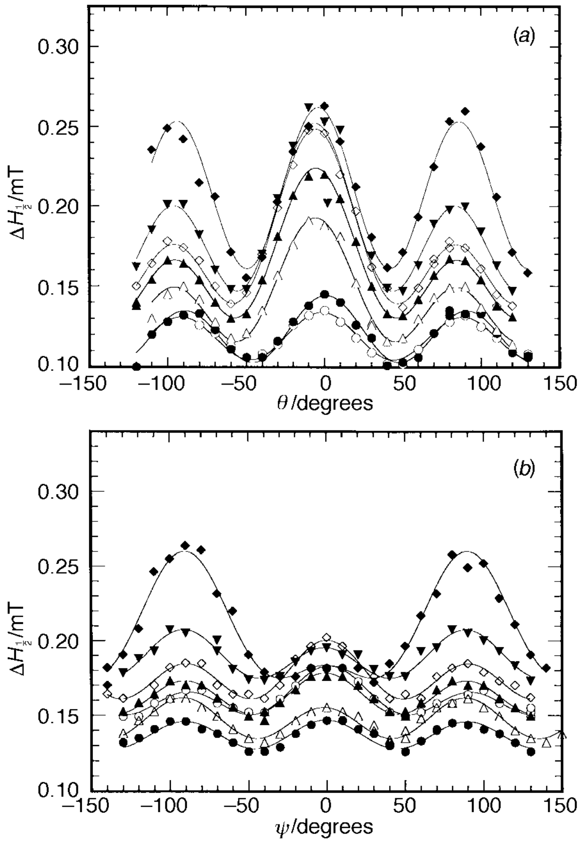

**Fig. 12** Temperature variation of the $\Delta H_{1/2}$ linewidth anisotropy (*a*) in the (*a,b*) plane, and (*b*) in the (*a,c**) plane for a β-form PcLi needle. The sample is kept under secondary vacuum in a sealed quartz tube. The full lines are obtained after fitting the experimental data with eqn. (2) (see text). (○) 4 K, (●) 10 K, (△) 25 K, (▲) 50 K, (◇) 100 K, (▼) 200 K, (◆) 300 K.

which implies that the relative values for the *a*, *b* and *c* parameters were fixed. The hypothesis of low dimensionality was supported by the columnar arrangement of the PcLi molecules, which favours strong molecular orbital overlap along the *c* stacking direction in the x structure. A similar analysis was tried in the case of the $\beta$ structure of PcLi but the results were not satisfactory. First, the fitting of the linewidth anisotropy in the (*a,b*) plane using eqn. (2) shows that the second non-secular term is dominant in the temperature range 4–300 K. Secondly, the analysis of the linewidth anisotropy in the (*a,c**) plane appears to be much more complicated since the location of the linewidth maximum changes with temperature from $\theta=90°$ for $T>200$ K down to $\theta=0°$ for $T<200$ K. Nevertheless, as for the anisotropy in the (*a,b*) plane, the second non-secular term is dominant. Accordingly, it is impossible to evidence a low dimensional behaviour of the magnetic properties in the $\beta$ structure of PcLi. The angular variations of the linewidth are believed to be mainly governed by dipolar couplings without any clear contribution from the spin–spin correlation functions as observed in low-dimensional systems.[35,41,42] As a consequence, the general expression used in the present case for the fitting of the linewidth anisotropy may be nothing else but a simple trigonometric fit.

## Discussion

The present study shows the very different magnetic behaviours of the three polymorphs of lithium phthalocyanine. In the following we will show that the mechanism proposed by Mc Connell[44] for the magnetic couplings in solid free $\pi$-radicals can account for the differences in the magnetic behaviours of the PcLi polymorphs.

According to Mc Connell, the hamiltonian for the exchange interaction between two molecules A and B can be approximated by the form:

$$H_{AB} = -S^A \cdot S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B \qquad (3)$$

where $S^A$ and $S^B$ are the total spin operators for A and B and $\rho_i^A$ and $\rho_j^B$ are the $\pi$ spin densities on atom *i* and *j* of molecules A and B, respectively. $J_{ij}^{AB}$ is the interatomic exchange integral between atom *i* of molecule A and atom *j* of molecule B.

Two situations are possible: (i) the spin densities on adjacent molecules are all positive and the largest exchange integrals $J_{ij}^{AB}$ are negative leading to antiparallel spin alignment (antiferromagnetic couplings) or (ii) there are positive and negative $\pi$ spin densities and molecules are stacked such as to show couplings between spin densities of opposite signs which favours parallel spin arrangements (ferromagnetic couplings).

The spin densities of lithium phthalocyanine have been determined experimentally by using the $^{13}$C Overhauser shift and by theoretical intermediate neglect of differential overlap (INDO) calculations for the PcLi x structure.[45] Calculations of the spin densities have shown that the carbon atoms of the inner macrocycle have positive spin densities of *ca.* 0.178 while the nitrogen atoms show negative spin densities of between $-0.074$ and $-0.082$. Spin densities of the other atoms of the PcLi molecule are smaller by at least one order of magnitude. The polymorphism observed in PcLi is very unusual and three different stacking modes are possible (Fig. 1). Thus, in the framework of the Mc Connell's mechanism, PcLi appears as a potential candidate for ferromagnetic and antiferromagnetic couplings. Fig. 13 schematises two neighbouring molecules within the stacks of the x, $\alpha$ and $\beta$ structures along the stacking direction in order to visualise the shortest interatomic contacts between atoms of successive molecules within a stack and the corresponding distances are collected in Table 2. The nitrogen molecules are shown as dark spheres for negative spin densities and the carbon atoms as light spheres for positive spin densities. For the x structure, we see that the only relevant overlaps are between carbon $p_z$ orbitals of neighbouring molecules which show positive spin densities. Accordingly, we should observe an antiparallel arrangement of the spins in the stacks *i.e.* antiferromagnetic couplings. This is verified experimentally since most of the spins are EPR silent in the x structure and only a small fraction of the spins are observed. The case of the $\alpha$ structure is quite opposite to the previous one. The stacking mode of the molecules in the $\alpha$ structure indicates that the shortest intermolecular atomic distances and thus the most

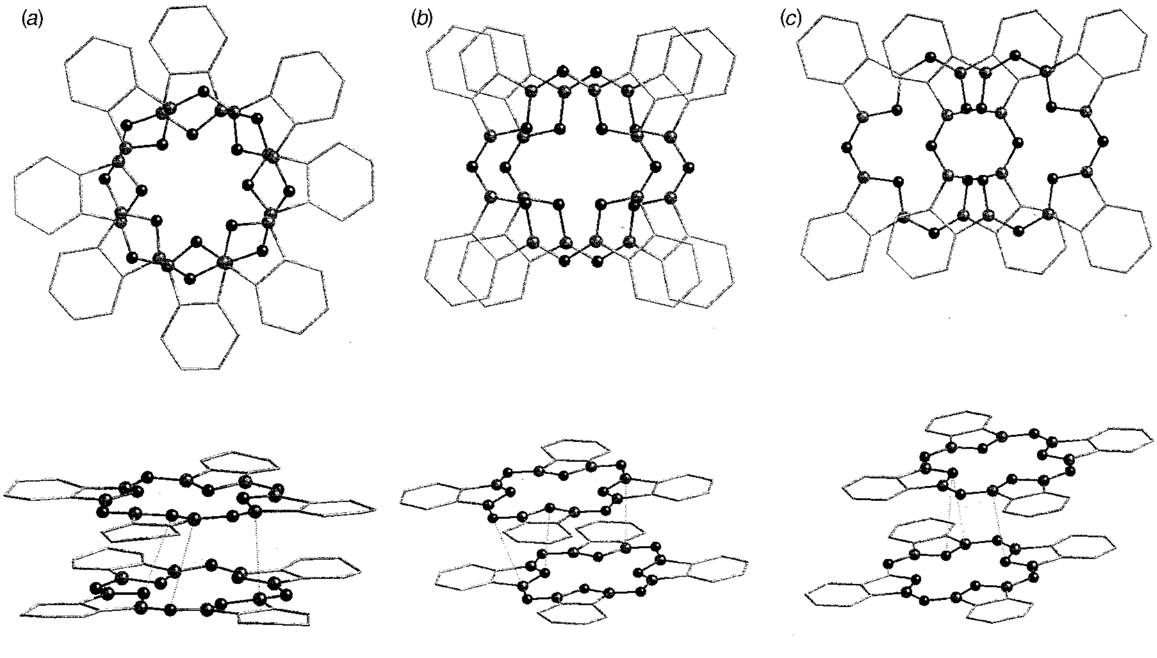

**Fig. 13** Molecular packing within the stacks of the x, $\alpha$ and $\beta$ structures of PcLi [(*a*), (*b*) and (*c*) respectively]. The positive spin densities of the carbon atoms are shown as light spheres and the negative spin densities of the nitrogen atoms as dark spheres (Cerius Molecular Modelling Software Package For Material Research, Molecular Simulations Inc.). The shortest interatomic C—C, N—N and C—N distances are also shown (see Table 2).

important $\pi$ orbital overlaps are between nitrogen and carbon atoms, *i.e.* between sites of opposite spin densities (Table 2). This observation is in favour of ferromagnetic couplings between successive molecules in the stacks which is experimentally observed. The low Curie–Weiss temperature and thus the small ferromagnetic couplings may hint at small molecular orbital overlaps as compared to the x structure.

The $\beta$ form of PcLi is more complicated. Indeed, as seen from the susceptibility of the system, an overall antiferromagnetic behaviour is observed ($T_{\mathrm{CW}}$ *ca.* −60 K in powders and $T_{\mathrm{CW}}$ *ca.* −37 K in needles). We thus expect, according to Mc Connell's mechanism, that the strongest orbital overlaps are between atoms of identical spin densities. However, if we consider the $\beta$ structure of PcLi [Fig. 13(*c*)], we see that the smallest interatomic distances are between carbon and nitrogen atoms of opposite spin densities within the stacks (see Table 2) and thus ferromagnetic couplings between successive molecules within the stacks are expected, which is not the case. Nevertheless, it should be mentioned that the present analysis does not take into account the possible magnetic couplings between the stacks of PcLi molecules. It is quite possible that the molecules show dominant ferromagnetic couplings inside the stacks and global antiferromagnetic couplings between the stacks. This situation is probable in the case of the $\beta$ structure since the mean distance between columns is quite short (*d ca.* 9.6 Å along the *a* axis) as compared to that observed in the x and the $\alpha$ structures (*d ca.* 14 Å in the x form and *ca.* 12 Å in the $\alpha$ form) for which the low dimensionality of the spin diffusion is well established. Correlatively, the shortest interatomic C···C, N···N and C···N distances are fairly isotropic in the $\beta$ structure as opposed to the x and $\alpha$ structures. The present application of the mechanism proposed by Mc Connell to the case of PcLi shows that the occurrence of relevant and well defined interatomic contacts, *i.e.* well defined neighbour molecules is required. The later requirement is fulfilled in the x and $\alpha$ structures of PcLi and but not in the $\beta$ structure.

## Conclusion

The magnetic properties of the x, $\alpha$ and $\beta$ polymorphs of lithium phthalocyanine have been investigated by EPR spectroscopy. The three polymorphs show very different magnetic properties as observed from the magnetic susceptibility or the linewidth temperature dependences. The x structure shows an efficient exchange narrowing of the EPR line (5.5 μT *in vacuo* at 300 K) which is very sensitive to oxygen. Exchange narrowing is much less efficient in the $\alpha$ and $\beta$ structure which results in a linewidth in the range 0.13–0.08 mT at 300 K. A Curie–Weiss susceptibility is observed for the $\alpha$ phase with a mean-field temperature $T_{\mathrm{CW}}$ *ca.* $4.5 \pm 1$ K characteristic of ferromagnetic couplings. The x polymorph shows a thermally activated contribution to the susceptibility with an activation energy $E_{\mathrm{a}}$ *ca.* 0.04 eV as well as a Curie–Weiss component ($T_{\mathrm{CW}}$ *ca.* −3 K). A Curie-Weiss-like susceptibility with $T_{\mathrm{CW}}$ *ca.* $-60 \pm 5$ K is observed for $T > 50$ K in $\beta$-form powders but no AF ordering occurs below $T_{\mathrm{CW}}$. The overall magnetic properties of the PcLi polymorphs are tentatively interpreted in the framework of Mc Connell's mechanism for ferromagnetism and antiferromagnetism in solid free radicals. A qualitative agreement is found between the experimental results and the prediction derived from Mc Connell's mechanism for the $\alpha$ and x structures. The magnetic properties of $\beta$ PcLi needles have also been investigated. In particular the linewidth anisotropy has been studied in the temperature range 4–300 K within the (*a,b*) and (*a,c**) planes. No clear evidence for low dimensionality is obtained. Moreover, adsorbed oxygen is shown to alter strongly the magnetic properties in PcLi $\beta$-form needles and powders at temperatures below 55 K.

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## References

1 C. C. Leznoff and A. B. P. Lever, *Phthalocyanines Properties and Applications*, VCH, 1989, 1993, 1994 and 1996, vol. 1, 2, 3 and 4.
2 P. Turek, J.-J. André, A. Giraudeau and J. Simon, *Chem. Phys. Lett.*, 1987, **134**, 471.
3 P. Turek, J.-J. André, J. Simon, R. Even, B. Boudjema, G. Guillaud and M. Maitrot, *J. Am. Chem. Soc.*, 1987, **109**, 5119.
4 F. Bensebaa and J.-J. André, *J. Phys. Chem*, 1992, **96**, 5739.
5 K. Yakushi, T. Ida, A. Ugawa, H. Yamakado, H. Ishii and H. Kuroda, *J. Phys. Chem.*, 1991, **95**, 7636.
6 M. Brinkmann, C. Chaumont, H. Wachtel and J.-J. André, *Thin Solid Films*, 1996, **283**, 97.
7 M. Brinkmann, J.-C. Wittmann, C. Chaumont and J.-J. André, *Thin Solid Films*, 1997, **292**, 192.
8 (*a*) M. Moussavi and A. De Cian, personal communication, 1993; (*b*) H. Sugimoto, M. Mori, H. Masuda and T. Taga, *J. Chem. Soc., Chem. Commun.*, 1986, 962.
9 H. Wachtel, J.-C. Wittmann, B. Lotz, M. A. Petit and J.-J. André, *Thin Solid Films*, 1994, **250**, 219.
10 H. Homborg and Chr. L. Teske, *Z. Anorg. Allg. Chem.*, 1985, **527**, 45.
11 C. J. Schramm, R. P. Scaringe, D. R. Stojakovic, B. M. Hoffman, J. A. Ibers and T. J. Marks, *J. Am. Chem. Soc.*, 1980, **102**, 6702.
12 M. Almeida, M. G. Kanatzidis, L. M. Tonge, T. J. Marks, H. O. Marcy, W. J. Mc Carthy and R. Kannewurf, *Solid State Commun.*, 1987, **63**, 457.
13 J.-J. André and M. Brinkmann, *Synth. Met.*, 1997, **90**, 211.
14 M. Brinkmann, P. Turek and J.-J. André, *Thin Solid Films*, 1997, **303**, 107.
15 M. A. Petit, T. Thamia and R. Even, *J. Chem. Soc., Chem. Commun.*, 1989, 15.
16 C. J. Brown, *J. Chem. Soc. A*, 1968, 2488.
17 M. Ashida, N. Uyeda and E. Suito, *J. Cryst. Growth*, 1971, **8**, 45.
18 F. Iwatsu, *J. Phys. Chem.*, 1988, **92**, 1681.
19 H. Klapper, M. Kobayashi, T. Kobayashi and K. Sato, in *Organic Crystals*, ed. H. C. Freyhardt and G. Müller, Springer Verlag, Berlin, 1991.
20 M. Y. Ogawa, J. Martinsen, S. M. Palmer, J. L. Stanton, J. Tanaka, R. L. Greene, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, 1987, **109**, 1115.
21 M. Y. Ogawa, B. M. Hoffman, S. Lee, M. Yudkowsky and W. P. Halperin, *Phys. Rev. Lett.*, 1986, **57**, 9.
22 J.-L. Stanger, J.-J. André, P. Turek, Y. Hosokoshi, M. Tamura, M. Kinoshita, P. Rey, J. Cirujeda and J. Veciana, *Phys. Rev. B*, 1997, **55**, 8398.
23 J.-L. Stanger, *PhD Thesis, ULP*, Strasbourg, France, 1995.
24 S. Takagi and M. Date, *Physica B*, 1989, **155**, 425.
25 P. Turek, *PhD Thesis, ULP*, Strasbourg, France, 1989.
26 H. Wachtel, J.-J. André, W. Bietsch and J. U. von Schütz, *J. Chem. Phys.*, 1995, **102**, 9606.
27 P. Turek, M. Moussavi, P. Petit and J.-J. André, *Synth. Met.*, 1989, **29**, F65.
28 R. Foster, *Molecular Association*, Academic Press, New York, 1975, p. 70.
29 P. Turek, J.-J. André, M. Moussavi and G. Fillion, *Mol. Cryst. Liq. Cryst.*, 1989, **176**, 535.
30 S. Baker, M. C. Petty, G. G. Roberts and M. V. Twigg, *Thin Solid Films*, 1983, **99**, 53.
31 J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, 1964, **135**, 640.
32 F. Palacio in *Magnetic Molecular Materials*, ed. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, NATO ASI Series, Kluwer Academic, Serie E, vol. 198, p. 22.
33 P. Grobet, L. Van Gerven and A. Van den Bosch, *J. Chem. Phys.*, 1978, **68**, 5225.
34 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.
35 P. M. Richards, *Proc. Int. School of Physics*, 'Enrico Fermi', LIX, North Holland, 1976.

36 S. Mitra, A. K. Gregson, W. Hatfield and R. R. Weller, *Inorg. Chem.*, 1983, **22**, 1729.
37 F. Bensebaa, P. Petit and J.-J. André, *Synth. Met.*, 1992, **52**, 57.
38 J. Simon and J.-J. André in *Molecular Semiconductors*, Springer Verlag, Berlin, 1985, pp. 98–101.
39 L. C. Isett, G. A. Reynolds, E. M. D. Schneider and J. H. Perlstein, *Chem. Phys. Lett.*, 1979, **67**, 71.
40 C. G. Barraclough, R. L. Martin, S. Mitra and R. C. Sherwood, *J. Chem. Phys.*, 1970, **53**, 1638.
41 J. E. Drumheller, *Magn. Res. Rev.*, 1982, **7**, 123.
42 D. Gatteschi and R. Sessoli, *Magn. Res. Rev.*, 1990, **15**, 9.
43 M. Dumm, P. Lunkenheimer, A. Loidl, B. Assmann, H. Homborg and P. Fulde, *J. Chem. Phys.*, 1996, **104**, 5048.
44 H. M. McConnell, *J. Chem. Phys.*, 1963, **39**, 1910.
45 B. Gotschy and G. Denninger, *Mol. Phys.*, 1990, **71**, 169.

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