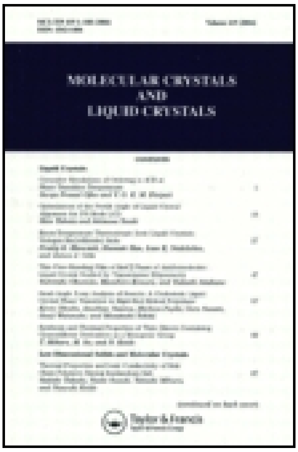

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SPIN CORRELATIONS IN ORGANIC RADICAL MAGNETS

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Abstract The Electron Paramagnetic Resonance (EPR) technique is described as a valuable tool in order to probe the spin correlations in π-radical magnets. The peculiar features of the EPR response of low dimensional exchange coupled spin systems are recalled. The extreme sensitivity of the resonance field to both magnetic and dipolar interactions is emphasized. The example materials include phthalocyanine radical derivatives and nitronyl nitroxide radical derivatives. Both exhibit either *antiferromagnetic or ferromagnetic intermolecular interactions.*

1. INTRODUCTION.

The search for bulk ferromagnetism in molecular materials has been very active for the past five years. Well documented reports on workshops and reviews have recently been devoted to this topic.[1-3] As a matter of fact, there has been a great deal of work yielding successful results concerning the ferromagnetic properties of the metal complexes and/or the charge transfer salts.[3-5] The goal of this paper is to highlight some of the information that have been obtained with the help of the EPR technique in the case of the restricted class of organic radical magnets. Therefore, we will mainly deal with interacting spins belonging to π molecular orbitals, the latter orbitals being characteristic of a single molecule. The first observation of bulk ferromagnetism in an organic radical has been reported very recently.[6,7] We except the ferromagnetic polymers due to the lack of reproducible experiments.[8] The physical background of the EPR properties of low dimensional magnets will be first recalled (Section 2. Spin correlations and EPR), as it is one of the best suited technique for the study of organic radicals. The experimental results that have been selected depict first the peculiar behavior of a class of materials described as *molecular semiconductors*[9,10]: the lutetium bisphthalocyanine and the lithium phthalocyanine π-radical compounds (Section 3. Phthalocyanine radicals). Low dimensional effects on spin exchange narrowed EPR spectra have been intensively studied in these materials.[11-14]. The EPR properties of α-substituted nitronyl nitroxide radicals are presented in the next section (Section 4. Nitronyl nitroxide derivatives). We will focus on the temperature dependent shift of the resonance field that has been observed in these organic magnets.

2. SPIN CORRELATIONS AND EPR.

There are well known different experimental techniques probing the behavior of the spin correlation function.[15] They divide into two classes depending upon whether the space and/or time scale that they provide for the observations. The macroscopic properties such as the specific heat or the magnetic susceptibility are related to the static correlation function. The dynamical behavior is probed through, e.g. the neutron scattering, the Nuclear Magnetic Resonance, and the EPR. The choice of EPR as the leading technique for our studies is shortly justified hereafter on an experimental point of view. Its high sensitivity, currently 10^{13} $\text{spins.cm}^{-3}.\text{G}^{-2}$, allows to perform experiments on a very low mass of sample e.g. a few μg. This corresponds to the usually small single crystals that are obtained through chemical synthesis and crystallization. It is worth noting that EPR yields a great accuracy on the resonance field and the linewidth. However, depending upon the signal to noise ratio the accuracy may be rather poor concerning the lineshape. This is especially true, as one has to consider the far wings of the spectrum of a low-D material. In such a case, the pulsed EPR experiment is more suitable, as we will briefly report. The theoretical analysis of the EPR absorption has been basically settled down within the frame of the theory of the linear response.[16-17] The so-called exchange narrowing effects were then first investigated.[17,18] Following further improvements of the basic theory, the present state-of-the-art has been reported in numerous review works until very recently.[19-23] Therefore, we will only give a short overview of the theoretical predictions. This will not be complete, but restricted to the frame of the experimental results that we present on organic radicals.

The time-dependent spin-spin correlation function

$$g(\underline{r},t)=<S_n^i S_m^j(t)> \qquad (1)$$

is the relevant mathematical tool for the analysis of the parameters that are derived from an experimental EPR absorption spectrum: linewidth, lineshape, and resonance field. It expresses the probability for the spin component S^j (j=x,y, or z) at the site m to take account of the state $S_n{}^i$ after a time t. The brackets stand for a thermal average. Instead of the space-time $g(\underline{r},t)$, its full Fourier transform is often used as $g(\underline{q},\omega)$. The interacting spins always experience the Zeeman interaction introduced by the applied field. They further probe the dipolar field, H_D, and the exchange field, H_E. Whereas the dipolar interaction is responsible of the homogenous broadening of the EPR line, the exchange interaction induces a line narrowing. The narrowing effect is due to the modulation of the dipolar interaction by the exchange field. Assuming the isotropic exchange coupling, J, i.e. Heisenberg interaction, it has been shown theoretically in the limit $H_E \gg H_D$ that a diffusion process results for the spin motion at high temperature, $kT \gg J$, in the paramagnetic state. This means that the long time behavior of $g(\underline{r},t)$ or equivalently the low frequency behavior of $g(\underline{q},\omega)$ will be of utmost interest. During an EPR experiment, the q=0 mode (diffusive mode) is probed at the frequency $\omega=0$, ω_e, and $2\omega_e$ ($\omega_e=10^{10}$ rad.s^{-1} for the usual X-band), if one assumes the quadratic Heisenberg interaction between the total spin operators. The effects of the lattice dimensionality are then to emphasize the $\omega=0$ mode relatively to the ω_e and $2\omega_e$ modes. The lower the dimensionality, the higher is the relative importance of the $\omega=0$ mode.

How such effects are detected through EPR is the purpose of the following summary of the theoretical predictions. It is obvious that these peculiar features require a geometrical analysis, since the dimensionality of the spin lattice is involved. There are some relevant magnetic axes. The spin lattice itself is often closely related to the molecular arrangement within the crystal lattice. Therefore, we will mainly deal with anisotropy experiments. The sample consists in a single crystal. It is rotated with respect to the direction of the applied magnetic field, H_0.

2.1. EPR lineshape.[16-20]

The pure dipolar coupling yields a gaussian resonance lineshape. Extreme exchange narrowing in a 3-D system will result in a lorentzian lineshape, whatever the orientation of the sample.[16-18] The low dimensionality of the spin system enhances the role of the null frequency mode, or secular contribution.[19,20] We are therefore expecting an intermediate lineshape for 1-D and 2-D compounds, in between gaussian and lorentzian. This should be observed at any orientation, except the magic angle $\theta=55°$, where the secular contribution to the dipolar interaction vanishes. The lineshape is expected to be lorentzian at this orientation. For a 1-D magnetic chain, the lineshape is proportional to the Fourier transform of $\exp(-t^{3/2})$. For a 2-D layered compound, the time dependence within the exponential decay is logarithmic. As a summary, the lineshape is essentially non-lorentzian for 1-D and 2-D systems, except at the magic angle. The departure from the lorentzian shape is less important for a 2-D compound, due to the less drastic role of the secular contribution.

2.2. EPR linewidth.[19,20]

The overall angular dependence of the EPR linewidth also demonstrates the prominent role of the null frequency mode as the dimensionality decreases. This is mainly observed through the existence of a minimum at the magic angle at low dimension. Due to the peculiar time decay of the correlation function at 1-D and 2-D, the power law of the secular dipolar contribution is different in 1-D and 2-D. As the spectral density of the spin correlation function exhibits a flat frequency dependence for a 3-D exchange narrowed EPR line, the aforementioned peculiarities are not observed. The angular dependence of the half-width at half-maximum, $\Delta H_{1/2}$, may be summarized as follows[19]:

1-D: $\Delta H_{1/2} \propto |3\cos^2\theta - 1|^{4/3}$ (2)

2-D: $\Delta H_{1/2} \propto (3\cos^2\theta - 1)^2$ (3)

3-D: $\Delta H_{1/2} \propto (1 + \cos^2\theta)$ (4)

It is worth mentioning that these relations are not strictly correct at 1-D and 2-D. The reason is that we have solely considered the angular dependence of the secular contribution, which is expected to be dominant. However, a behavior in between low-D and 3-D will be observed as the effects of the non-secular contributions at ω_e and $2\omega_e$ will arise.[20] The efficiency of the interchain or interplane interactions will induce such a departure, either as the temperature decreases or as they are rather strong.

2.3. EPR g-factor.

As we will present our own new results concerning the temperature dependence of the g-factor, we will discuss more about this section. A temperature dependent shift of the resonance field, or equivalently a g-shift, has been observed in low dimensional antiferromagnetic[24-27], ferrimagnetic[28-30] and ferromagnetic[31] metal complexes.[32] The shift is anisotropic. It depends upon the direction of the applied magnetic field with respect to the orientation of the crystal sample. This occurs at low temperature, within the temperature range where the effects of the short range magnetic order (SRMO) are expected to become important in low-D magnets. The theoretical explanation was suggested in the frame of the Kubo-Tomita theory[17] taking into account the effects of the SRMO.[24,25,33-35]. However, Boucher[36] has shown that at least in the case of the 1-D antiferromagnetic compound TMMC, these effects should be attributed mostly to the anisotropy induced by the dipolar field rather than to the applied magnetic field. Most of the reported observations indicate at least semi-quantitative agreement with the theory elaborated by Nagata.[24] Basically, the relative shift of the g factor is given as[27]:

$$\Delta g_i/g_i=(3\cos^2\theta-1)(\chi_{//}/g^2_{//}-\chi_\perp/g^2_\perp)/(2\chi_i/g^2_i) \qquad (5)$$

This relation states that the shift along the i direction is proportional to the anisotropy of the susceptibility along the principal directions. The shift along the magnetic axis is predicted to be positive for both ferromagnetic and antiferromagnetic interactions owing to the temperature dependence of the susceptibility.[34,35] It has been shown to be negative in the case of ferrimagnetic interactions in chain compounds.[28-30] It is worth noting the geometrical term which expresses the anisotropy induced by the dipolar interaction. Moreover, this correspond to the secular contribution, the role of which we have already much emphasized. In the case of a uniaxial system, either 1-D or 2-D, we recognize that the shift along the magnetic axis should be simply minus twice the shift along the perpendicular direction. Another point of interest is that there should be no shift at the magic angle.

From the preceding remarks, we feel that we have very simple ways to check experimentally the described behavior. However, the theoretical results of the preceding subsections have been mainly checked for low dimensional metal complexes. In particular, the theory of the g-shift assumes the classical spin limit, i.e. large spin value such as e.g. 5/2 for Mn complexes. We may wonder about the extension to the radical 1/2 π-spin, although the conclusions have been shown to be valid for the spin 1/2 of Cu.[26] Moreover, we are expecting a weak anisotropy for the π-radical compounds as compared to the transition metal complexes. For instance, the spin-orbit coupling is usually very weak in the organic radicals. Let us assume that the above theoretical background may be at least qualitatively valid, due to the basic ideas such as spin exchange and dipolar coupling in low-D systems that are involved. We should then be able to determine the magnetic axis for the exchange interactions. Therefore, the analysis of the molecular packing may yield indications about the relevant chemical groups for the magnetic interactions. Such a possibility will be investigated in section 4. We next recall the experimental results concerning the phthalocyanine radical derivatives, known as molecular semiconductors submitted to spin exchange narrowing.

3. PHTHALOCYANINE RADICALS.

We have intensively studied the EPR properties of the radical compounds lutetium bisphthalocyanine, Pc_2Lu (Fig. 1a), and lithium phthalocyanine, PcLi (Fig. 1b), with special emphasis both on their electrical and magnetic properties.[10-14,37-42] We will focus on the spin exchange narrowing mechanisms leading to spin diffusion processes that have been observed in these materials.

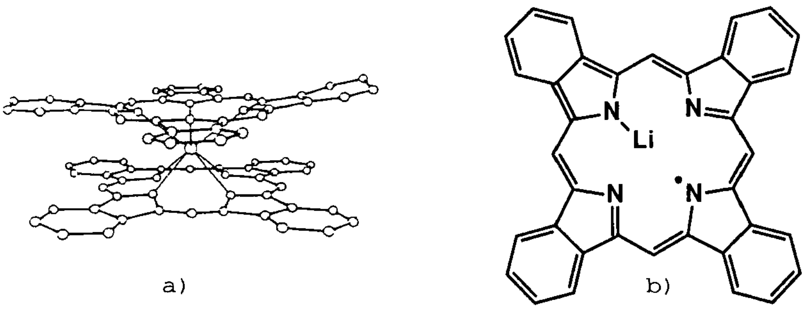
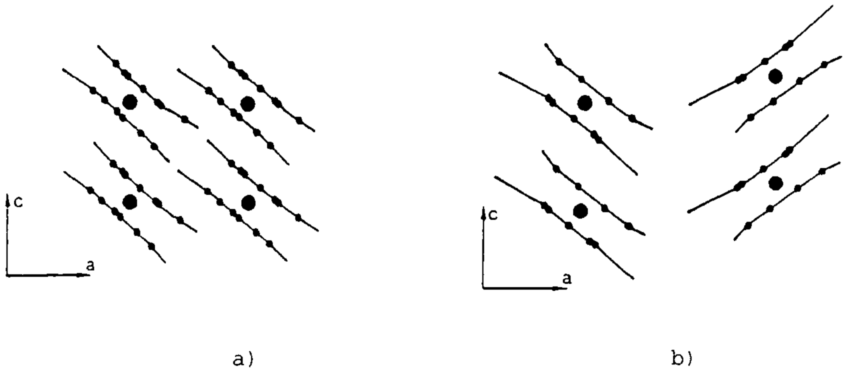


FIGURE 1. Schematic representation of a) Pc_2Lu, and b) PcLi molecules.

3.1. Lutetium bisphthalocyanine.

The lutetium bisphthalocyanine has been studied in two different crystalline forms. Whereas the single crystals of Pc_2Lu exhibit a 2-D molecular arrangement (Fig. 2a), the solvated compound, $Pc_2Lu.CH_2Cl_2$, yields a 1-D packing (Fig. 2b).

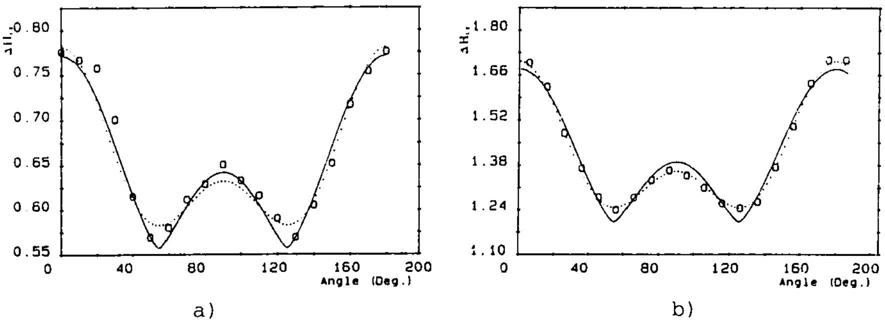
The exchange narrowing may be first inferred from the line narrowing occurring between the condensed state ($0.5\ G<\Delta B_{pp}<2\ G$ for both molecular arrangements[11,12]) and the isolated molecule into solution ($\Delta B_{pp}=11$ G).[41] Both compounds are seen to exhibit intermolecular magnetic interactions. The temperature dependence of the EPR spin susceptibility of a polycrystalline sample of $Pc_2Lu.CH_2Cl_2$ is Curie-Weiss like, with a positive Weiss temperature of about 5K.[11] This suggests a ferromagnetic coupling between the molecular units. However, due to the lack of sample the static magnetic properties could not be studied in order to assess such a behavior. A similar behavior is observed for a single crystal of Pc_2Lu yielding a Weiss temperature of about -6 K, thus suggesting the intermolecular antiferromagnetic coupling. However, like as the solvated compound, more accurate experiments could not be performed.



a) b)

FIGURE 2. Schematic crystal packing in a) Pc_2Lu, and b) $Pc_2Lu.CH_2Cl_2$.

The spin diffusion processes have been shown to characterize these exchange coupled localized spin systems. Such a behavior could be accurately probed with the help of the EPR technique. The study of the anisotropy of the linewidth and the study of the lineshape have been performed (Fig. 3). The results nicely fit with the previously recalled



a) b)

FIGURE 3. Variation of the linewidth as a function of the angle between the magnetic axis and the applied magnetic field for a) $Pc_2Lu.CH_2Cl_2$[11], and b) Pc_2Lu[12].

theoretical results (see sect. 2.1. and 2.2.). The 1-D character of the spin diffusion in $Pc_2Lu.CH_2Cl_2$ is suggested by the angular dependence of the linewidth at room temperature[11] (Fig. 3a). The observed behavior is well represented by Eq. (2) of sect. 2.2. Such an agreement between experiment and theory is also found for the 2-D Pc_2Lu. The angular dependence of the linewidth of Pc_2Lu at room temperature is well described by eq. (3) of sect. 2.2 (Fig. 3b).[12]

The analysis of the lineshape along the magnetic axis and at the magic angle yields a good agreement with the expected behavior (see sect. 2.1.). Whereas the lineshape at the magic angle is close to lorentzian for Pc_2Lu, a departure from the lorentzian shape was observed along the magnetic axis.[12] The pure 1-D diffusive behavior of $Pc_2Lu.CH_2Cl_2$ could be directly checked with the help of the pulsed EPR technique. The free induction decay at 0° exhibits the time dependence fitted by the $\exp(-t^{3/2})$ law as mentioned in sect. 2.1 (Fig. 4).[37]

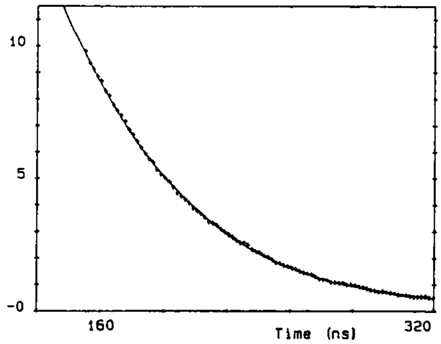


FIGURE 4. Pulsed EPR experiment: free-induction decay of $Pc_2Lu.CH_2Cl_2$ along the magnetic axis fitted by an $\exp(-t/T_2)^{3/2}$ law.[37]

3.2. Lithium phthalocyanine.

The lithium phthalocyanine radical condenses in the quadratic lattice. The 1-D molecular packing is observed along the c axis (Fig. 5).The most interesting feature is the possibility of the absorption of dioxygen, O_2, between the chains of macrocycles. The overall magnetic behavior of PcLi is closely related to the observed coupling of the radical spins with the triplet spin of O_2.[14,40] Whereas the linewidth of the isolated molecule is about 6 G[43], the line may be as narrow as a few mG in the solid state. The linewidth of single crystals depends

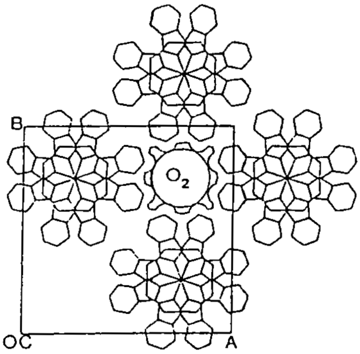
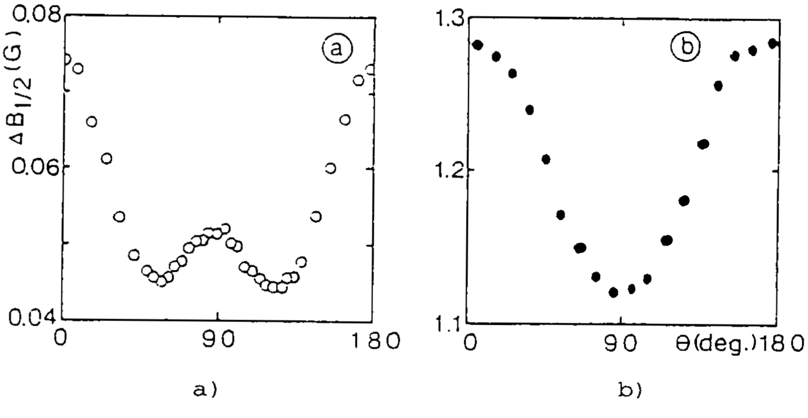


FIGURE 5. Projection of the crystal structure of PcLi along the c-axis. The absorption channels for the O_2 molecules are indicated.

strongly upon the O_2 partial pressure.[14,38] The magnetic history of PcLi is complex, due to the presence of O_2. There are different spin species whose concentration depends upon the O_2 content. The local interaction of the radical spins with the triplet spins of O_2 has been shown to result in a high spin state S=3.[14]

At room temperature, the EPR line of samples held under vacuum is very narrow. This signal has been attributed to the free spins, those which have little interaction with O_2. Its angular dependence exhibits the minimum at the magic angle, then suggesting the spin diffusion in a low-D system (Fig. 6a).

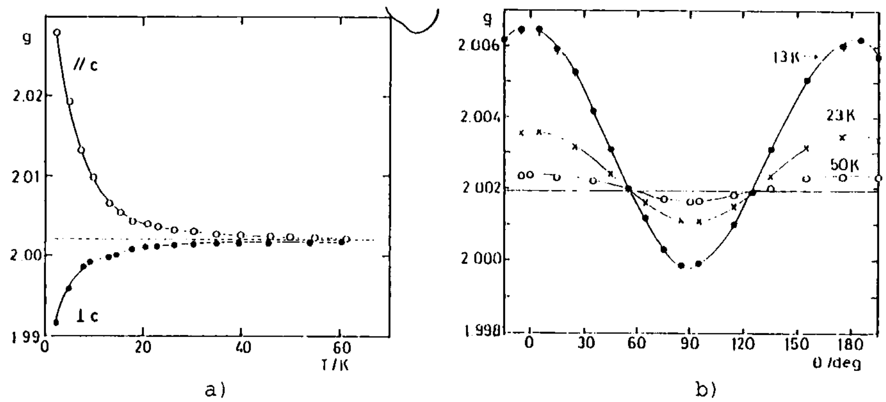


a) b)

FIGURE 6. Angular variation of the linewidth of PcLi between the c-axis and the applied magnetic field a) for a sample held under vacuum, b) for a sample exposed at the air.

However, a much broader line is observed for a sample kept at ambient atmosphere, i.e. in the presence of O_2. The behavior is then typical of isotropic spin diffusion (Fig. 6b). As for the low-D behavior, it is not possible to directly evidence a 1-D spin diffusion by use of eq. (2) as expected from the molecular packing. Here we have a good example of the break of the pure 1-D spin diffusion as we mentioned in section 2.2. The residual molecules of O_2, which have been shown to be always present[14], induce a cutoff of the spin diffusion along the chain axis. Therefore, the non-secular contributions to the spectral density of the spin correlation function do play a role.

The temperature dependence of the g-factor of the spin species attributed to the coupling with O_2 reveals an anisotropic shift at low temperature (Fig. 7a). The g-tensor is isotropic at room temperature with g=2.0020. We observe a positive shift along the chain axis. It is about twice the negative shift in the perpendicular direction. The anisotropy of the g-factor at different temperatures below 50 K underlines the absence of a shift at the magic angle (Fig. 7b).



a) b)

FIGURE 7. a) Temperature dependence of the g-factor of PcLi along the parallel and perpendicular orientations relative to the c-axis; b) angular variation of the g-factor at different temperatures.

These observations fully agree with the basic features outlined by eq. (5), as already mentioned in sect. 2.3. Assuming the validity of the proposed theoretical frame, we may infer the magnetic axis to correspond to the molecular stacking axis. In the present case this is rather obvious, since the p_z molecular orbitals of the C atoms overlap along the c axis yielding high spin density channels.[13,44]

However, let us think of a crystal structure exhibiting different close intermolecular contacts. The determination of the relevant axis for magnetic interactions is then ambiguous given the usual lack of a large enough sample for a neutron diffraction experiment. It is the purpose of the next section to show that we may have the possibility to predict the direction of the magnetic axis by performing the temperature dependence of the g-tensor.

4.NITRONYL NITROXIDE DERIVATIVES.

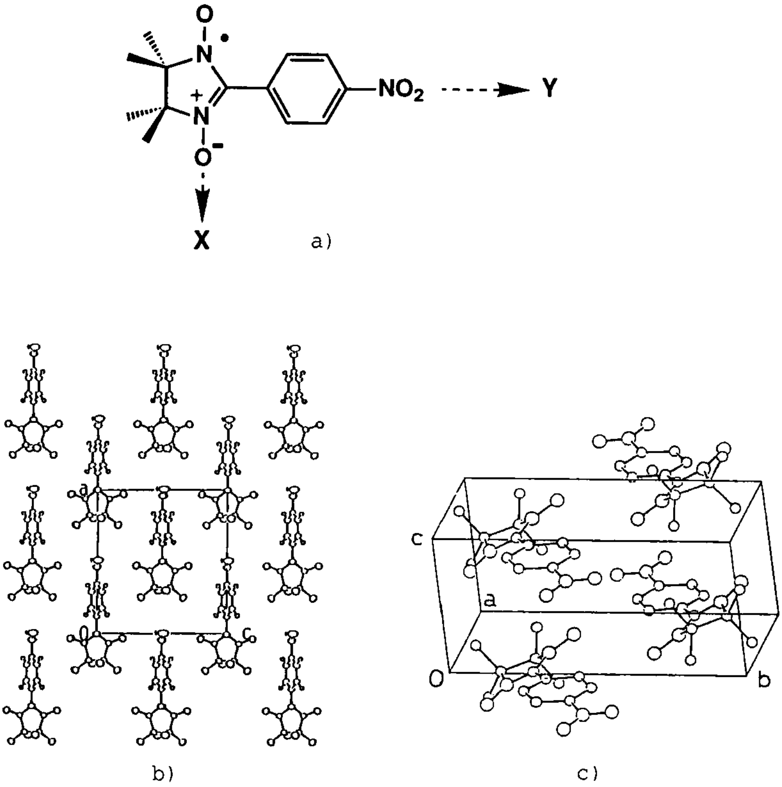


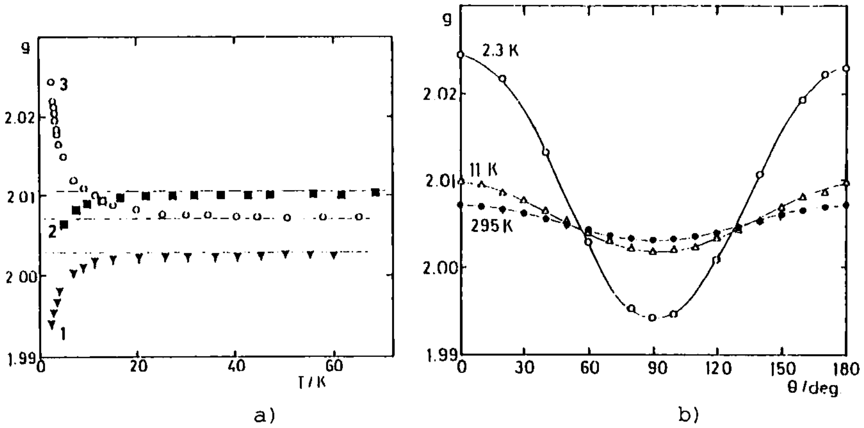
FIGURE 8. a) Scheme of the p-NPNN molecule, b) crystal structure of β-NPNN (projection along the b axis)[50], c) crystal structure of γ-NPNN (projection along the a axis).[47]

The single crystals of the p-nitrophenyl nitronyl nitroxide radical, p-NPNN (Fig. 8a), exhibit polymorphism.[7,45-47] We will present the results obtained on the temperature dependence of the g-tensor of two different phases, namely β-NPNN (Figure 8b) and γ-NPNN (Fig. 8c). The intermolecular ferromagnetic coupling is observed in both phases.[45,47]

It has been demonstrated that γ-NPNN is a good example of the spin 1/2 quasi-1D Heisenberg ferromagnetic chain[48,49] down to about 0.65 K, where it orders antiferromagnetically.[7,49] Moreover, β-NPNN undergoes a transition towards a bulk ferromagnetic ordered state below 0.6 K.[7,50]

4.1. β-NPNN.

The principal values of the g-tensor are determined at room temperature as g_c=2.0106, g_a=2.0070, and g_b=2.0030. The principal axes are found to coincide with the crystal axes a,b,c. The molecular frame is such as X is pointing along the nitroxide direction on the twisted five-membered ring, Y is the symmetry axis of the molecule pointing to the nitro group, and Z is the perpendicular to the (X,Y) plane (Figure 8a). The g-tensor is anisotropic. It exhibits a slight departure from the free-electron g-value. This is well understood, because most of the spin density is expected at the NO site and the spin-orbit coupling occurs at this site.



a)

b)

FIGURE 9. a) Temperature dependence of the g-factor of β-NPNN along three perpendicular directions (see text), b) angular variation of the g-factor within the (1,3) plane (see text) at different temperatures.

The temperature dependence of the g-factor has been recorded down to 2.3 K along three perpendicular orientations (Fig. 9a), given the crystal shape. The experimental frame (1,2,3) is such as the 3.axis coincides with the a axis, equivalently the Y molecular axis. The 1 and 2 axes are nearly aligned with the b and c axes respectively. At room temperature, we get g_1=2.0026, g_2=2.0106 and g_3=2.0071. A shift of the g-factor is observed below c.a. 30 K. As expected (see sect 2.3), the shift is much smaller than observed in transition metal complexes.[24-31]

It is positive along the a axis being about twice the shift along the two other directions. It is worth mentioning that the anisotropy of the linewidth is not detectable. This has to be linked to the almost isotropic dipolar field expected from the highly symmetrical molecular arrangement. However, the role of the secular term of the dipolar coupling (see sect. 2.3) is well evidenced on Fig. 9b. The angular variation of the g-factor is recorded within the (1,3) plane at different temperatures. There is no g-shift at the magic angle, as previously noted for the PcLi compound (sect. 3.2.).

Assuming the qualitative validity of the previously described theoretical frame, such a behavior may indicate that i) the magnetic system is of uniaxial symmetry, and ii) the magnetic axis corresponds to the a axis. It is worth noting that the thermal behavior of the spin susceptibility does not reveal the peculiar features of a low dimensional magnetic lattice.[7,52] The existence of a 2-D network of intermolecular contacts between the side NO group and the nitrogen atom of the NO_2 group has been first emphasized for the β-phase.[51] However, short intermolecular distances are also found between the side NO and the side of the phenyl ring. This suggests a 3-D molecular packing. But our results on the g-shift point to the a axis as a unique symmetry axis for the magnetic properties of β-NPNN. This may indicate the existence of 2-D layers within the (a,b) plane (or 1,2 plane for our experiments). As a matter of fact, the usual geometry for the 2-D magnetic materials is such as the magnetic axis of the 2-D lattice is perpendicular to the magnetic layers. The full understandig of the origin of the behavior of the g-tensor should be considered in order to consistently relate the observed anisotropic g-shift with the isotropic magnetic behavior of this compound. There is the need to keep in mind that the suggested anisotropy may not be fully attributed to the only but one exchange interaction. The contribution of the dipolar field itself might have to be considered in such a case, although it is expected to be almost isotropic.[53]

4.2. γ-NPNN.

The analysis of the triclinic structure of the γ-phase (Fig. 8c) yields the same intermolecular short contacts than in the β-phase. The shortest intermolecular distances are found along the c axis, between NO and NO_2. The principal values of the g-tensor at room temperature are $g_X=2.0115$, $g_Y=2.0052$, and $g_Z=2.0035$. The (X,Y,Z) frame corresponds to the molecular frame as previously defined.

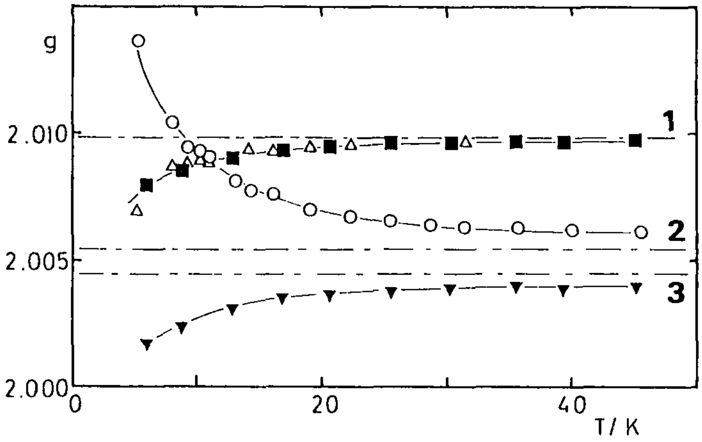


FIGURE 10. Temperature dependence of the g-factor of γ-NPNN along three perpendicular directions (see text).

For the study of the temperature dependence of the g-factor, the experimental frame (1,2,3) was such that the c-axis coincides with the 1 axis. The a*-axis corresponds to the 3-axis and the 2-axis is perpendicular to the (a*,c) plane. The temperature dependence of the g-factor along 1,2 and 3 is represented in figure 10, with $g_1=2.0097$, $g_2=2.0060$, and $g_3=2.0044$ at room temperature.

It is well observed the largest positive g-shift along the c axis, about twice the negative shift along the two other orientations. Therefore, the magnetic axis is suggested to point along the c axis. As the magnetic behavior of γ-NPNN has been well assessed as quasi-1D ferromagnetic Heisenberg[48,49], we may conclude that the ferromagnetic chain is parallel to the c-axis. This indicates the ferromagnetic intermolecular interaction between the NO and the NO_2 chemical groups. It has been recently proposed that the weak interchain interaction in γ-NPNN consists of the ferromagnetic and the antiferromagnetic coupling.[49] The latter one induces the antiferromagnetic order below 0.65 K. From the behavior of both the β-phase and the γ-phase, we reach the conclusion that the intermolecular contact between the side of the phenyl ring and the NO group cannot yield the antiferromagnetic coupling, given the highly probable relashionship between the short intermolecular contacts and the magnetic interactions. If it was the case, the ferromagnetic ordering could not occur in the β-phase,

5. CONCLUSION.

We have recalled the efficiency of the EPR technique as a probe of the spin correlations in low-D organic magnets. This has been demonstrated with the help of different π-radical materials. The relevance of the theoretical background, which was mainly checked in the case of metal complexes, to the field of π-molecular compounds is at least qualitatively established. Moreover, we have suggested that the analysis of the temperature dependence of the g-factor of radical magnets may be of great help in order to get detailed information about the intermolecular magnetic interactions in organic radicals. The opportunity of such an sensitive experimental tool for the study of the magnetic interactions in organic radicals is suggested for the first time. As a summary, the anisotropic g-shift is observed in PcLi, and in both the β-phase and the γ-phase of p-NPNN. The importance of the role of the dipolar coupling is emphasized. However, in order to allow a more detailed discussion, there is the need of a theoretical frame well suited to the organic radicals. For instance, the g-shift in the γ-phase of NPNN seems to be directly related to the known magnetic properties of this material. However, the corresponding behavior in the β-phase points to some anisotropy which is not obviously related to the magnetic behavior of this phase. The full analysis of the results on the g-factor of the nitronyl nitroxide radical derivatives will be reported in a forthcoming publication.[53]

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REFERENCES

1. NATO ARW Molecular Magnetic Materials, edited by D. Gatteschi, O. Kahn, J.S. Miller and F. Palacio, E198, (1991).
2. H. Iwamura, Adv. Phys. Org. Chem., 26, 179 (1990).
3. J. S. Miller and A.J. Epstein, Chemtech, 168 (March 1991).
4. K. Nakatani, P. Bergerat, E. Codjovi, C. Mathoniäre, Yu Pei and O. Kahn, Inorg. Chem., 30, 3977 (1991)
5. A. Caneschi, D. Gatteschi, R. Sessoli and P. Rey, Acc. Chem. Res., 22, 392 (1989).
6. M. Kinoshita, Ph. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe and Y. Maruyama, Chem. Lett., 1225 (1991).
7. Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshitą and M. Ishikawa, ISSP technical report, No 2521, (1992).
8 J. S. Miller, Adv. Mat., 4, 298 (1992).
9. Ph. Turek, P. Petit, J.-J. Andre, J Simon, R. Even, B. Boudjema, G. Guillaud and M. Maitrot, J. Am. Chem. Soc., 109, 5119 (1987).
10. J.-J. Andre, in Nanostructures Based on Molecular Materials, edited by W. Gopel and Ch. Ziegler (VCH, Weinheim-New York-Basel-Cambridge, 1992), p. 251.
11. P. Petit, K. Holczer and J.-J. Andre, J. Physique, 48, 1363 (1987)
12. P. Petit and J.-J. Andre, J. Physique, 49, 2059 (1988).
13. Ph. Turek, M. Moussavi, P. Petit and J.-J. Andre, Synth. Met., 29, F65 (1989)
14. Ph. Turek, J.-J. Andre, M. Moussavi and G. Fillion, Mol. Cryst. Liq. Cryst., 176, 535 (1989).
15. M. Steiner, J. Villain and C. G. Windsor, Adv. Phys., 25, 87 (1976).
16. R. Kubo, in Lectures in Theoretical Physics, (Intersciences Publishers, New York, 1959), 1, p. 120.
17. R. Kubo and K. Tomita, J. Phys. Soc. Japan, 9, 888 (1954).
18. P. W. Anderson and P. R. Weiss, Rev. Mod. Phys., 25, 269 (1953).
19. P. M. Richards, in Local Properties at Phase Transitions, (North-Holland, Amsterdam, 1976), p. 539.
20. H. Benner and J.-P. Boucher, in Physics and Chemistry of Materials with Low Dimensional Structure, vol. IX: Magnetic Properties of Layered Transition Metal Compounds, edited by L. J. de Jongh (Kluwer Academic Pub., Dordrecht-Boston-London, 1990), p. 323.
21. J. E. Drumheller, Magn. Res. Rev., 7, 123 (1982).
22. D. Gatteschi and R. Sessoli, Magn. Res. Rev., 15, 1 (1990).
23. A. Bencini and D. Gatteschi, EPR of Exchange Coupled Systems, (Springer-Verlag, Berlin-Heidelberg, 1990).
24. K. Nagata and Y. Tazuke, J. Phys. Soc. Japan, 32, 337 (1972).
25. K. Nagata, Y. Tazuke and K. Tsushima, J. Phys. Soc. Japan, 32, 1486 (1972).
26. K. Oshima, K. Okuda and M. Date, J. Phys. Soc. Japan, 41, 475 (1976).
27. K. Nagata, I. Yamamoto, H. Takano and Y. Yokozawa, J. Phys. Soc. Japan, 43, 857 (1977).
28. D. Gatteschi, O. Guillou, C. Zanchini, R. Sessoli, O. Kahn, M. Verdaguer and Yu Pei, Inorg. Chem., 28, 287 (1989).
29. A. Caneschi, D. Gatteschi, J.-P. Renard, P. Rey and R. Sessoli, Inorg. Chem., 28, 1976 (1989); 28, 3314 (1989)
30. A. Caneschi, D. Gatteschi, P. Rey and R. Sessoli, Inorg. Chem., 30, 3936 (1991).

31. R. Hoogerbeets and A.J. Van Duyneveldt, Physica, 121B, 233 (1983).
32. ref. 23 , p. 162.
33. K. Nagata, Physica, 86-88B, 1283 (1977).
34. H. Okamoto and T. Karasudani, J. Phys. Soc. Japan, 42, 717 (1977).
35. T. Karasudani and H. Okamoto, J. Phys. Soc. Japan, 43, 1131 (1977).
36. J.-P. Boucher, J. Magn. Magn. Mat., 15-18, 687 (1983).
37. P. Petit, Synth. Met., 46, 147 (1992).
38. P. Petit and J.-J. Andre, BRUKER Report, 2, 7 (1989).
39. Ph. Turek, J.-J. Andre and J. Simon, Solid State Commun., 63, 741 (1987)
40. Ph. Turek, M. Moussavi and J.-J. Andre, Europhys. Letters, 8, 275 (1989).
41. P. Petit, thesis, Strasbourg (France), unpublished (1987).
42. Ph. Turek, thesis, Strasbourg (France), unpublished (1989).
43. Ph. Turek, J.-J. Andre, A. Giraudeau and J. Simon, Chem. Phys. Lett., 134, 471 (1987).
44. B. Gottschy, private communication (1989).
45. K. Awaga and Y. Maruyama, Chem. Phys. Lett., 158, 556 (1989); J. Chem. Phys., 91, 2473 (1989).
46. P.M. Allemand, C. Fite,G.Srdanov, N. Keder, F. Wudl and P. Canfield, Synth. Met., 41-43, 327 (1991).
47. Ph. Turek, K. Nozawa, D. Shiomi, K. Awaga, T. Inabe, Y. Maruyama and M. Kinoshita, Chem. Phys. Lett., 180, 327 (1991).
48. M. Takahashi, Ph. Turek, Y. Nakazawa, M. Tamura, K. Nozawa, D. Shiomi, M. Ishikawa and M. Kinoshita, Phys. Rev. Lett., 67, 746 (1991).
49. M. Takahashi, M. Kinoshita and M. Ishikawa, ISSP technical report, No 2544, (1992).
50. M. Kinoshita, Mat.Res. Symp. Proc., 247, 429 (1992).
51. K. Awaga, T. Inabe, U. Nagashima and Y. Maruyama, J. Chem. Soc. Chem. Commun., 1617 (1989); 520 (1990).
52. M. Kinoshita, this conference.
53. Ph. Turek et al., to be published.