

Role of the demagnetizing field on the EPR of organic radical magnets

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It has been long thought that microscopic mechanisms related to magnetic short-range order were responsible for the temperature dependence of the electron paramagnetic resonance \mathbf{g} tensor in low-dimensional magnetic systems. We show here that the demagnetizing field can explain qualitatively and quantitatively the observed features, i.e., (i) the g shift, variation of the g value, (ii) the presence of magic angles where there is no g shift, and (iii) the reorientation of the \mathbf{g} tensor with temperature. These features are discussed theoretically and supported experimentally in purely organic insulating compounds. Previous results obtained on two different nitroxide derivatives are revisited in this framework. The role of the demagnetizing field may probably be generalized to most low-dimensional molecular materials. [S0163-1829(97)07213-5]

I. INTRODUCTION

The effects of the demagnetizing field are well known in ferromagnetic and in superconducting materials.¹ Demagnetization is not a new concept introduced in magnetic resonance spectroscopy (e.g., ferromagnetic resonance), but it is usually neglected in the study of weakly coupled magnetic materials, since it is expected that it would have only a small influence on the resonance field. However, the great sensitivity in the magnetic field measurement (≈ 1 mG) of electron paramagnetic resonance (EPR) spectroscopy allows the detection of small shifts even in purely paramagnetic compounds. We studied² several series of purely organic compounds derived from the nitronyl nitroxide radical. These compounds show different types of magnetic “dimensionality” [from zero dimensions (0D) to 3D] and various kinds of magnetic exchange interaction (ferromagnetic or antiferromagnetic). The magnetic dimensionality of the spin system might be inferred from the study of the temperature dependence of the EPR \mathbf{g} tensor. Such information is of utmost importance for the understanding of the magnetic properties of molecular compounds. The ease of assessment of the magnetic axis of a low-dimensional magnetic system from an EPR study is very attractive, as compared to more sophisticated and rather heavy techniques, such as neutron diffraction and/or very-low-temperature experiments, i.e., below

the transition temperature. The rapidly growing field of molecular magnetism urged us to check the validity of this method.

It will be shown in this work that our own experiments performed on purely organic compounds are well understood in terms of the demagnetizing field effects. Our conclusions rule out any possible determination of the magnetic axis within the frame of the previous model. The experimental results and the previous theoretical background are first recalled and summarized (Sec. II). The theoretical predictions for the effects of the demagnetizing field on the EPR response are derived in the following sections (Secs. III–V), and the predictions are compared to our experimental results. It is shown that the demagnetizing field explains well all observed features in organic magnetic materials. Moreover, a critical survey of previous experimental results shows that it is difficult to assess any effect of short-range magnetic order, given the estimated effects of the demagnetizing field (Sec. VI).

II. LOW-DIMENSIONAL BEHAVIOR

A large amount of evidence for a temperature-dependent shift of the elements of the \mathbf{g} tensor in low-dimensional magnets has been brought about since the early 1970s.^{3,4} The g shifts were observed for compounds exhibiting either ferro-

magnetic or antiferromagnetic exchange coupling. The materials studied may be metal alloys, metal complexes, or purely organic compounds. It is widely accepted that it is possible to deduce information on the magnetic anisotropy of low-dimensional exchange-coupled spin systems from the temperature dependence of the \mathbf{g} tensor.^{3,4} The observed "standard" behavior may be summarized as follows.

(i) A downwards or upwards shift of the resonance field is observed as the temperature decreases in uniaxial low-dimensional magnetic system, depending on the orientation of the crystal with respect to the applied static field.

(ii) The absolute value of the shift along the anisotropy axis is twice its absolute value along orthogonal orientations.

Nagata and co-workers^{3(e),3(f),3(l)} set up a theoretical treatment in order to rationalize the above depicted behavior in antiferromagnetic chains of metal complexes. This model was further extended to the case of 2D antiferromagnets,^{3(m)} and 1D ferromagnets⁵ and ferrimagnets.^{4(e)} As a summary of these theoretical results, a weak uniaxial dipolar anisotropy is responsible for the g shift. Essentially, it is related to the anisotropy of the magnetic susceptibility. The relationship to the short-range magnetic order in low-dimensional magnets is given through the temperature dependence of the spin correlation function estimated within the classical spin limit.^{3(c),3(f)} It is worth noting the rule for the predicted g shift parallel (\parallel) and perpendicular (\perp) to the magnetic chain:

$$\Delta\omega_{\parallel} + 2\Delta\omega_{\perp} = 0. \quad (1)$$

The wide use of these results is based on their ability to describe qualitatively the observed behavior at a more or less high level of accuracy.

Some comments and complements have to be noticed in the following.

The resonance field is given by the statistical first moment of the resonance line. Therefore, the g shift cannot occur except for an anisotropic field whether internal or external, e.g., microscopic (anisotropic exchange interaction, single-ion anisotropy, dipole-dipole couplings) or macroscopic terms (demagnetizing field). These anisotropic fields are also responsible for the anisotropy of the magnetic susceptibility. We stress that the effects of the short-range magnetic order in low-dimensional magnets, thoroughly referred to in most previous works, may be recognized only through the sign of the temperature dependence of the g shift and not by the g shift itself.

Although Nagata *et al.*^{3(e),3(f)} have mentioned the demagnetizing field corrections in their work, they found them to be negligible compared to the effects of the short-range magnetic order in their work. This point will be discussed in Sec. VI. To our knowledge, Ajiro and Miura^{3(h)} were the first to consider qualitatively the demagnetizing field to account for the g shift observed in EPR experiments.

The influence of the sample shape and temperature on the EPR linewidth above the Curie point of a ferromagnet has been proposed^{3(i),3(j)} the frame of a phenomenological theory. This theory ascribes the behavior of the resonance field to the anisotropy of the macroscopic magnetic susceptibility.

Nagata *et al.* have drawn similar conclusions.^{3(m)} They also include the secular dipolar contribution ($3\cos^2\theta - 1$) in

the uniaxial case. Therefore it is stated that no g shift occurs at the magic angle ($\theta_d = 54.7^\circ$), i.e., the vanishing of the dipolar contribution.

The only severe criticism of Nagata's theory has been made by Boucher.⁶ The latter suggests that the dipolar interaction alone is responsible for the g shift observed in the 1D antiferromagnetic chain compound TMMC.^{3(e)}

The above summary is the present state of the art of the g shift and its theoretical background in inorganic materials. As already mentioned, Nagata's results are appealing owing to the easy check they provide for the dimensionality and for the anisotropy of the magnetic system. We have investigated the EPR properties of pure organic magnetic materials in order, if possible, to extend the frame of these ideas to π -radical compounds.^{2,4(i)} Recently, ferromagnetic resonance experiments⁷ performed at very low temperature have shown that the g shift^{4(i),4(k)} observed in the paramagnetic regime of the β phase of the organic ferromagnet p -NPNN (Ref. 8) was due merely to demagnetizing field effects.

Starting from these facts and from some of the above comments on Nagata's theory, it is necessary to clearly state which effect (demagnetization vs dipolar interaction or short-range magnetic order) is responsible for the g shift at least in organic magnets. We now turn to the evaluation of the effects of the demagnetizing field on the \mathbf{g} tensor.

III. TEMPERATURE-DEPENDENT g SHIFT

The internal magnetic field \mathbf{H}_i within a magnetic material does not coincide with the applied external field \mathbf{H}_e . It must be corrected by the demagnetizing field, which is related to the magnetization \mathbf{M} via the demagnetizing tensor \mathbf{N} :

$$\mathbf{H}_i = \mathbf{H}_e - \mathbf{N}\mathbf{M} = \mathbf{H}_e(1 - \mathbf{N}\chi), \quad (2)$$

where χ is the volume susceptibility. The demagnetizing tensor is a rank-2 symmetric tensor ($\text{Tr } \mathbf{N} = 1$ in SI units and $\text{Tr } \mathbf{N} = 4\pi$ in cgs units), which depends on the shape of the sample. The principal values of \mathbf{N} for a spherical sample are equal: $N_x = N_y = N_z$. The relations between principal values are $N_x = 0$, $N_y = N_z = 2\pi$ for a needle elongated along x , and $N_x = N_y = 0$ and $N_z = 4\pi$ hold for a disk within the (xy) plane. The principal values of \mathbf{N} for a general ellipsoid ($N_i \neq N_j \neq N_k$ and $N_{ij} = 0$ with $i, j, k \equiv x, y, z$ and $N_i \equiv N_{ii}$) have been given.^{9,10} The \mathbf{N} tensor of a sample with a rectangular parallelepiped shape may be estimated upon considering the inscribed ellipsoid. Any departure requires a numerical computation at a difficulty level proportional to the complexity of the shape.¹¹ Further discussions will be limited to shapes close to the rectangular parallelepiped.

The resonance condition (Larmor frequency) for a magnetic material within an external field \mathbf{H}_e directed along the z axis is given by the so-called "Kittel's ferromagnetic formula" derived for the ferromagnetic resonance:¹²

$$\omega_0^2 = \gamma^2 [H_e + (N_y - N_z)M_z][H_e + (N_x - N_z)M_z], \quad (3)$$

where γ is the electron gyromagnetic ratio. This expression holds for a general ellipsoid. It is easily adapted to the principal values of the \mathbf{g} tensor for a paramagnet:

$$g_i(T) = g_{ei} \sqrt{[1 + (N_j - N_i)\chi(T)][1 + (N_k - N_i)\chi(T)]}, \quad (4)$$

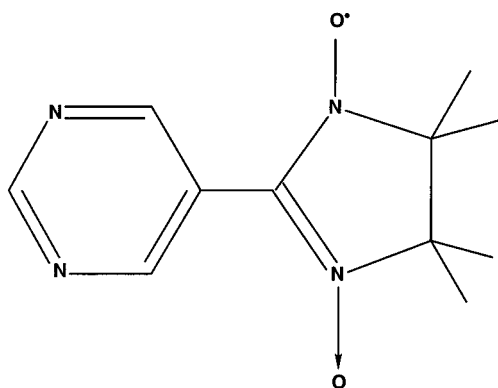


FIG. 1. Molecular structure of PymNN.

where $g_i(T)$ is the temperature-dependent principal value of the \mathbf{g} tensor along the i direction ($g_i \equiv g_{ii}$) and g_{ei} corresponds to the same component measured at infinite temperature without demagnetization effects. Experimentally, it will be replaced by the value measured (g_{iref}) at room temperature (RT). The susceptibility $\chi(T)$ will be considered as nearly isotropic in purely organic compounds. Reasonably considering that $\chi(T) \ll 1$, a first-order expansion gives

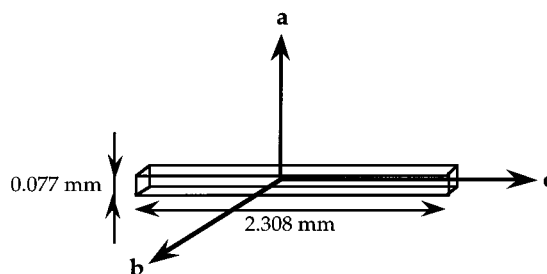
$$g_i(T) \approx g_{iref} \left[1 + \frac{1}{2} (N_j + N_k - 2N_i) \chi(T) \right] \approx g_{iref} [1 + f_i \chi(T)], \quad (5)$$

where f_i is a geometrical factor determined entirely by the principal values of the \mathbf{N} tensor. Equation (5) shows that there will be no g shift for a sphere owing to the equality of the principal values of the \mathbf{N} tensor. In the following two simple cases, it is found (in cgs units) that

needle	along x :	$g(T) \approx g_{ref} [1 + 2\pi\chi(T)]$,
	along y or z :	$g(T) \approx g_{ref} [1 - \pi\chi(T)]$,
disk:	along x or y :	$g(T) \approx g_{ref} [1 + 2\pi\chi(T)]$,
	along z :	$g(T) \approx g_{ref} [1 - 4\pi\chi(T)]$.

It is worthwhile noting that in the two cases the predicted behavior of the g shift is the same as that predicted by Nagata's theory; i.e., they fulfil the condition of Eq. (1). Here \parallel means along the main axis of the needle or perpendicular to the flat part of the disk. Moreover, the disk shape gives rise to the same behavior as that predicted by Nagata in the antiferromagnetic case:^{3(e),3(f),3(g)} The larger shift is negative.

To illustrate our discussion, we show an example of an organic magnetic system: 2-(5-pyrimidinyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-3-oxoimidazol-1-oxyl (or 3,5-pyrimidyl nitronyl nitroxide, shortened PymNN) (Fig. 1). The structural and magnetic properties of this compound are published elsewhere.¹³ The PymNN crystallizes in the tetragonal space group $P4_2bc$. The magnetic properties may be represented by a one-dimensional ferromagnetic chain with an intrachain exchange of +26.2 K and a weaker antiferromagnetic interchain coupling of -1.1 K. The studied sample has a needle shape elongated along the c axis (Fig. 2). The lengths of the edges along the a and b directions are equal within our experimental accuracy (ca. ± 0.025 mm). The principal values of the \mathbf{N} tensor are estimated as $N_a = N_b = 0.498$ and $N_c = 0.004$. These values, calculated us-

FIG. 2. Shape and dimensions of the studied PymNN single crystal. The a , b , and c directions correspond to the crystalline axes.

ing Osborn's results,⁹ are inserted in Eq. (4) in order to simulate the g shift along the crystallographic axes (Fig. 3). The g shifts are expressed here in percent of the g value at room temperature (g_{iref}). One should first note that the largest observed shift of 0.3% is small compared to inorganic systems. The precision of our measurements is not surprising in EPR experiments, since the usual homogeneity and stability of the magnetic field allow an accuracy much better than 0.1 G over 3000 G (X band, 9.5 GHz).

The shift along the needle axis (c) is positive and twice that along the perpendicular directions, which are of opposite sign. The goodness of the simulation of the behavior following Eq. (4) indicates that (i) the demagnetizing field is responsible for most of the shift of the resonance field and (ii) the shape of the sample is very well approximated using Osborn's abaci.⁹ A small discrepancy between the shift along the a and b directions indicates that the opposite faces of the needle are not completely equivalent. The temperature dependence of the averaged g factor of PymNN has also been measured on a powder (Fig. 4).¹⁴ The relative g shift is then much smaller than the one observed in a single crystal: There is no shift of the mean value of the g factor, $g = (g_x + g_y + g_z)/3$. Therefore we conclude that no microscopic effects affect the g factor of PymNN within our experimental accuracy.

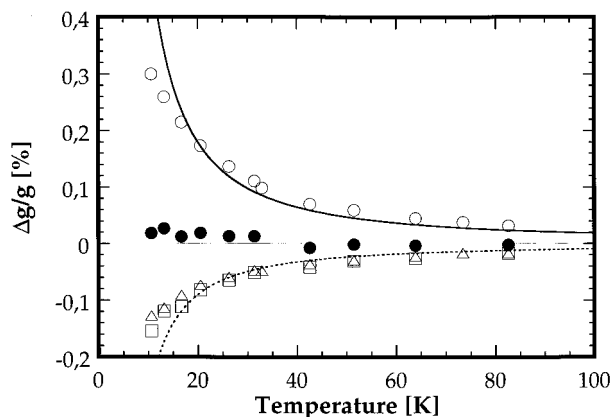


FIG. 3. Temperature dependence of the \mathbf{g} tensor of the PymNN single crystal depicted in Fig. 2 relative to its high-temperature value $\Delta g(T)/g$ and along the crystallographic axes: along c (open circles), along b (open triangles), and along a (open squares); sum of the contributions along a , b , and c : solid circles. The lines represent the fits to Eq. (4): dotted line for the perpendicular direction, solid line for the parallel direction.

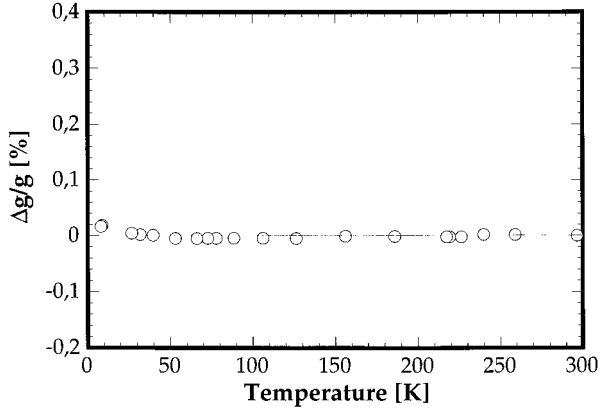


FIG. 4. Temperature dependence of the \mathbf{g} tensor of a powder of PymNN relative to its high-temperature value $\Delta g(T)/g$. Note that the scale is the same as in Fig. 3.

The case of a powder sample may be further discussed. The random orientation of the microcrystals depends on several factors such as (i) the shape of the sample holder, (ii) the shape of the crystallites, and (iii) the value of the applied magnetic field. Points (i) and (ii) are related: For instance, putting needles in a bowl (i.e., the bottom of an EPR tube which is hemispherical) would not give the same orientation distribution as that of needles put on a flat surface. Point (ii) results in the uncomplete cancellation of the demagnetizing field in the EPR spectra of powdered compounds with anisotropic g tensors,¹⁵ except for the spherical grains or a homogeneous distribution of the sample shape. Point (iii) means that in high magnetic field,¹⁶ the crystallites may align with the applied magnetic-field as a result of either anisotropic susceptibility¹⁷ or demagnetizing field.¹⁸ The powder sample would then mimic a single crystal.

In this section, we have shown that the effects of the demagnetizing field in the case of needle or disk are similar to the theoretical predictions for short-range magnetic order. In the case of organic compounds, a quantitative agreement is only obtained with the effects of the demagnetizing field.

IV. MAGIC ANGLES

Section II recalls that the previous theoretical models dealing with the temperature-dependent g shift predict a null effect at the magic angle ($\theta_d = 54.7^\circ$) corresponding to the vanishing of the secular dipolar contribution. For the sake of consistency, we have to check that this also applies for the demagnetizing field effects.

The anisotropy of the \mathbf{g} tensor of a uniaxial system within the (i, j) plane is given by

$$g^2(\theta) = g_{ii}^2 \cos^2 \theta + 2g_{ij}^2 \sin \theta \cos \theta + g_{jj}^2 \sin^2 \theta. \quad (6)$$

The existence of some magic angles θ_m is defined the equivalence of the g factor for two different temperatures as follows:

$$g^2(\theta_m, T_1) - g^2(\theta_m, T_2) = \Delta_{ii} \cos^2 \theta_m + 2\Delta_{ij} \sin \theta_m \cos \theta_m + \Delta_{jj} \sin^2 \theta_m, \quad (7)$$

with

$$\begin{aligned} \Delta_{ii} &= g_{ii}^2(T_1) - g_{ii}^2(T_2), \\ \Delta_{ij} &= g_{ij}^2(T_1) - g_{ij}^2(T_2), \\ \Delta_{jj} &= g_{jj}^2(T_1) - g_{jj}^2(T_2). \end{aligned} \quad (8)$$

The solutions are

$$\theta_m = \tan^{-1} \left(\frac{-\Delta_{ij} \pm \sqrt{\Delta_{ij}^2 - \Delta_{ii} \Delta_{jj}}}{\Delta_{jj}} \right). \quad (9)$$

Therefore, Eq. (7) will be fulfilled for $\Delta_{ij}^2 - \Delta_{ii} \Delta_{jj} \geq 0$. The physical solution corresponds to opposite variations of the \mathbf{g} tensor with the temperature along orthogonal directions, i.e., for $\Delta_{ii}(T)$ and $\Delta_{jj}(T)$, since the off-diagonal components are much smaller than the diagonal ones, typically $g_{ii} \approx 2000g_{ij}$.

The next step is to show that the demagnetizing field allows such a temperature-independent magic angle. The coefficients Δ of Eq. (9) are derived from Eq. (5) as

$$\Delta_n = 2f_n g_{n\text{ref}}^2 [\chi(T_1) - \chi(T_2)], \quad (10)$$

with $n = ii, jj, ij$. Equation (9) then reads

$$\theta_m = \tan^{-1} \left(\frac{-g_{ij\text{ref}}^2 f_{ij} \pm \sqrt{g_{ij\text{ref}}^4 f_{ij}^2 - g_{ii\text{ref}}^2 g_{jj\text{ref}}^2 f_{ii} f_{jj}}}{g_{jj\text{ref}}^2 f_{jj}} \right). \quad (11)$$

Thus the demagnetizing field affords the temperature-independent magic angle, because the g factor depends linearly upon the magnetic susceptibility. This result stresses the fact that both the former theories and that presented here for the demagnetizing field do predict qualitatively the same major features.

A simple application of our results is to consider that the off-diagonal terms are zero; i.e., the \mathbf{g} tensor and \mathbf{N} tensor have the same referential, as in high-symmetry lattices (orthorhombic and higher). For instance, a rectangular-parallelepiped-shaped single crystal will have an \mathbf{N} tensor with its principal axes perpendicular to the faces of the crystal. Since the \mathbf{g} tensor of high-symmetry lattices reflects the symmetry of the unit cell, the two set of coordinates may have the same principal axes. Note that the principal values of the \mathbf{g} tensor of organic radicals are very close to the free electron g value, and inserting Eq. (5) into Eq. (11) yields

$$\begin{aligned} \theta_m &= \pm \tan^{-1} \left(\frac{g_{ii\text{ref}}}{g_{jj\text{ref}}} \sqrt{-\frac{f_{ii}}{f_{jj}}} \right) \\ &\approx \pm \tan^{-1} \left(\sqrt{-\frac{f_{ii}}{f_{jj}}} \right) \\ &= \pm \tan^{-1} \left(\sqrt{-\frac{1-3N_i}{1-3N_j}} \right). \end{aligned} \quad (12)$$

Applying Eq. (12) to the case of a needle with, e.g., $N_i = 0$ and $N_j = 1/2$, one gets $\theta_m = \pm 54.7^\circ$. The same result is obtained for a disk with $N_i = 1$ and $N_j = 0$.

It is concluded that in analytical cases the effects of the demagnetizing field are similar to the effects of the dipolar field and/or the short-range magnetic order: θ_m does correspond to the dipolar magic angle.

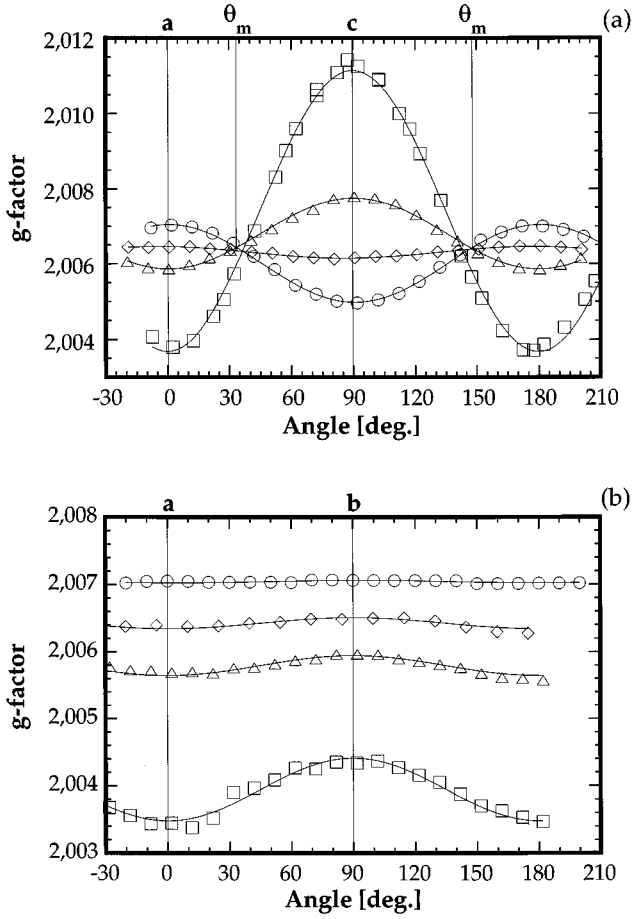


FIG. 5. The \mathbf{g} -tensor anisotropy of the PymNN single crystal depicted in Fig. 2: (a) in the (a,c) plane and (b) in the (a,b) plane at 10 K (squares), 25 K (triangles), 50 K (diamonds), and room temperature (circles). The solid lines correspond to the fits to Eq. (6).

The conclusive experiments are presented with the PymNN sample already discussed. The EPR experiments have been performed at different temperatures and in orthogonal crystal planes (Fig. 5). One observes in Fig. 5(a) the magic angles denoted as θ_m . These magic angles lie at $\pm 57.3^\circ$ of the c direction, i.e., 2.6° apart from the dipolar magic angle of 54.7° . This small discrepancy is easily ascribed to the shape of the sample, which is not a perfect needle as previously mentioned, and to the use of Osborn⁹ approximation in the calculation of the principal values of the demagnetizing tensor. In Fig. 5(b), the lack of any magic angle in the orthogonal plane is fully understood, since $N_i = N_j$ in Eq. (12).

V. ANGULAR DISPLACEMENT

During the course of our studies of organic magnets,^{2,19} we have often observed a rotation of the principal axes of the \mathbf{g} tensor with temperature. As this effect has not been reported previously^{3,4} it is relevant to check its importance within the present study of the demagnetizing field effects. We have already noted this phenomenon¹⁹ without further analysis.

The position of the extrema of the \mathbf{g} tensor within a plane is calculated from Eq. (6):

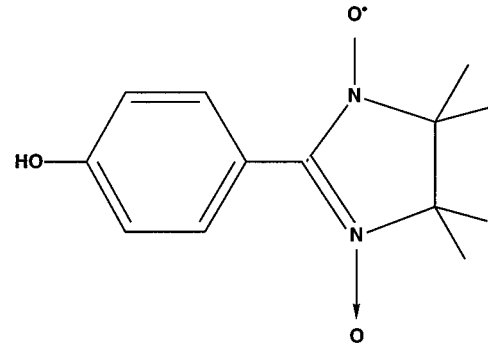


FIG. 6. Molecular structure of 4-OHPNN.

$$\theta_e = \frac{1}{2} \tan^{-1} \left(\frac{2g_{ijref}^2}{g_{iiref}^2 - g_{jjref}^2} \right) + n \frac{\pi}{2}, \quad n=0,1,2,\dots \quad (13)$$

This may be rewritten with the use of Eqs. (10) and (11):

$$\theta_e = \frac{1}{2} \tan^{-1} \left(\frac{2g_{ijref}^2 [1 + 2f_{ij}\chi(T)]}{g_{iiref}^2 [1 + 2f_{ii}\chi(T)] - g_{jjref}^2 [1 + 2f_{jj}\chi(T)]} \right). \quad (14)$$

The trivial case $g_{ijref} = 0$ occurs as the coordinates of both \mathbf{g} and \mathbf{N} tensors coincide and there is no possible reorientation of the \mathbf{g} tensor. The extrema of $g(\theta)$ are oriented along the axes of the \mathbf{N} tensor for any given temperature. This is the case for the PymNN derivative (see above). The case $g_{ijref} \neq 0$ is more complex owing to number of solutions that may exist. If we restrict ourselves to the rectangular parallelepiped shape case, f_{ij} will be zero, neglecting the off-diagonal elements of the \mathbf{N} tensor.⁹ Equation (14) then reads

$$\theta_e = \frac{1}{2} \tan^{-1} \left(\frac{2g_{ijref}^2}{(g_{iiref}^2 - g_{jjref}^2) + 2\chi(T)(g_{iiref}^2 f_{ii} - g_{jjref}^2 f_{jj})} \right). \quad (15)$$

Assuming a Curie-Weiss temperature dependence for weakly coupled $S=1/2$ magnets and for temperatures higher than the mean-field temperature, higher-order terms may be neglected in the expansion of the \tan^{-1} function in odd power series:

$$\theta_e = \left(\frac{\pi}{4} - a + \frac{a^3}{3} \right) - b\chi(T)(1 + a^2) = A - B\chi(T), \quad (16)$$

with

$$A = \frac{\pi}{4} - a + \frac{a^3}{3}, \quad B = b(1 + a^2),$$

$$a = \frac{g_{iiref}^2 - g_{jjref}^2}{2g_{ijref}^2}, \quad b = \frac{g_{iiref}^2 f_{ii} - g_{jjref}^2 f_{jj}}{g_{ijref}^2}.$$

Equation (16) points towards a rough hyperbolic dependence of the angular shift with temperature. The aforementioned studies¹⁹ dealing with the 2D organic ferromagnet 2-(4-hydroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxoimidazol-1-oxyl (or 4-hydroxy-phenyl nitronyl nitroxide, shortened 4-OHPNN) (Fig. 6) may be reanalyzed within this frame. Let us recall that the compound 4-OHPNN crystallizes in the orthorhombic space group $Pca2_1$. Its magnetic behavior is consistent with a weak 2D ferromagnetic behav-

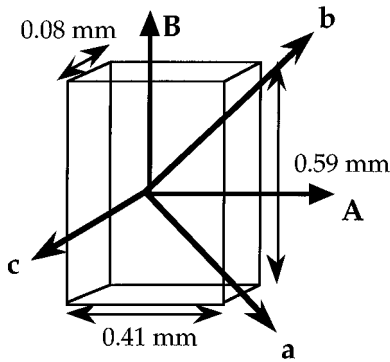


FIG. 7. 4-OHPNN single crystal: shape and crystal dimensions. The a , b , and c directions represent the crystalline axes and A, B, c refer to the principal axes of the demagnetizing tensor.

ior with $J = +0.63$ K in the nearly quadratic (a, b) plane with a weaker interlayer antiferromagnetic coupling. The principal axes of the \mathbf{g} tensor coincide with the crystallographic axes. The shape of the samples was a rectangular parallelepiped with the c -axis perpendicular to the larger face (Fig. 7). The principal values of the \mathbf{N} tensor are estimated⁹ as before: $N_c = 0.780$, $N_A = 0.138$, and $N_B = 0.082$. These lead to the geometrical factors $f_c = -1.340$, $f_A = +0.586$, and $f_B = +0.754$. In Fig. 7 the A and B directions correspond to the principal axes of the demagnetizing tensor. As the principal axes of the \mathbf{g} tensor do not coincide with the principal axes of the \mathbf{N} tensor, a reorientation of the \mathbf{g} tensor with the temperature is expected from the previous discussion. This was confirmed (Fig. 8). We have previously, tentatively, interpreted this phenomenon at a microscopic level,¹⁹ arguing for a dominant intermolecular magnetic interaction along the A axis. The present discussion stresses the fact that the demagnetizing field is responsible for the observed behavior. The relative angular shift [e.g., $\Delta\theta = \theta_{\max}(T) - \theta_{\max}(RT)$] is plotted versus temperature in Fig. 9. Equation (16) may be exploited with respect to the known principal values and principal axes of the \mathbf{g} tensor yielding $g_A = 2.00918$, $g_B = 2.00913$, and $g_{AB} = 0.04713$, and a Curie-Weiss law for the magnetic susceptibility¹⁹ ($C = 0.00196$ emu K cm⁻³ and

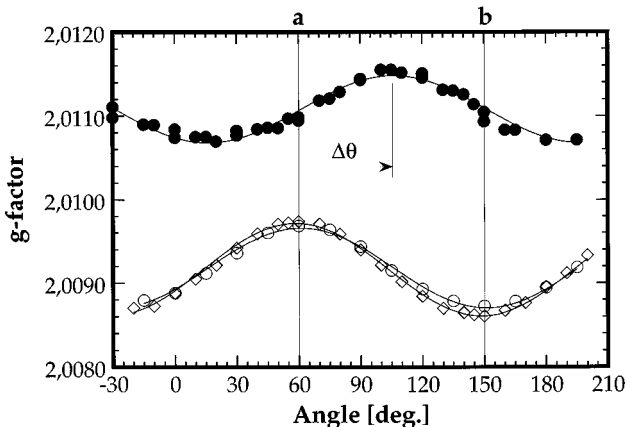


FIG. 8. The \mathbf{g} -tensor anisotropy within the (a, b) plane of the 4-OHPNN single crystal depicted in Fig. 7: $T = 4$ K (solid circles), $T = 50$ K (diamonds), and room temperature (open circles). The solid lines correspond to the fits to Eq. (6).

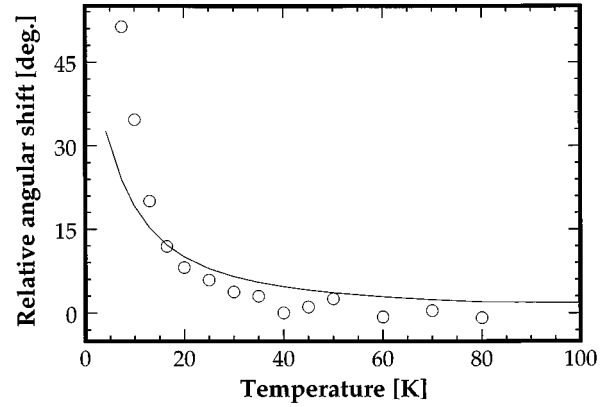


FIG. 9. Temperature dependence of the extrema of the \mathbf{g} -tensor anisotropy in the (a, b) plane of the 4-OHPNN single crystal. The solid line is a fit to Eq. (16).

$\theta = +0.63$ K). The calculated temperature dependence of the relative shift shows a good qualitative agreement with the experimental data. The lack of a quantitative agreement is easily understood for the same reasons as given before. Nevertheless, the temperature dependence of the angular shift is fairly well described by Eq. (16) within the experimental accuracy. The last point stresses the importance of the demagnetizing field in the measurements of the EPR field for organic magnets.

VI. DISCUSSION

The effects of the demagnetizing field have been demonstrated theoretically and illustrated by experimental observations on organic radicals. To further the use of the present results, we examine some previously reported g shifts for some organic radicals and organometallic compounds. The effects of short-range magnetic order on the \mathbf{g} tensor may be summarized as

$$\frac{\Delta g_i(T)}{g_i} = f_i \chi_c(T) n(x), \quad (17)$$

with

$$\frac{\Delta g_i(T)}{g_i} = \frac{\hbar \omega(T) - g_i \mu_B H}{g_i \mu_B H}, \quad f_i = f_{\parallel} = -\frac{18}{5N a^3} = -2 f_{\perp},$$

where $\chi_c(T)$ is the Curie law, $n(x)$ is a function of the temperature derived from the temperature dependence of the spin-spin correlation functions within the classical spin approximation,^{3(e),3(f)} and a the distance between neighboring spins. Equation (17) is very similar to Eq. (5) for the demagnetizing field effects.

It is not possible to estimate quantitatively the effects of the demagnetizing field for the previously reported experiments for metal complexes or organic radicals,^{3,4} since the shape of the samples has not been described. It is worth noting that the most commonly observed and larger shifts of the resonance field so far reported are of the order of 100–500 G in the paramagnetic regime. The largest shifts have been observed at the Q band, i.e., at a frequency around 35 GHz. The demagnetization field in Eq. (5) varies linearly with the microwave frequency, since the magnetization of an

unsaturated paramagnet is linear with the magnetic field. These effects are also proportional to the magnetic moment of the compound as the spin susceptibility varies as $S(S+1)$. For organic radicals with $S=1/2$ and at the X band (9 GHz), the larger shifts measured at 4 K are at most a few gauss. For a given shape, there is a factor of about 45 in the shift if one considers a spin $S=5/2$ at the Q band. Shifts of the resonance field as large as a few hundred gauss are then expected.

It is noted that the demagnetizing field is always present for nonspherical samples. The situation may be mastered experimentally in the case of metal alloys as one can machine the sample to the desired shape. However, it is almost impossible for crystals of metal complexes or organic radicals which grow as thin plates or thin needles. Therefore, in the absence of the desired shape of the sample, it is difficult to ascertain whether short-range magnetic order or the demagnetizing field is the relevant phenomenon for the discussion of the experimental results.

In our opinion, the theories concerned with the short-range magnetic order cannot be disregarded, but one has to define its limits. In some studies this was already emphasized.^{6,7} The theory of the short-range magnetic order effect^{3(e),3(f),3(l),3(m)} assumes a weak anisotropic dipolar field and, hence, a quantization axis field along the applied magnetic field direction. This is not always true as argued by Boucher in the case of TMMC.⁶ Considering the present results for purely organic compounds, one may doubt the efficiency of the local microscopic effects such as the short-range magnetic order at temperatures as far as 20 or more times the transition temperature even in low-dimensional magnetic systems.²⁰ Recent careful magnetic measurements show that short-range magnetic order effects, if present, should manifest much closer to the transition temperature.⁷ The observed effects are then much weaker than the effects of the demagnetizing field. The secular term of the dipolar field involved in the short-range magnetic order theory just yields a factor of 2 between orthogonal orientations, as does

the demagnetizing field. This is quite misleading for the interpretation of the experimental results as has been stressed above. However, it is physically well understood, since the demagnetizing field originates from the long-range magnetic dipolar interactions.²¹

VII. CONCLUSION

The effects of the demagnetizing field on the resonance field measured during EPR experiments have been considered in organic radical magnetic materials. It has been shown that these quantitatively explain the observed temperature-dependent shifts of the g values, the absence of effect at the dipolar magic angle, and a newly reported rotation of the g tensor as a function of temperature. A critical discussion of previous theoretical and experimental results for metal complexes and organic compounds, dealing with short-range magnetic order in low-dimensional magnets, indicates that it is difficult to ascertain the origin of the g shifts. The present study might be useful for explaining the reported effects for metal complexes.^{3(b)-3(h),4(e)} Although it is appealing, it is hardly possible to define the magnetic axes of a given material in a study of its temperature-dependent resonant field through EPR. The generality and validity of the effect of short-range magnetic order may have been overextended without paying sufficient attention to its limitation, as the present study on organic materials and recent ferromagnetic resonance experiments have revealed.⁷

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¹See, e.g., C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1967).

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