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EPR anisotropy induced by a magnetic field in the smectic A phase of a mesogenic Cu(II) complex derived from a Schiff's base

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The Q-band electron paramagnetic resonance (EPR) spectrum of the frozen smectic phase of the mesogenic compound bis[*N*-(4′-*n*-pentoxyphenyl)-4-*n*-decyloxysalicylaldiminate] copper(II) is studied. An anisotropic EPR spectrum is observed if freezing from the SmA phase is done in the presence of a magnetic field; the sample tends to orient with the director perpendicular to the magnetic field. The relative intensities of the EPR signal of this exchange coupled system are discussed in relation to the orientational distribution of the molecules. The results appear to be compatible with a biaxial magnetic susceptibility in the SmA phase. This suggests that an ordering of the short axes of the molecules in the plane perpendicular to the director in the SmA mesophase may take place.

1. Introduction

The molecular shape of some metallomesogenic complexes derived from Schiff's bases noticeably deviates from those of classical calamitic molecules and can be better described as brick-like instead of rod-like, see figure 1(*a*). Breaking the molecular uniaxial symmetry opens up new possibilities for molecular organization in the mesophases. In fact the existence of some local order in the plane perpendicular to the director, see figure 1(*b*), has been suggested from X-ray diffraction and extended X-ray absorption fine structure (EXAFS) studies [1], as well as from electron paramagnetic resonance (EPR) measurements [2, 3].

In the first case, correlation peaks at about 3.8 and 8.5 Å that roughly correspond to the molecular width and thickness were observed. In the second case, the EPR spectra of some copper derivatives of Schiff's bases show a completely smeared out hyperfine structure indicating that an exchange interaction occurs. However the components of the g tensor in the plane perpendicular to the director are only partially averaged. Taking into account the similar magnitudes of the hyperfine and g tensor anisotropies, both facts can only happen together if nearby molecules keep their short axes nearly parallel.

The studies cited above have only given evidence for the existence of local order (within a length of ten or more molecules, which is the number of exchange interacting molecules needed for a complete averaging of the hyperfine structure) for the short axes, and this does not necessarily imply the existence of a biaxial order over typical director correlation lengths in the mesophase [1]. On the other hand, new arguments in favour of the existence of biaxial order have recently been afforded when we studied the orientation of the director by a moderate magnetic field in the case of some brick-like metallomesogens derived from Schiff's bases. We proposed a model which relates this orientation with the mesophase structure [4]. According to that model, the orientation of some Cu(II) complexes with the director perpendicular to the magnetic field has to be associated with the existence of some degree of macroscopic biaxial order. In the present paper we report on the orientation induced by a magnetic field in the smectic A phase of one of these Cu(II) metallomesogen complexes by studies of the induced anisotropy in the EPR spectrum of the frozen smectic phase. We will see that our observations are in agreement with the above mentioned model.

To continue our earlier experiments, we have exploited the capability of obtaining mesophase orientation by using relatively moderate magnetic fields. This capability is a direct consequence of the anisotropic magnetic susceptibility of the phase. It is interesting to remember that a set of independent molecules cannot show a macroscopic net orientation in the presence of a moderate magnetic field because the individual molecular magnetic energy is very small compared with the thermal energy.

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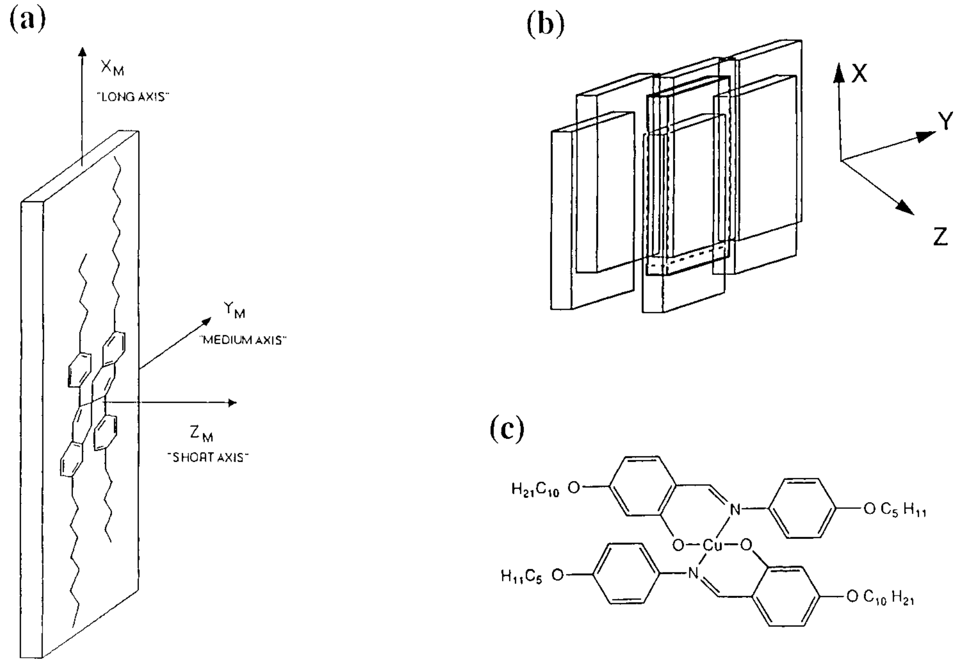

Figure 1. (*a*) A sketch of the molecular shape of CuCL. Molecular (X_M, Y_M, Z_M) axes are indicated. (*b*) A diagram of the local environment of the brick-like molecules in the mesophases. The principal *g* tensor (X, Y, Z) axes, that correspond to the local molecular equilibrium direction (e.g. the z-axis is the director) are indicated (see text). (*c*) Molecular formula of CuCL.

On the other hand, the magnetic field can interact with the director when its correlation length is long enough to allow a set of more than 10^8–10^9 molecules with practically the same equilibrium orientation of the long axes. The global magnetic anisotropy arises from a co-operative effect arising from the orientation of the molecules (that are held together by the anisotropic interactions responsible for the order of the mesophase) and the magnetic anisotropy of the molecules themselves [4–7]. Magnetic field orientation has to be carried out in the fluid mesophase. From the experimental point of view, it is also of great help that in many cases the high temperature mesophase structure can be frozen in by fast cooling of the sample to room temperature. In the presence of the magnetic field the frozen sample yields an anisotropic distribution of molecular orientations. Thus, information about the anisotropy of the magnetic susceptibility can be obtained by lower temperature measurements. A biaxial magnetic susceptibility proves that an ordering of the molecular short axes occurs, thereby defining an additional ‘director’.

In particular we have carried out a study by EPR spectroscopy of some frozen phases of a Cu(II) mesogenic compound derived from a Schiff’s base: bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxysalicylaldiminate] copper(II) (hereafter referred to as CuLC). The corresponding chemical formula is shown in figure 1 (*c*). We have chosen this compound because its SmA phase can be oriented by an applied magnetic field in such a way that the director tends to be perpendicular to the magnetic field. Therefore, according to the model given in [4], this phase will show a biaxial magnetic susceptibility and the shortest molecular axis will tend to orient parallel to the field. Although the compound also shows a SmC phase at lower temperatures, no orientation can be achieved in this phase by applying a magnetic field. This can be understood by considering the increase of the sample viscosity as the temperature decreases. In addition, the EPR spectra of this compound have been thoroughly studied both in its solid phases and in its mesophases [8].

2. Experimental

The CuLC complex was prepared as described in [9]. Its phase sequence is Cr → 125°C → SmC → 130°C → SmA → 162°C → I on heating and I → 162°C → SmA → 130°C → SmC → 105°C → Cr on cooling. If the sample is frozen from the smectic phases the solid keeps the smectic texture as revealed by optical microscopy. The Cr phase is again restored by heating the frozen smectic to about 100°C.

Room temperature (r.t.) Q-band EPR measurements (microwave frequency about 34 GHz) were performed with an ESP380E Bruker spectrometer. The samples were introduced into a quartz tube of 1 mm diameter. For this sample size, the wall effects are negligible. Frozen phases were produced by first heating the sample in a ERV411T variable temperature set-up from Bruker and then by quenching in water at r.t. The sample temperature was monitored by attaching a thermocouple to the quartz tube. The temperature error was estimated to be lower than 0.5°C and the stability better than 0.1°C. Quenching was done either in the absence or in the presence of a magnetic field of about 2 T.

3. Results

As has been previously reported [8], the r.t. EPR spectrum of a fresh CuLC sample is associated with exchange coupled Cu(II) paramagnetic entities ($S = 1/2$). The exchange interaction is responsible for the collapse of the hyperfine structure associated with the copper nucleus ($I = 3/2$) and the 'strong exchange' condition is fulfilled. So, the EPR signal can be described by the following spin-Hamiltonian:

$$H = \mu_B \{ g_{xx} B_x S_x + g_{yy} B_y S_y + g_{zz} B_z S_z \} \quad (1)$$

where μ_B represents the Bohr magneton, $S = 1/2$ and g_{xx}, g_{yy} and g_{zz} are the principal values of the 'exchange averaged' g tensor. The g tensor principal frame is shown in figure 1 (*b*). Given that there exists a spatial averaging because of the exchange interaction, the axes refer to the local equilibrium orientation of the molecular axes imposed by the phase structure and not to that of the isolated molecules. Furthermore, an anisotropic linewidth needs to be considered in order to explain the spectrum. We have to remember that in this material the actual linewidth is driven by the dipolar and exchange interactions and both are, in principle, anisotropic. A similar anisotropic linewidth has been used by Ghedini *et al.* [10] to explain the EPR signal in other Cu complexes from mesogenic Schiff's bases.

The powder spectrum can be reproduced assuming a Lorentzian lineshape and using the following g values and signal widths:

$$g_{xx} = 2.044 \qquad g_{yy} = 2.080 \qquad g_{zz} = 2.207$$

$$W_x = 2.0\ \text{mT} \qquad W_y = 3.0\ \text{mT} \qquad W_z = 4.5\ \text{mT}$$

together with the following interpolating halfwidth formula:

$$W^2(l_x l_y l_z) = W_x^2 l_x^2 + W_y^2 l_y^2 + W_z^2 l_z^2 \quad (2)$$

where l_x, l_y, l_z are the director cosines of the magnetic field with respect to the principal axes of the g tensor. Although the former expression does not have a theoretical basis, it can be used in an empirical way. In fact, we have also used other interpolating formulae like $W(l_x l_y l_z) = W_x l_x^n + W_y l_y^n + W_z l_z^n$ ($n = 1$ and 2) and similar results are obtained. The goodness of expression (2) is understood as being due to the fact that the aspects of the powder spectra depend mainly on the lineshape of the transitions corresponding to the orientation of the magnetic field along the principal g tensor directions.

The principal g tensor axes have been chosen such that $g_{xx} < g_{yy} < g_{zz}$. It is interesting to note that although the g_{xx} and $(g_{zz} + g_{yy})/2$ values are the same as for isolated molecules in a frozen toluene solution [8], a reduction in the $\delta g = g_{zz} - g_{yy}$ difference in the concentrated solid sample is observed. This indicates that a partial exchange induced averaging of the Y and Z principal components of the g tensor takes place, presumably because the corresponding axes of the interacting molecules do not have perfect coaxial orientation throughout the solid.

The EPR spectrum we obtained after freezing from the SmA phase in the absence of any magnetic field is shown in figure 2. Of course, the spectrum is isotropic, as it does not depend on the magnetic field orientation. Only minor changes are observed in this spectrum as compared with that of a fresh sample. Again the absence of hyperfine structure means that the intermolecular exchange also takes place in this frozen smectic phase and the 'strong exchange' limit also applies. Consequently we followed the same analysis procedure as in the previous case and obtained for the principal g values and the halfwidths of the absorption lines:

$$g_{xx} = 2.044 \qquad g_{yy} = 2.086 \qquad g_{zz} = 2.199$$

$$W_x = 2.0\ \text{mT} \qquad W_y = 5.0\ \text{mT} \qquad W_z = 7.0\ \text{mT}.$$

The calculated spectrum using these parameters is given by the dotted lines in figure 2. It is worth noting that for this kind of calculation we have to consider, in principle, both the orientational distribution function of

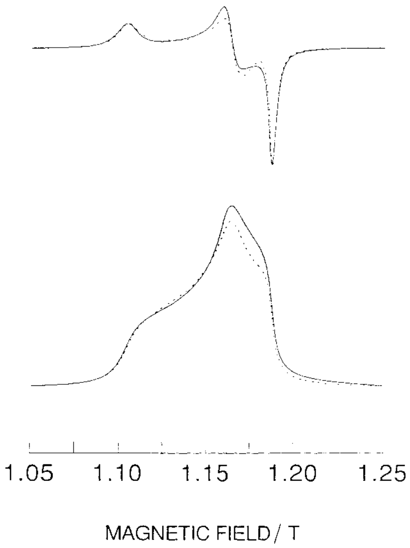

Figure 2. Q-band EPR spectra, measured at r.t., of a CuLC sample quenched from the SmA phase in the absence of a magnetic field. The continuous lines give the experimental spectra and the dotted lines the calculated spectra (see text). Upper part, first derivative spectra; lower part, absorption spectra.

the molecules with respect to the principal g tensor axes and the distribution function of the orientation of those equilibrium axes throughout the sample. In our case the exchange interaction between molecules produces, as has been mentioned above, a spatial averaging of the molecular tensor [3]. Consequently, the first distribution is responsible only for the changes in the g tensor principal values with respect to that of isolated molecules [3, 11]; also as consequence of the exchange interaction, the measured g tensor corresponds to a kind of spatial 'averaged molecule', in the same way that a fluid system in the 'fast motion limit' is described by time averaged molecular tensors. This contrasts with the situation found in mesogenic systems where the exchange interaction between paramagnetic entities is absent [12], such as, for example, systems of diamagnetic mesogens where paramagnetic probes are introduced in order to study the phase order by means of EPR spectroscopy. The effect of the exchange averaging and the relationship between the equilibrium frame and the director distributions will be discussed below. The non-oriented sample has a uniform distribution of orientations and a typical, isotropic powder spectrum is measured.

The g_{xx} and $(g_{zz}+g_{yy})/2$ values remain unchanged, but a further reduction of δg together with an increase in W_y and W_z is observed for the frozen sample. Such effects, which have been previously observed with other mesogenic copper(II) complexes derived from Schiff's bases [8, 13], are a consequence of some orientational distribution of the short axes of the molecules around their equilibrium directions in the frozen phase.

It is important to note here that the g_{yy} and g_{zz} components are far from being completely averaged—both equal to $(g_{zz}+g_{yy})/2$—as would be expected for a random orientational distribution of the short axes of exchange-coupled molecules as observed in [11].

We have pointed out elsewhere [3, 8] that these kinds of EPR results on exchange coupled mesogenic Schiff's base complexes support the concept of a local order of molecular short axes such as that shown in figure 1 (*b*). Exchange consists in a kind of weak bonding between paramagnetic entities that can be described as a non-commuting term in the spin-Hamiltonian [3]. Such systems can be interpreted in a 'dynamical' way: electronic spin is not localized, but has a probability (proportional to the exchange energy) of 'hopping' from one paramagnetic centre to another. In this way both exchange and motion effects can be treated with a similar formalism [14]. In a sample with long range exchange coupling, the spin-Hamiltonian anisotropy is spatially averaged between the molecules 'visited' by an electron spin in a time shorter than that associated with the anisotropy frequency. This allows us to define an 'exchange length' (that depends on the exchange strength and on the anisotropy to be averaged) as the length over which the spatial averaging takes place. It is worth noting that all molecules in a region of the exchange length size have common equilibrium axes.

Some estimations about the exchange length in our sample can be obtained from the experimental results. The collapse to zero of the hyperfine structure implies that the exchange length must be larger than ten molecules in order to average the maximum hyperfine anisotropy. It has to be noted that in our copper centres the maximum hyperfine anisotropy is comparable to the maximum Zeeman anisotropy. Since the Zeeman anisotropy is far from being completely averaged, there is a clear indication that the three principal molecular axes have a strong spatial correlation over a length of more than ten molecules. The conclusion from EPR studies on non-oriented samples is that the equilibrium directions for the three principal axes of the molecules are constant, at least for a few tens of molecules.

Considering all these points and previous results [3, 11], the slight Zeeman anisotropy exchange averaging observed can be understood as being due to the distribution of the axes of individual molecules within the exchange length around the equilibrium orientations. Then, as has been discussed above, the g tensor principal axes correspond to the equilibrium directions of the molecular axes. Consequently the distributions of the axes of the molecules with respect to the equilibrium directions do not affect the relative intensities in EPR measurements on an oriented sample.

The question now is whether this detected local order extends over a long range (that is, whether the phase is globally biaxial). Taking into account that the orientation of the director by a magnetic field is driven by the anisotropy of the global magnetic susceptibility [5], we have studied the spectra of samples frozen in the presence of a magnetic field.

After freezing the sample from the SmA phase to r.t. in the presence of a magnetic field, B_0, the spectrum becomes anisotropic as it depends on the relative orientation of the measuring magnetic field, B_m, and B_0. It is important to remember that if the freezing is done from the SmC phase under the same conditions, no anisotropy is observed in the EPR spectrum. The spectra of a CuLC sample frozen from the SmA phase, measured with B_m either parallel or perpendicular to B_0, are shown in figures 3 (*a*) and 3 (*b*), respectively. For the sake of brevity we have denoted them as the *parallel* and *perpendicular* spectra. Both absorption and first derivative spectra are shown. In the *parallel* spectrum, figure 3 (*a*), a strong decrease is observed in the intensity of the g_{xx} component, together with a very important increase in that of the g_{zz} component, as compared with the values for the non-oriented sample. It is noteworthy that the g_{zz}

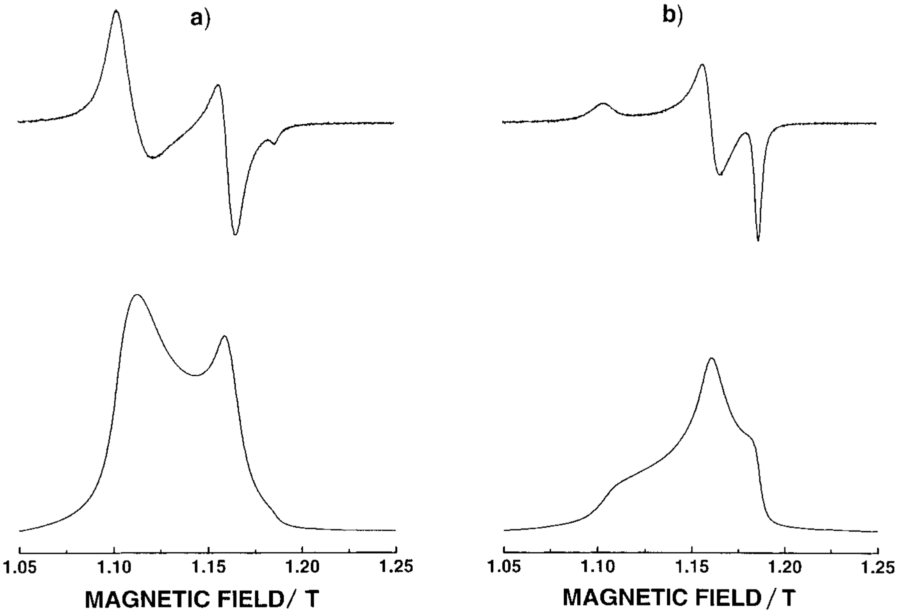

Figure 3. Q-band *parallel* (*a*) and *perpendicular* (*b*) EPR spectra of a CuLC sample quenched from the SmA phase in the presence of a 2 T magnetic field. Upper parts, first derivative spectra; lower parts, absorption spectra.

signal reaches an absolute maximum of absorption. This spectrum indicates than an orientation with the Z (shortest molecular axis) equilibrium direction nearly parallel to the field has been strongly favoured. For the *perpendicular* spectrum a decrease of the intensity of the g_{zz} component occurs, whereas the other components in the region of the g_{xx} and g_{yy} features are intense and dominate the spectrum, see trace 3(*b*). Again the absence of hyperfine structure indicates that the exchange interaction does not disappear within the orienting process.

4. Discussion

From the last experiment it follows that our sample *can* be oriented by applying a magnetic field in the SmA mesophase. This orientation can be frozen by quenching to r.t. in the presence of the magnetic field. Now we go on to see if it can be determined whether the magnetic susceptibility of the SmA phase is uniaxial or biaxial.

Let us consider first the case of a uniaxial mesophase. In such a situation the magnetic susceptibility tensor is given by:

$$\chi = \chi_0 + \frac{\Delta\chi}{3}\begin{pmatrix} -1 & & \\ & -1 & \\ & & 2 \end{pmatrix} \qquad (3)$$

where $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ gives a measurement of the magnetic susceptibility anisotropy. As the magnetic susceptibility is axial, the probability of finding the director in a region of the sample making an angle between α and $\alpha + \mathrm{d}\alpha$ with the orienting magnetic field, B_0, is given by:

$$f(\alpha)\,\mathrm{d}\alpha = f_0 \exp(-K \cos^2\alpha)\,\sin(\alpha)\,\mathrm{d}\alpha \qquad (4)$$

where f_0 is a normalization constant and K is proportional to the anisotropy of the magnetic energy, $-\Delta\chi\ |B_0|^2$, and increases as the correlation length of the director increases. If the director tends to orient itself parallel to the magnetic field, $K < 0$ and in the opposite case $K > 0$.

The orientation process causes an anisotropic orientation of the molecular axes in the sample. As a matter of fact, the experimentally detected distribution of orientations will be, strictly speaking, a convolution of the director distribution with respect to the orienting field, and the orientational distribution of the local equilibrium axes with respect to the director. As we have discussed above, and as a consequence of the exchange interaction in the 'strong exchange limit', the distribution of the individual molecules with respect to the equilibrium directions causes only the small g value averaging detected and has no effect on the signal intensities. In the simplest description of the phase, the equilibrium molecular long axis coincides with the director. Therefore, in a first approximation we can neglect the influence of the second distribution. On the other hand, in the case of a uniaxial phase, the director distribution with respect to the magnetic field is given by a function like (4).

Then, for a uniaxial mesophase and using this distribution function, we calculated the *parallel* and *perpendicular* EPR spectra. In a uniaxial oriented sample, the Z and Y molecular short axes must be uniformly distributed as they are not oriented. In our case the g_{xx} feature decreases in the *parallel* spectrum, see figure 3(*a*), so it would correspond to a mesophase oriented with the director perpendicular to the magnetic field, i.e. $K > 0$. In figure 4 we show both the *parallel* and *perpendicular*

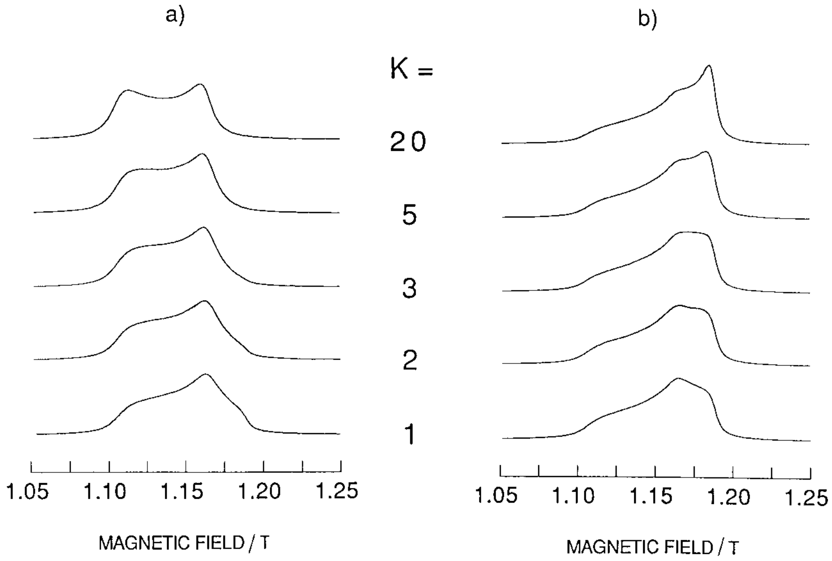

Figure 4. Calculated *parallel* (*a*) and *perpendicular* (*b*) absorption spectra of an oriented sample assuming a uniaxial distribution of orientations for different values of K (see the text).

spectra calculated for different positive values of K for a uniaxial distribution.

It is easy to verify that both the *parallel* and *perpendicular* experimental spectra are absolutely incompatible with such a uniaxial mesophase. In the case of a completely ordered uniaxial distribution with the director aligned perpendicular to the orienting magnetic field, the *parallel* and *perpendicular* spectra would be like those given in figure 4 for high K values. In such a case, the *parallel* spectrum corresponds to a distribution of resonance lines between g_{zz} and g_{yy} which produces an EPR spectrum with two main features at these principal g values and of equal intensity (the differences observed in figure 4 are due to the anisotropy on the linewidths). For a uniaxial phase, the g_{zz} component could never reach an absolute maximum in the *parallel* spectrum (as experiments show) provided that the signal in this region is clearly broader. On the other hand the simulated *perpendicular* spectrum for high K values consists of a pronounced absorption near to g_{xx} and only small shoulders at g_{zz} and g_{yy}. This clearly cannot explain the relative intensity of the g_{yy} component in the experimental *perpendicular* spectrum. It has to be pointed out that these simulated spectra are qualitatively independent of the uniaxial distribution used, since in the case of strong orientation (high K) there will always be a uniform angular distribution probability between g_{zz} and g_{yy} for the *parallel* spectra and a strong absorption near g_{xx} for the *perpendicular* cases.

We conclude then that the formerly drawn model fails to describe, even qualitatively, the main experimental facts given in figure 3. Therefore we have to revisit the two main hypotheses of this model where we assumed a negligible influence of the distribution of the equilibrium axes with respect to the director and a uniaxial distribution of orientations of the director like that given by equation (4). Now we analyse the first hypothesis. It is well known that classical studies of mesophase order from motional averaging in the EPR signals of paramagnetic probes dissolved in liquid crystals considered that motion of the probe around its equilibrium orientation gave a good picture of the global phase order. This is only true when it is assumed that all the long axis equilibrium directions nearly coincide with the director. Even if there exists some distribution of the long axial equilibrium direction around the director, the short axes of the equilibrium frame always lie almost perpendicular to the director and it is very unlikely that this distribution imposes an important difference on the intensities of the signals corresponding to the orientations of the short axes, Z and Y, in our spectra of oriented samples.

Alternatively, and it seems to be a simpler explanation, we go on to see that our results can be qualitatively explained by using a simple model that accounts for a biaxial magnetic susceptibility. In the biaxial case, if λ_x, λ_y, λ_z are the cosines of the angles that the magnetic field makes with the x, y, z principal axes of the magnetic susceptibility, the probability of finding the orienting magnetic field within a differential solid angle $d\Omega$ around the direction defined by λ_x, λ_y, λ_z is given by:

$$f'(\lambda_x\lambda_y\lambda_z)\,d\Omega = f'_0 \exp\{A(\lambda_x^2+\lambda_y^2)+B(\lambda_x^2-\lambda_y^2)\}\,d\Omega. \qquad (5)$$

The axial case corresponds to $A = K$ and $B = 0$, with $d\Omega = \sin(\alpha)\,d\alpha$.

Using this expression we have calculated the *parallel* and *perpendicular* spectra. To a first approximation, we

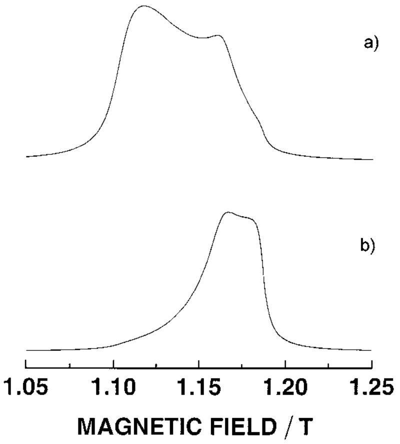

Figure 5. Calculated *parallel* (*a*) and *perpendicular* (*b*) absorption spectra of an oriented sample assuming an orthorhombic distribution of orientations given by $A = 2.0$ and $B = 0.6$ (see the text).

have also assumed the principal axes of the magnetic susceptibility and of the g tensor to be coaxial [2, 4, 5]. Then:

$$l_x = \lambda_z, \qquad l_y = \lambda_y, \qquad l_z = \lambda_x. \tag{6}$$

As an example, we show in figure 5 the result of such a calculation with $A = 2.0$, and $B = 0.6$ and the same g values and halfwidths quoted above. The introduction of an othorhombic contribution ($B > 0$ that favours the orientation of the shortest axis, Z, parallel to the field) induces an increase of the g_{zz} contribution in the *parallel* spectrum and a decrease of the g_{zz} signal in the *perpendicular* one. A direct comparison of the calculated with the experimental spectra (see figure 3) is not easy because we do not know the actual orientation of the principal magnetic susceptibility axes or the angular dependence of the halfwidth and lineshape in this exchange narrowed system. In spite of that we can see that the introduction of an orthorhombic contribution to the magnetic susceptibility in the mesophase can account for all the qualitative facts observed in the EPR signal of a sample frozen in the presence of a magnetic field.

At this point we want to re-emphasize the fact that an anisotropy cannot be induced by freezing the sample from the SmC phase in presence of the B_0 magnetic field. Consequently, the anisotropy of the oriented frozen samples is a direct consequence of the orientation in the SmA phase.

As a conclusion, our results provide strong evidence that the molecular organisation of the mesogen CuCl in the SmA mesophase is such that the magnetic susceptibility seems to be biaxial, and the equilibrium orientations of the molecular short axes have a correlation length comparable to that of the director. This would be a strong indication that the SmA phase of the Schiff's base bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxysalicylaldiminate] copper(II) is a biaxial phase. More work in order to check whether these unusual low symmetry effects translate into other properties of the mesogen must be done. Moreover, this kind of study has to be extended to other Schiff's base derivatives of Cu(II) that orient *perpendicular* to the magnetic field in a classically described uniaxial mesophase.

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References

[1] Barberá, J., 1996, *Metallomesogens: Synthesis, Properties and Applications*, edited by J. L. Serrano (Weinheim: VCH), Chap. 8.

[2] Alonso, P. J., 1996, *Metallomesogens: Synthesis, Properties and Applications*, edited by J. L. Serrano (Weinheim: VCH), Chap. 9.

[3] Martínez, J. I., Marcos, M., Serrano, J. L., Orera, V. M., and Alonso, P. J., 1995, *Liq. Cryst.*, **19**, 603.

[4] Alonso, P. J., and Martínez, J. I., 1996, *Liq. Cryst.*, **21**, 597.

[5] Alonso, P. J., 1996, *Metallomesogens: Synthesis, Properties and Applications*, edited by J. L. Serrano (Weinheim: VCH), Chap. 10.

[6] De Gennes, P. G., and Prost, J., 1993, *The Physics of Liquid Crystals*. 2nd Edn. (Oxford: Clarendon Press).

[7] Vertogen, G., and de Jeu, W. H., 1987, *Thermotropic Liquid Crystals: Fundamentals* (Berlin: Springer).

[8] Alonso, P. J., Marcos, M., Martínez, J. I., Orera, V. M., Sanjuán, M. L., and Serrano, J. L., 1993, *Liq. Cryst.*, **13**, 585.

[9] Marcos, M., Romero, P., Serrano, J. L. Bueno, C., Cabeza, J. A., and Oro, L. A., 1989, *Mol. Cryst. liq. Cryst.*, **167**, 123.

[10] Ghedini, M., Morrone, S., Gatteschi, D., and Zanchini, C., 1991, *Chem. Mater.*, **3**, 752.

[11] Martínez, J. I., Bruce, D. W., Price, D. J., and Alonso, P. J., 1995, *Liq. Cryst.*, **19**, 127.

[12] See for instance Schwerdtfeger, C. F., and Diehl, P., 1969, *Mol. Phys.*, **17**, 417; Diehl, P., and Schwerdtfeger, C. F., 1969, *Mol. Phys.*, **17**, 423; James, P. G., and Luckhurst, G. R., 1971, *Mol. Phys.*, **20**, 761.

[13] Campillos, E., Marcos, M., Serrano, J. L., Barberá, J., Alonso, P. J., and Martínez, J. I., 1993, *Chem. Mat.*, **5**, 1518.

[14] For a description of the treatment of exchange coupling as a Markofian discrete 'jumping' process, see Anderson, P. W., 1954, *J. phys. Soc. Japan*, **9**, 316.