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^{3}He NMR in Liquid Crystals: Measurement of Local Magnetic Fields

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^{3}He NMR in Liquid Crystals: Measurement of Local Magnetic Fields

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Temperature dependences of NMR chemical shifts of ^{3}He and ^{129}Xe in the liquid crystals K15 (5CB) and ZLI1167 orienting parallel and perpendicular to the external magnetic field, respectively, are measured. From the slopes of the ^{3}He shifts, their behaviour at the phase transition and from a comparison with corresponding data for ^{129}Xe shifts we conclude that the local shift anisotropy σ_a represents an important contribution to the ^{3}He shifts. σ_a is responsible for the sign of the shift jump when going from the isotropic to the nematic phase, which is found positive in 5CB and negative in ZLI1167. By appropriate corrections for susceptibility and by scaling the ^{3}He van der Waals shift contributions from ^{129}Xe data the temperature dependence of σ_a for ^{3}He can be obtained. A theoretical model is introduced which explains the experimental results and shows that the σ_a values in the oriented phase are dominated by the isotropic susceptibility. In the isotropic phase however the susceptibility anisotropy is the determining factor.

1. INTRODUCTION

NMR of noble gas atoms dissolved in various solids and liquids has been found to be a very useful tool providing information on the physical and chemical properties of the solvents. In particular, ^{129}Xe has become very popular, since its chemical gas-to-solution solvent shift ranges over 300 ppm for liquid solvents. For this reason it has been used extensively to study the properties of organic solvents, clathrates, zeolites and bioorganic systems (See for example [1,2,3]). The ^{129}Xe nucleus is also an excellent probe for the detection of phase transitions of liquid crystals and of the formation of induced smectic phases [4]. Moreover, the ^{129}Xe shielding anisotropy of xenon gas dissolved in liquid crystals was determined [5]. On the other hand, ^{131}Xe, ^{83}Kr and ^{21}Ne were used to study solvent shifts and quadrupolar relaxation [6,7,8]. Having a quadrupole moment these nuclei can be used to probe static electric field gradients in various liquid crystals [7,9] and to determine macroscopic order parameters [10,11].

The ^{129}Xe nuclear shielding has its origin in the deformation of the relatively large electron cloud due to repulsive and attractive van der Waals forces, whereas the local effects are of minor importance. On the contrary, ^{3}He provides an excellent nucleus for the detection of minute local magnetic fields at the site of the noble gas atom, since its total solvent medium shift range is only about 0.8 ppm [12]. Hence the changes in ^{3}He chemical shift for the gas dissolved in a liquid surrounding may be assumed to be governed by the bulk magnetic susceptibility (σ_b) and the local anisotropy (σ_a) of the neighbouring molecules.

In this work we introduce a theoretical model to interpret our experimental chemical shift data of ^{3}He as a function of temperature. Quantitative values of σ_a in K15 (often denoted as 5CB) and ZLI1167 are presented.

2. EXPERIMENT

The manufactured sample tubes (outer diameter 8 mm, wall thickness 1.5 mm) contained $\sim$ 1.5 g liquid crystal. The samples were evacuated and oxygen was carefully removed in a vacuum line. The liquid crystals ZLI1167 (mixture of 4-*n*-alkyl-trans, trans-bicyclohexyl-4′-carbonitrile) and 5CB (4′-*n*-pentyl-4-biphenylcarbonitrile) were both products from Merck Darmstadt. Each sample was filled with 10 atm of helium gas (at least 99.95 atom percent enriched, delivered by Isotec Inc. Miamisburg, Ohio) and subsequently sealed with a flame. In order to reach this pressure the sample tubes were cooled in a dewar containing liquid helium. The ^{3}He spectra were recorded on a Bruker AC250 spectrometer operating at 190.5 MHz. The samples were spinning at 16 Hz, but contained no lock substance. A specially tuned probe head was necessary for the ^{3}He measurements and 1024 data points were recorded in 8 scans leading to a signal-to-noise ratio of appproximately 100. A line broadening factor of 1 Hz was applied before the Fourier transformation of the ^{3}He data. The chemical shift of ^{3}He was measured with respect to a sample having a pressure of 1 atm ^{3}He gas. A further correction to zero pressure is negligible as reported in reference [12]. The error of the ^{3}He gas to solution shifts is less than 0.005 ppm.

The ^{129}Xe spectra were recorded on the same instrument using a commercial 10 mm BB probe head tuned to 69.2 MHz. A pressure of 5 atm natural xenon gas (delivered by Messer–Griessheim, Duesseldorf, Germany; the natural abundance of ^{129}Xe is 26.44 at%) was brought into the sample tubes (inner diameter 8 mm,outer diameter 10 mm) equipped with a Young valve by condensing the gas with liquid nitrogen. The same amount of liquid crystals were used in the Young valve samples as in the sealed ones. The samples were neither spinning nor contained any lock substance. 4096 data points were taken in a single FID and after application of a line broadening of 5 Hz and of Fourier transformation of the data, a signal-to-noise ratio of about 20 was achieved, with an uncertainty of the peak position not larger than 0.01 ppm. The ^{129}Xe shifts were measured with respect to a gas sample containing 5 atm natural xenon gas and corrected for infinitely diluted gas.

3. RESULTS AND DISCUSSION

In Figure 1 and 2 the temperature dependent gas to solution shifts for ^{3}He and ^{129}Xe in the liquid crystals 5CB and ZLI1167 are presented. Figure 1 shows that ^{3}He also provides an excellent probe for phase transitions, although its chemical shift sensitivity is 320 times smaller than the one of ^{129}Xe [12].

Also the smectic to nematic transition in ZLI1167 at a reduced temperature of 0.85 is clearly visible with ^{3}He. Due to its small size, ^{3}He does not perturb so much the liquid crystal and consequently it may be an even more favourable probe than ^{129}Xe.

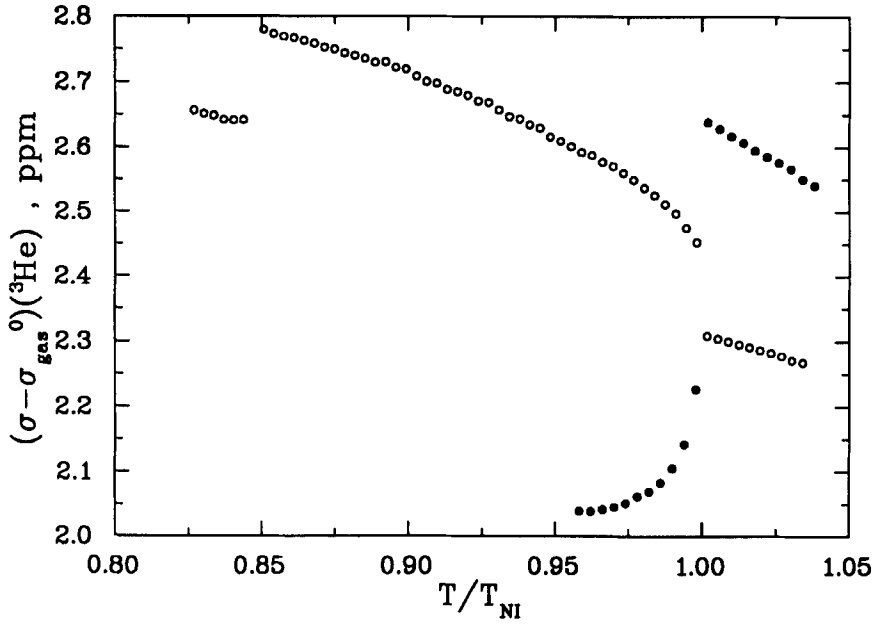

FIGURE 1 Gas to solution shifts for ^{3}He (gas at zero pressure) in the liquid crystals 5CB (●) and ZLI1167 (○) versus temperature.

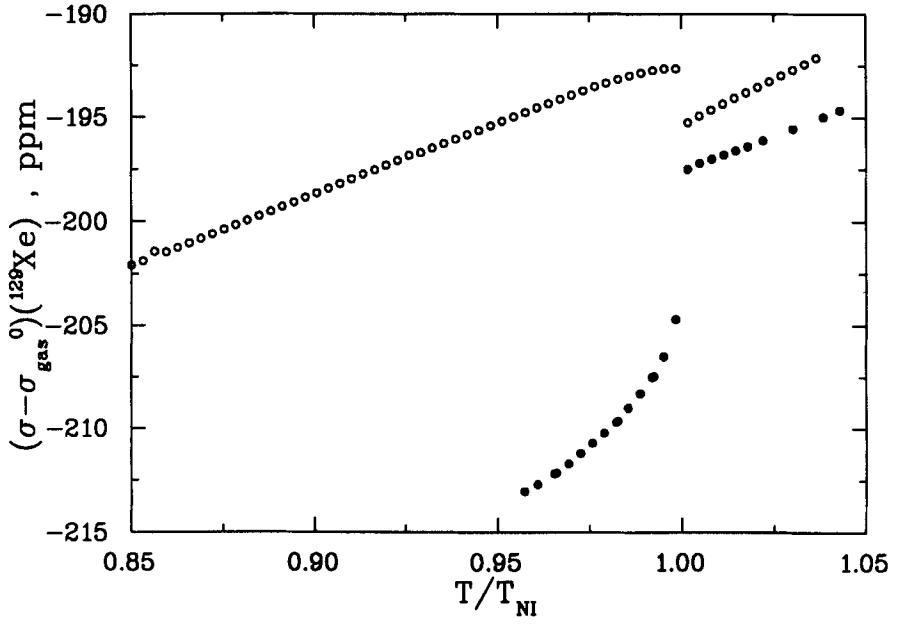

FIGURE 2 Gas to solution shifts for ^{129}Xe (gas at zero pressure) in the liquid crystals 5CB (●) and ZLI1167 (○) versus reduced temperature.

Although the direction of the chemical shift jumps at the NI-transition is the same for ^{3}He as for ^{129}Xe, this is based, as explained below, on different physical reasons. The ^{3}He and ^{129}Xe shift dependences on reduced temperature show two distinct differences. The first is the opposite sign of the shifts and the second the opposite overall slope of the curves. Both features are explained by the dominance of the van der Waals term σ_w in the case of ^{129}Xe and of the susceptibility term σ_b in the case of ^{3}He. The shift contributions [13] are as follows:

$$\sigma - \sigma^0_{\text{gas}} = \sigma_w + \sigma_a + \sigma_b \tag{1}$$

with

$$\sigma_b = -\left(\frac{4\pi}{3} - g\right)\chi_{\text{vol},\parallel}$$

where σ_w stands for the van der Waals contribution, but should include here for simplicity also the polar term σ_{E^2} and the shielding anisotropy, i.e., all E^2 effects and therefore all scalable shift contributions. σ_a is the local anisotropy and σ_b the bulk susceptibility correction for a cylinder parallel to the field with a geometrical correction factor g due to the finite length of the solvent column. The unscalable parts are estimated to be $|\sigma_a| < 0.5$ ppm [14, 15] and $\sigma_b \sim 3$ ppm. For an estimation of the contribution of σ_w^{He} its scalability is assumed according to the formula (see [12])

$$\sigma_w^{He} = \sigma_w^{Xe} \cdot 0.00313 + 0.316 \tag{2}$$

i.e., σ_w^{He} is expected as ~ -0.3 ppm. Thus the positive sign of $(\sigma - \sigma^0_{\text{gas}})^{He}$ is explained. For an interpretation of the opposite overall slopes of the ^{3}He and ^{129}Xe shift variation with temperature the density dependence must be taken into account. In σ_b it enters via the relation between mass and volume susceptibility,

$$\sigma_b = -\left(\frac{4\pi}{3} - g\right)\chi_{m,\parallel} \quad \rho = \sigma_b' \, \rho \tag{3}$$

and for σ_w a linear density rule is adopted

$$\sigma_w = \sigma_{w0} + \sigma_{w1}(\rho - \rho_0) + \cdots \tag{4}$$

where σ_{w1} is assumed to be temperature independent, which, at least for the temperature range considered, is well fulfilled [16]. σ_a can of course also be density dependent, but this may be neglected, because the variations with density of σ_b for ^{3}He and of σ_w for ^{129}Xe are proportional to the absolute values. The different signs of the slopes in Figures 1 and 2 follow because the factor σ_b' is positive while σ_{w1} is negative and $d\rho/dT$ is < 0.

If the chemical shift jumps of ^{3}He at the NI-transition were exclusively due to the susceptibility term σ_b, the jumps in both liquid crystals should have the same direction, because the liquid crystal molecules always orient such that the axis of lower diamagnetic susceptibility lies parallel to the field. The van der Waals term produces shift jumps into the observed direction for ^{3}He, but the expected contributions to $(\sigma_N - \sigma_I)^{He}$

at the phase transition of -0.02 ppm in 5CB and $+0.008$ ppm in ZLI1167 (according to Equation 2) are too small to account for the observed effects which are bigger than 0.1 ppm. Hence the local anisotropy σ_a must play an important role for the unexpected ^{3}He shift behaviour.

To extract the σ_a information from the ^{3}He shift data, corrections for σ_b and σ_w^{He} must be performed. For the former it is necessary to know the mass susceptibility and the temperature dependence of the density (see Equation 3) of each liquid crystal considered. The geometry correction applied was $g = 0.1$, and corresponds to a solvent column with a ratio of length to diameter of approximately 10. The isotropic mass susceptibility was estimated by use of Pascal's Method [17], as no experimental data were available. Thus the value for 5CB is $\chi_m^{iso} = -0.685 \cdot 10^{-6}\,\mathrm{cm^3\,g^{-1}}$ and for ZLI1167 $\chi_m^{iso} = -0.775 \cdot 10^{-6}\,\mathrm{cm^3\,g^{-1}}$. For the magnetic anisotropy an expression of the form [18]

$$\Delta\chi_m = \Delta\chi_{m0}\left(1 - y\frac{T}{T_{NI}}\right)^z \tag{5}$$

was used. The values for 5CB were taken from [19]: $\Delta\chi_{m0} = 0.17 \cdot 10^{-6}\,\mathrm{cm^3\,g^{-1}}$, $y = 0.9995$ and $z = 0.141$. For the mixture ZLI1167 these values are known only for the component 7CCH [19]. The same temperature characteristic and therefore the same parameters y and z are assumed also for the mixture. However the saturation value $\Delta\chi_{m0}$ is adjusted in order to obtain $\Delta\chi_m = -0.042 \cdot 10^{-6}\,\mathrm{cm^3\,g^{-1}}$, as reported in [20] for 295 K. Hence the parameters for ZLI1167 are: $\Delta\chi_{m0} = -0.052 \cdot 10^{-6}\,\mathrm{cm^3\,g^{-1}}$, $y = 0.9996$ and $z = 0.114$. The quantity $\chi_{m,\parallel}$ used in Equation 3 depends then on the type of liquid crystal used, i.e., parallel ($\parallel$) or perpendicular ($\perp$) orientation with respect to the magnetic field:

$$\begin{aligned} \parallel, \mathrm{5CB} \quad & \chi_{m,\parallel} = \chi_m^{iso} + \tfrac{2}{3}\Delta\chi_m \\ \perp, \mathrm{ZLI1167} \quad & \chi_{m,\parallel} = \chi_m^{iso} - \tfrac{1}{3}\Delta\chi_m \end{aligned} \tag{6}$$

With the assumption that the shift is directly proportional to the density, which is fulfilled quite well, since the σ_b is the leading term, a density variation in a 10 K range of the isotropic phase, for example in 5CB (steeper slope), of less than 4% is derived. It is then possible to estimate the variation of σ_b to be about 0.12 ppm and of σ_a to be less than 0.002 ppm, if one also considers that in the isotropic phase the σ_a values are smaller than 0.05 ppm as theoretical calculations show below. Furthermore it is reasonable to assume a direct proportionality of σ_a with the density since this term contains a $1/r^3$ dependence with r being of the order of intermolecular distances. Finally $\Delta\sigma_w$ is scaled down from the ^{129}Xe data by means of Equation 2 to give ~ 0.01 ppm in the 10 K range. Consequently, the error introduced in the determination of $d\rho/dT^*$, neglecting σ_a, is less than 2%. Equation 3 and 4 can then be transformed to:

$$\frac{d(\sigma - \sigma_{\mathrm{gas}}^0)^{Xe/He}}{dT^*} = (\sigma_{w1}^{Xe/He} + \sigma_b')\frac{d\rho}{dT^*} \tag{7}$$

TABLE 1

Density Dependence of van der Waals shift Contribution σ_{w1}^{Xe} and Density Variation with Reduced Temperature as Determined from Equation 7 and 2 for the two Liquid Crystals Used.

Liquid Crystal	σ_{w1}^{Xe} ppm $cm^3 g^{-1}$	$d\rho/dT^*$ $g cm^{-3}$
5CB	−68	−1.04
ZLI1167	−184	−0.49

where T^* is the reduced temperature T/T_{NI}. With Equation 2 it is possible to scale σ_{w1} so that $\sigma_{w1}^{He} = \sigma_{w1}^{Xe}/320$ results. Subsequently with the measured slopes of the shifts in the isotropic phase Equations 2 and 7 can be solved to yield the results presented in Table 1. In the nematic phase the same slope in density was used, but a density jump of 0.5% was assumed at the phase transition. Finally one density point was fixed by a separate experiment at 295 K for each liquid crystal, i.e., $\varrho(5CB) = 1.025\,g cm^{-3}$ and $\varrho(ZLI1167) = 0.945\,g cm^{-3}$.

The correction for σ_w^{He} is based simply on Equation 2. σ_w^{Xe} is obtained from the experimental $(\sigma - \sigma_{gas}^0)^{Xe}$ values by neglect of σ_a and by application of a susceptibility correction with a constant density of 1. This coarse consideration of σ_b is admissible, since the effects are subsequently scaled down for ^3He by a factor 320.

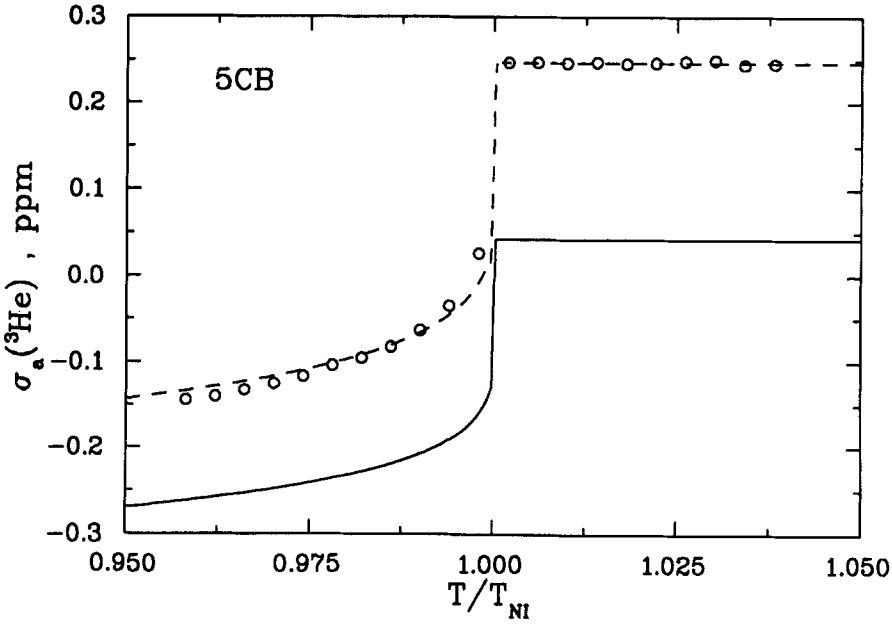

FIGURE 3 Local shift anisotropy for ^3He in 5CB. ○ denote the extracted data from the experimental gas to solution shifts. The lines are calculated according to a model considering the liquid crystal molecules as magnetically polarizable ellipsoids. The continuous line corresponds to a fully stretched liquid crystal molecule. The dashed line is obtained for a long molecular axis shrunk by 13% and is shifted to fit the isotropic part of the experimental points.

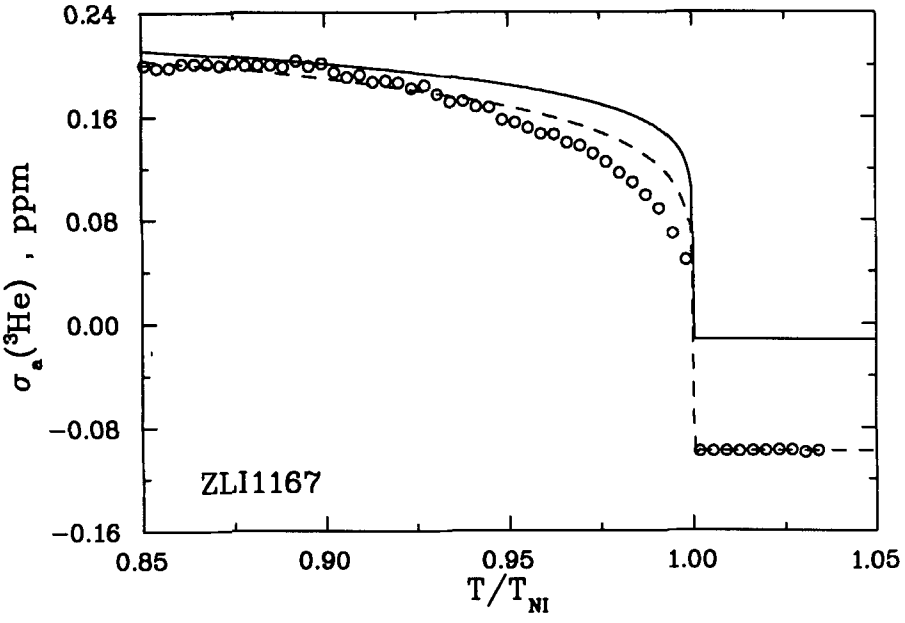

FIGURE 4 Local shift anisotropy for ^{3}He in ZLI1167. The same remarks apply as for the caption of Figure 3 except that the dashed line is for a shrinkage of 19%.

After the performance of all the described corrections, the σ_a values for ^{3}He are as shown in Figures 3 and 4. The overall behaviour remains the same as that of Figure 1, but the jump heights are now rather similar to each other. The reason is that at the phase transition the susceptibility correction has the same direction in both types of liquid crystals. Worth mentioning is the missing density dependence in σ_a, which is inherent in the corrections made and which could only be taken into account by a precise knowledge of the density in the temperature range considered.

In order to give a quantitative explanation of the observed local anisotropies, calculations were performed for a simplified model system, which is shown in Figure 5. The liquid crystal molecule is assumed to be a rotation ellipsoid with the long and short half axis c and a. The spherical ^{3}He atom of Radius R is allowed to move freely on the surface of the ellipsoid. The liquid crystal molecule, however is subject to an orienting potential of the form $U = -\lambda kT\cos^2\theta_{LC}$ [21], where λ is a function of the order parameter S and θ_{LC} is the angle between the symmetry axis of the molecule and the director. The liquid crystal molecule possesses a susceptibility tensor, whose elements in the molecule fixed coordinate system are determined by the two values

$$\chi^{iso} = \frac{M}{N_a}\chi_m^{iso} \qquad \Delta\chi = \frac{M}{N_a}\Delta\chi_{m0} \tag{8}$$

Herein M is the molecular weight, N_a the Avogadro constant and χ_m^{iso}, $\Delta\chi_{m0}$ are bulk mass susceptibilities. By means of this tensor for every position assumed by the

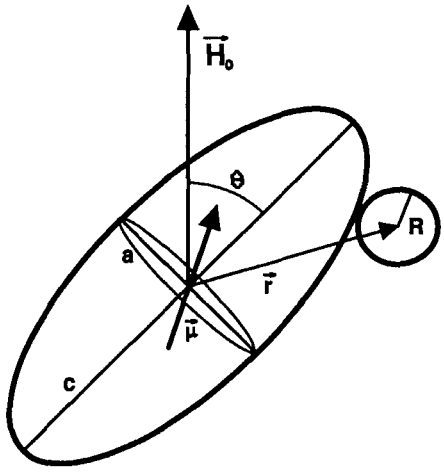

FIGURE 5 The ^{3}He atom and a neighbouring liquid crystal molecule, which has an induced magnetic dipole moment.

molecule and the atom the field component along $\vec{H}_0$ at the position of the ^{3}He nucleus can be calculated according to the field of the magnetic dipole induced at the center of the liquid crystal molecule. The average over all possible configurations taken with appropriate weights according to the orienting potential shall be interpreted as the local field effect. The complete procedure leads to the following expression:

$$\sigma_a = n(\Delta\chi + \alpha S(3\chi^{iso} + \Delta\chi))f(A, C) \tag{9}$$

i.e. the local anisotropy is represented by a susceptibility and a shape factor, for which a numerical integration must be performed:

$$f(A, C) = \frac{4\pi A}{3FC}\int_0^C \sqrt{A^2 + C^2 - r^2(z)}\,\frac{r^2(z) - 3z^2}{r^5(z)}\,dz$$

with

$$r(z) = \sqrt{A^2 + z^2\left(1 - \frac{A^2}{C^2}\right)} \tag{10}$$

Here the definitions $A = a + R$ and $C = c + R$ were introduced. F stands for the surface area of a rotation ellipsoid with the axes A and C, where C is the axis of rotation. The parameter α assumes the value 1 or $-1/2$ according to a liquid crystal that orients parallel (5CB) or perpendicular (ZLI1167) to the magnetic field. Finally n is the number of neighbours contributing, for which, regarding the small size of ^{3}He, a value of 2 was chosen. The order parameters S can be calculated from the formula $(1 - yT/T_{NI})^z$ with parameters y, z described above. The geometrical constants used in the simulation were derived for a fully stretched liquid crystal molecule; for 5CB: $a = 1.9$ Å $c = 9$Å; for ZLI1167: $a = 2.2$ Å $c = 9$ Å. The radius R of ^{3}He was assumed to be 1 Å. The result of

these calculations is shown as full lines in the Figures 3 and 4. The dashed lines correspond to a shortened long axis of the liquid crystal molecules and were shifted to fit the isotropic part of the experimental data.

The figures show that the model is in quite good agreement with the experimental result, as it predicts the σ_a-jump into the right direction and with the correct order of magnitude. The reason for the obvious offset between theoretical and experimental values are the imprecise values for the isotropic susceptibility used to correct for σ_b, which were estimated with Pascal's Method. In the case of 5CB a value increased by 7% and in the case of ZLI1167 decreased by 3% would cancel the offsets in the isotropic phase. But also if the curves are shifted to fit the isotropic part, the agreement in the nematic phase is only satisfactory, if the long axis of the liquid crystal molecule is reduced by about 13% for 5CB and 19% for ZLI1167. This could be attributed to the rather flexible alkyl tails, which let the effective length appear shorter than expected for a fully stretched molecule. In ZLI1167 the effect is more pronounced, because the cyclohexane rings are more flexible than the rigid phenyl rings in 5CB. Finally, the model calculation allows very interesting general conclusions on solvent effects observed in liquid crystals: Equation 10 shows that the existence of a shape anisotropy, i.e., $A \neq C$, is a necessary condition for a nonvanishing σ_a as well in the isotropic as in the oriented phase. In the former σ_a is very small (see the unshifted full lines in Figures 3 and 4), since it is detemined by the magnetic anisotropy $\Delta\chi$ of the liquid crystal molecules. In the oriented phase, however, no molecular magnetic anisotropy must be present to produce a σ_a. Here the isotropic molecular susceptibility in the term $3\chi^{iso}$ represents the dominating factor, which is at least ten times larger than $\Delta\chi$ for the two investigated liquid crystals. Hence considerably higher absolute values result in the nematic phase.

4. CONCLUSIONS

The presented results show that by NMR of ^{3}He atoms dissolved in a liquid crystal it is also possible to observe the phase transitions as with ^{129}Xe. However the information contained in the ^{3}He shifts is completely different, since these are dominated by the terms σ_b and σ_a, especially as far as the changes at the phase transitions are concerned. The jump in σ_a can even exceed the contribution of the susceptibility term, as it is the case for ZLI1167. This is due to the fact that in the oriented phase the local anisotropies can assume rather large values, since $3\chi^{iso}$ represents the important factor, whereas the σ_a values in the isotropic regime are determined by $\Delta\chi$, the susceptibility anisotropy. Provided that precise volume susceptibilities are known, the simultaneous measurement of ^{3}He and ^{129}Xe shifts offers the possibility of a determination of local anisotropies via a scaling of the van der Waals shift contributions from ^{129}Xe to ^{3}He.

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