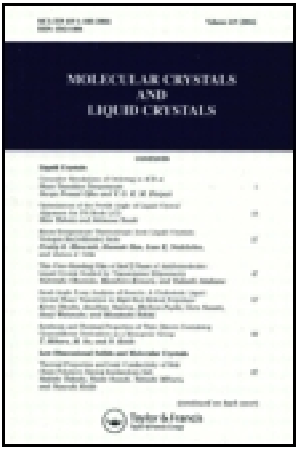

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^{129}Xe NMR in Liquid Crystals: Detection of Induced Smectic Phases in Binary Mixtures of Nematic Liquid Crystals by Use of Xenon Gas as a Probe

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^{129}Xe NMR in Liquid Crystals: Detection of Induced Smectic Phases in Binary Mixtures of Nematic Liquid Crystals by Use of Xenon Gas as a Probe

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The deuteron quadrupole splitting of d_2-EBBA and the nuclear shielding of the ^{129}Xe isotope of xenon gas dissolved in various binary mixtures of the nematic liquid crystals ZLI1132 and d_2-EBBA and in the mixture of S1114 (16.8 wt percent) and d_2-EBBA (83.2) were studied over the temperature range from 360 K to 280 K. The ^{129}Xe shielding is found particularly sensitive to phase transitions, and consequently, the ^{129}Xe NMR spectroscopy can be utilized in determining phase diagrams of liquid crystals. In the cases studied, $I - N$, $N - S_A$ (induced) and S_A (induced) $- S_B$ (induced) phase transitions have been detected, and the phase diagram of the ZLI1132/d_2-EBBA system is reported.

Keywords: *^{129}Xe NMR, xenon shielding, binary mixtures of liquid crystals, induced smectic phases*

1. INTRODUCTION

The NMR spectroscopy of noble gases adsorbed or dissolved in various solids or liquids can be utilized in many ways. In particular, the sensitivity of the shielding (and shielding anisotropy) of the ^{129}Xe isotope (spin 1/2) to its physical environment has been used to derive information about the structures of zeolites[1] and clathrates.[2] Recently, Bayle *et al.*[3] studied the ^{129}Xe shielding in nematic liquid crystals, and the present authors carried out measurements in various pure and mixed nematic phases and in a smectic A phase.[4]

Moreover, the nuclear resonances of the quadrupolar isotopes of noble gases, such as ^{83}Kr (spin 9/2) and ^{131}Xe (spin 3/2), in oriented phases of liquid crystals display quadrupolar splittings, and thus give insight into the electric field gradients interacting with the quadrupole moments of the nuclei.[5,6]

Recently, the ^{2}H NMR study of the solute d_3-acetonitrile and of d_2-EBBA in the mixture S1114 (16.84 wt%)/d_2-EBBA (83.16 wt%) yielded two induced smectic phases (smectic A and B) besides the nematic phase.[7] In the present work, we studied the phases of the same mixture with the aid of the ^{129}Xe NMR of dissolved

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xenon gas. Furthermore, the phase diagram of the ZLI1132/d_2-EBBA system was determined by applying the ^{129}Xe NMR. This system is particularly interesting, because, for example, the study of the orientation of a solute in a 50:50 mixture showed unexpected behaviour.[8] Furthermore, mixtures in various concentration ratios have been used in determining electric field gradients present in liquid crystals.[9] This study indicates that the mixtures with the concentration of d_2-EBBA between 70 and 85 wt% posses two smectic phases already at temperatures above 300 K.

2. EXPERIMENTAL

The xenon gas was delivered by Linde AG (Unterschleissheim, FRG) whereas the ZLI1132 and S1114 liquid crystals are products of Merck (Darmstadt, FRG). The d_2-EBBA was synthesized at Basel. The molecular formulas and the compositions of the liquid crystal used are given in Table I, while Table II lists the various mixtures.

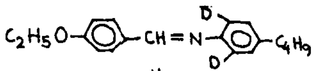
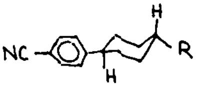
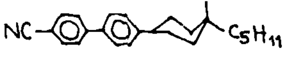
The samples were prepared into heavy-wall glass tubes (inner diameter 7 mm, outer diameter 10 mm). All the samples were degassed in a vacuum line and sealed on flame. The total pressure of xenon was ca. 7 atm in each sample.

Xenon has altogether nine stable isotopes. However, only two of them posses a non-zero spin: ^{129}Xe has a spin of 1/2, and ^{131}Xe a spin of 3/2. The natural abundances are 26.4% and 21.2%, and the absolute NMR sensitivities (with respect to ^{1}H) 5.60×10^{-3} and 5.84×10^{-4}, respectively. Thus the sensitivity is better than that of ^{13}C.

The ^{129}Xe as well as the ^{2}H NMR spectra were recorded without locking from non-spinning samples on a Bruker AC250 spectrometer using a tunable 10 mm probehead. The solubility of xenon in liquid crystals is so good that the spectrum

TABLE I

Formulas and compositions of the liquid crystals used.

Code name	Formula and composition		
d_2-EBBA			
ZLI1132[a]			
-S1103		R = C_3H_7	24 %
-S1114		R = C_5H_{11}	36 %
-S1115		R = C_7H_{15}	25 %
-S1131			15 %

[a] ZLI1132 (product of Merck AG, Darmstadt, FRG) is the mixture of the S -liquid crystals given below wit the concentrations shown in the rightmost column.

TABLE II

Compositions of the mixtures used.

Mixture	Composition[a]
A	ZLI1132(100)
B	ZLI1132(73.8)/d_2-EBBA(26.2)
C	ZLI1132(46.3)/d_2-EBBA(53.7)
D	ZLI1132(34.7)/d_2-EBBA(65.3)
E	ZLI1132(26.5)/d_2-EBBA(73.5)
F	ZLI1132(21.7)/d_2-EBBA(78.3)
G	ZLI1132(17.1)/d_2-EBBA(82.9)
H	d_2-EBBA(100)
I	S1114(16.8)/d_2-EBBA(83.2)

[a] The figures in parentheses stand for the concentration (in weigth per cent) of the component.

(single peak) with sufficiently good signal-to-noise ratio is obtained on one scan. This is an advantage because the spin-lattice relaxation time of the ^{129}Xe isotope in a liquid-crystalline phase has been found to be relatively long, 20 to 40 s.[10] For the ^{2}H spectra, up to ca. 10000 scans were accumulated, depending upon the concentration of d_2-EBBA.

3. RESULTS AND DISCUSSION

3.1. Phase transitions

Figure 1 illustrates the behaviour of the ^{129}Xe shielding as a function of temperature in the mixture S1114/d_2-EBBA (mixture I in Table II). At the various phase transitions (the identification of the smectic B phase is based on Reference 7), the shielding changes abruptly indicating changes in the degree of order and in the structure of the environment. This figure also yields information on the sensitivity to the temperature variation of the xenon shielding (we shall use the notation $\langle\sigma_{zz}(^{129}\text{Xe})\rangle$ for the shielding of the ^{129}Xe isotope. The total shielding may arise from several contributions, as discussed later in this paper and in Reference 4): the linewidth increases with increasing sensitivity, i.e. with increasing $|d\langle\sigma_{zz}(^{129}\text{Xe})\rangle/\text{d}T|$. This phenomenon is simply due to temperature gradients and temperature fluctuations over the sample volume. The third result that can be read from the figure is the possible existence of an extra phase (marked by a *) between the S_A and S_B phases. The temperature range, however, is so narrow that a detailed study on an NMR spectrometer without a high quality VT unit is not possible.

In Figure 2 are plotted the $\langle\sigma_{zz}(^{129}\text{Xe})\rangle$ and the ^{2}H quadrupole splitting, $\Delta\nu_Q$, of d_2-EBBA as a function of temperature in the mixture I.

It is seen that the absolute value of the xenon shielding jump is more than twice so large at the transitions $I - N$ (shielding decreases) and $S_A - S_B$ (shielding increases) as at the $N - S_A$ (shielding increases) transition. In the nematic phase and in the smectic B phase, the xenon shielding decreases towards lower temperature, whereas in the smectic A phase the situation is reverse. This different be-

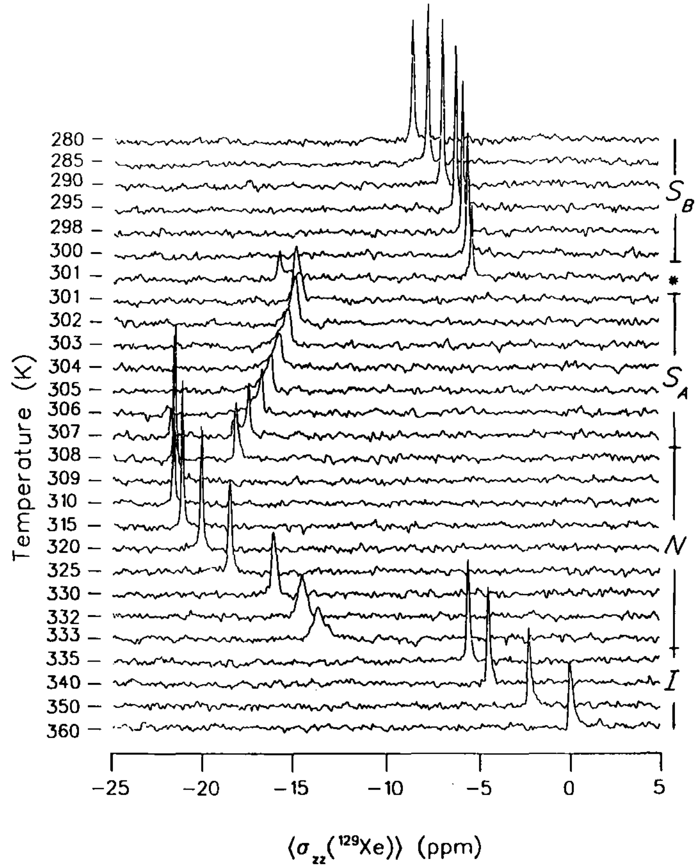


FIGURE 1 ^{129}Xe NMR spectrum of xenon gas dissolved in the mixture I at various temperatures. The jumps in the nuclear shielding show clearly the phase transitions $N - I$, $S_A - N$ and $S_B - S_A$. The spectra at 301 K were taken before and after connecting the cooling unit on. Very likely the spectrum marked by a * corresponds to a temperature between 300 K and 301 K, and may indicate a presence of an additional phase in between the S_B and S_A phases.

haviour in the nematic and smectic A phases was earlier observed for HAB,[4] and most probably displays the structural change (appearance of density waves) in the environment of xenon. On the contrary, the deuteron quadrupole splitting increases when moving to lower temperatures, except in the smectic B where it remains almost constant or slightly decreases. The quadrupole splitting can be presented in the form

$$\Delta\nu_Q = (3/2)\chi S_{zz}\left[P_2(\cos\Theta) + (1/2)\frac{S_{xx} - S_{yy}}{S_{zz}}\sin^2\Theta\right]\langle P_2(\cos\alpha)\rangle \qquad (1)$$

where χ is the quadrupole coupling constant, S_{zz} and $(S_{xx} - S_{yy})$ are the independent order tensor elements, $P_2 = 1/2(3x^2 - 1)$ is the second Legendre polynomial, and Θ and α are the angles between the C-D bond and the molecular z-axis and between

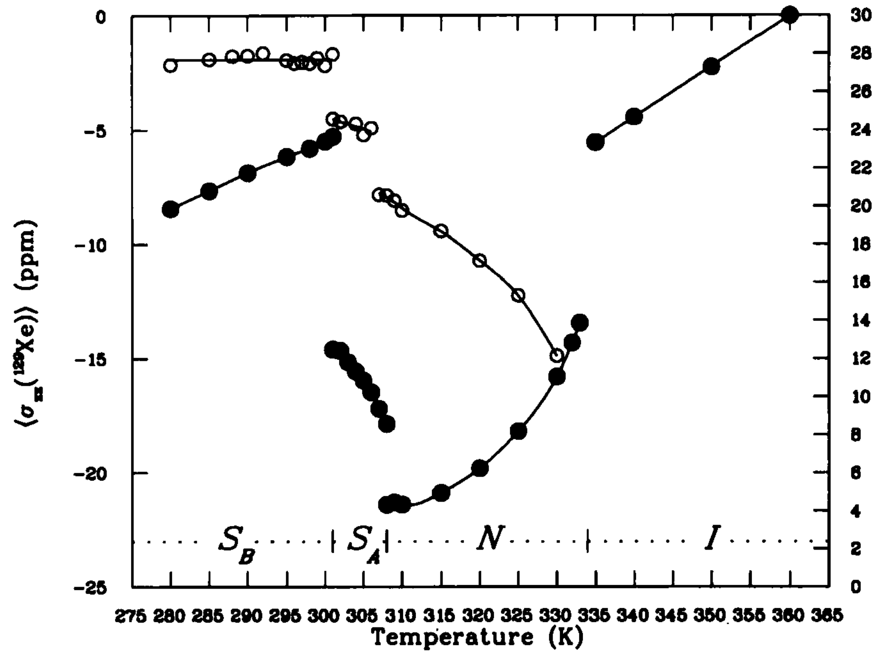


FIGURE 2 The ^{129}Xe shielding, $\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$ (●), of the xenon gas dissolved and the ^{2}H quadrupole splitting, $\Delta\nu_Q$ (○), of the deuterons in d_2-EBBA in the mixture I.

the liquid crystal director and the applied magnetic field, respectively. The ortho deuteron-proton dipolar coupling in turn can be written as

$$D_{HD} = -K_{HD}S_{zz}/r_{HD}^3 \tag{2}$$

where $K_{HD} = \mu_0\hbar\gamma_D\gamma_H/8\pi^2$ and r_{HD} is the proton-deuteron distance. Thus, the ratio of the quadrupole splitting and of the dipole-dipole coupling is

$$\Delta\nu_Q/D_{HD} = -(3\chi r_{HD}^3/2K_{HD})\left[P_2(\cos\Theta) + (1/2)\,\frac{S_{xx} - S_{yy}}{S_{zz}}\sin^2\Theta\right] \tag{3}$$

This ratio was found to be constant within the experimental uncertainty. Consequently, assuming constant geometry for the phenyl ring in d_2-EBBA the S_{zz} and $(S_{xx} - S_{yy})$ are linearly related and the quadrupole splitting can be regarded as a measure for the degree of orientation of the liquid crystal. The observed ^{2}H splittings indicate that the degree of order increases in the order nematic—smectic A—smectic B, as usual.

The ^{129}Xe shielding as a function of temperature in various mixtures of ZLI1132 and d_2-EBBA is shown in Figure 3, while Figure 4 illustrates the behaviour of the xenon shielding and of the deuteron quadrupole splitting as a function of temperature in the mixture F. The shielding value at the temperature of 360 K was chosen as reference in every case. The shielding is affected somewhat, for example, by

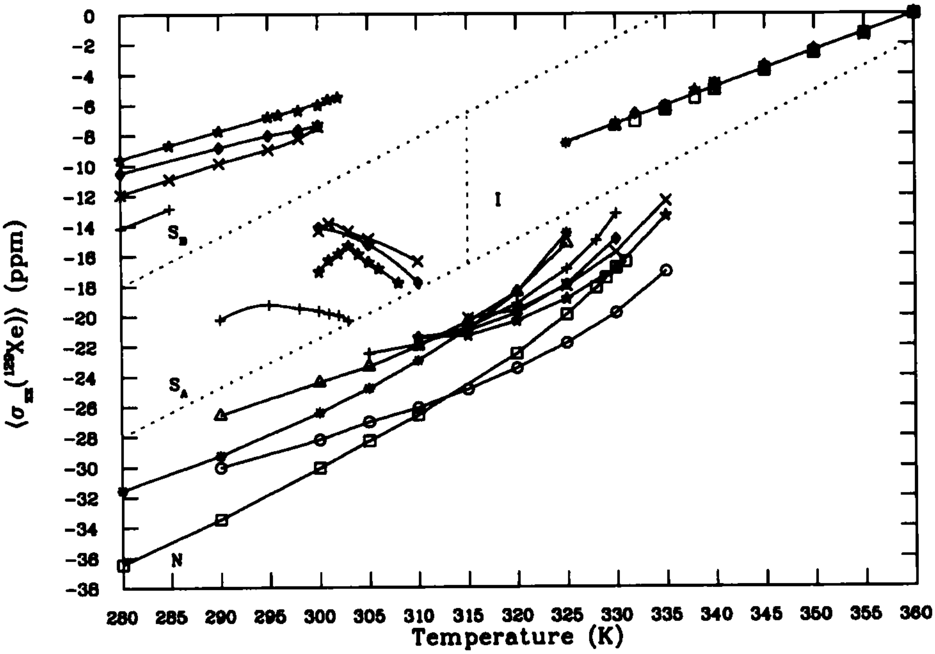


FIGURE 3 The ^{129}Xe shielding, $\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$, versus temperature for various mixtures of ZLI1132 and d_2-EBBA. The symbols are associated with the mixtures in the following way: (□) A, (*) B, (△) C, (+) D, (×) E, (⊗) F, (☆) G, and (○) H.

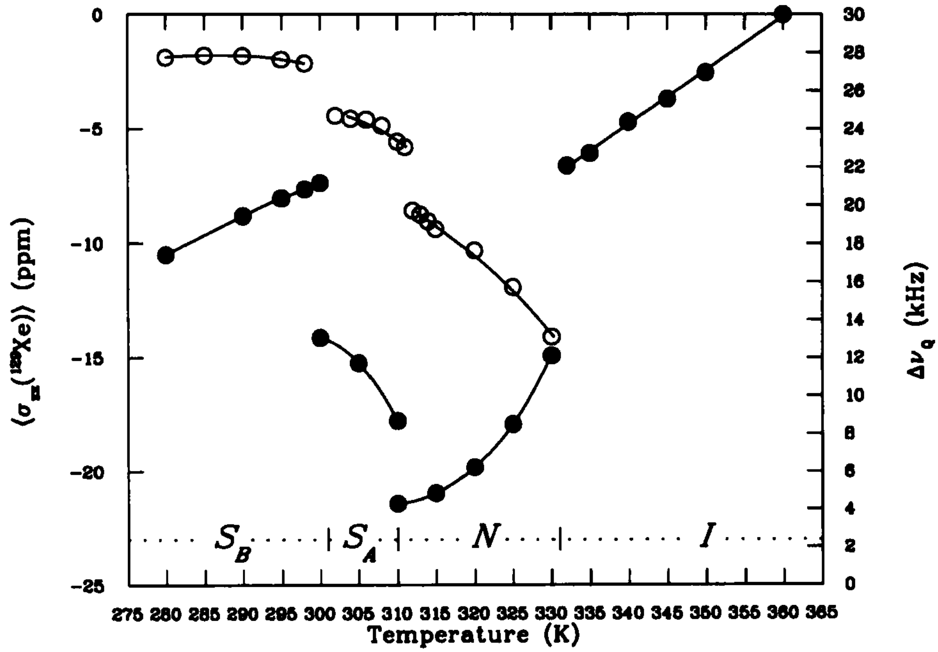


FIGURE 4 The ^{129}Xe shielding, $\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$ (●), of the xenon gas dissolved and the ^{2}H quadrupole splitting, $\Delta\nu_Q$ (○), of the deuterons in d_2-EBBA in the mixture F.

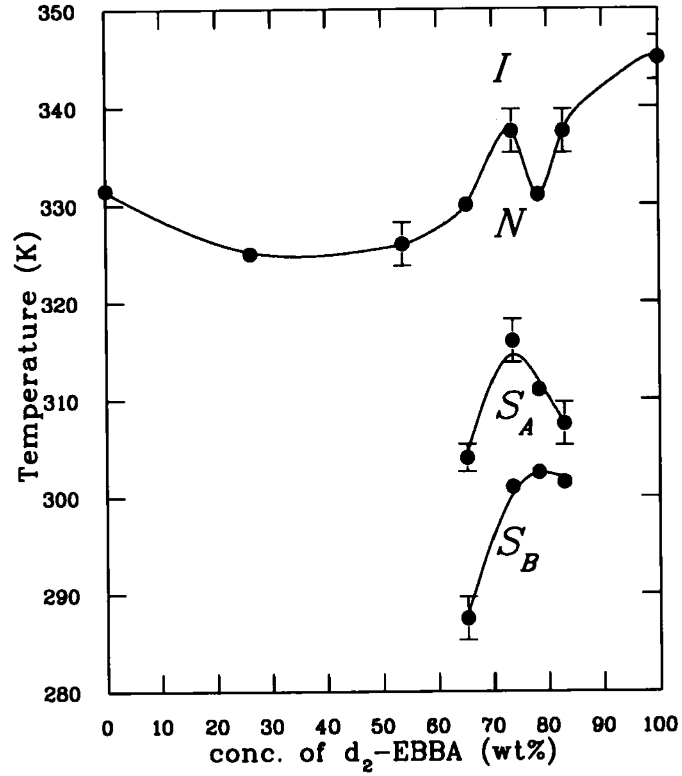


FIGURE 5 Phase diagram of the binary ZLI1132/d_2-EBBA system.

the bulk contribution, but this is estimated to be small compared to the total shift.[4] Anyway, it does not prevent one from observing the phase transitions. From Figure 3, it is possible to construct the phase diagram, shown in Figure 5. The phase transition temperatures are dependent upon the amount of xenon gas dissolved. No measurements about the solubility of xenon gas into liquid crystals has been made, but our earlier study indicated that for xenon/EBBA the T_{NI} decreased from ca. 346 K to ca. 340 K when the pressure of xenon gas increased from ca. 1 atm to ca. 5 atm.[4] For pure EBBA, T_{NI} = 352.5 K.[11] There are, however, no insurmountable obstacles to detect ^{129}Xe signals from less concentrated samples.

The diagram exhibits a maximum in the N-I transition boundary between the concentrations from ca. 60 to ca. 83 wt% of d_2-EBBA. Below this maximum, the smectic A and B regions may be detected. On the contrary, the transitions from the smectic B to the crystal phase could not be observed because of supercooling of samples. For example, the mixture F could be supercooled down to 220 K.

3.2. ^{129}Xe shielding

The total shielding of the ^{129}Xe isotope (or in general, of any nucleus) in a solution may be a result of various contributions, such as the bulk effect (due to the macroscopic diamagnetic susceptibility and its anisotropy), the local effect (due to the microscopic diamagnetic anisotropy of neighbour solvent molecules), van der Waals effect (due to the vdW interactions), electric field effect (due to the permanent electric dipole moment of solvent molecules), and particularly in anisotropic environments, shielding anisotropy effect (due to the anisotropy of the shielding tensor, which in the case of xenon arises from the deformation of the originally spherical electron cloud). It is considered that the most important contributions to the observed shielding jumps, $\Delta\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$, at the phase transitions stem from the change in the shielding anisotropy and from the change in the liquid crystal structure. These two contributions are most probably, at least partly, interrelated, i.e. the change in structure induces via the change in the deforming forces different shielding anisotropies. On the other hand, as the ^{2}H splittings indicate, the phases become more ordered when the sample is cooled. This should mean increasing shielding anisotropy of the ^{129}Xe isotope, and consequently, a monotonically decreasing $\langle\sigma_{zz}(^{129}\mathrm{Xe})\rangle$. This, however, is not the case. Presumably, the appearance of density waves in the smectic A and B phases and the hexagonal structure of the smectic B are responsible for the observed shielding behaviour.

In various regions of the sample, the ^{129}Xe isotope may experience very different shielding contributions, even the sign of the shielding anisotropy may change, as observed, for example, for molecular sieves[12] and clathrates.[2]

4. CONCLUSIONS

This study shows that the nuclear shielding of the ^{129}Xe isotope dissolved in a liquid-crystalline medium is very sensitive to phase transitions, and consequently, a property which can be utilized in deriving phase diagrams. This can be done, although the various effects contributing to the xenon shielding are not understood in all details.

Acknowledgments

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