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^{21}Ne and ^{131}Xe NMR study of electric field gradients and multinuclear NMR study of the composition of a ferroelectric liquid crystal

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This study has two goals. First, the electric field gradient (EFG) present in the liquid-crystalline phases of ferroelectric FELIX-R&D is determined using NMR spectroscopy of noble gases ^{21}Ne and ^{131}Xe . The ^{21}Ne and ^{131}Xe NMR spectra were recorded over a temperature range, which covers all the mesophases of FELIX-R&D: nematic N^* , smectic A, and smectic C^* . The spin quantum number of both ^{21}Ne and ^{131}Xe is $3/2$. Their electric quadrupole moment interacts with the EFG at the nuclear site, which in liquid-crystalline phases results in the NMR spectra of the triplet structure, instead of a singlet detectable in the isotropic phase. The total EFG experienced by the noble gas nuclei consists of two contributions; one arises from the quadrupole moments of the liquid crystal molecules (external contribution) and the other one from the deformation of the electron distribution of the atoms (deformational contribution). The total EFGs determined from the ^{131}Xe and ^{21}Ne quadrupole splittings are very similar in the nematic and smectic A phases but differ in the smectic C^* phase, being about twice larger in the ^{21}Ne case which stems from the larger deformation of the xenon electron cloud than that of neon. For the first time, EFG was determined also in the smectic C^* phase applying noble gas NMR spectroscopy. Second, the structure of molecules which, as a mixture, compose the used ferroelectric liquid crystal, FELIX-R&D, is determined by applying a number of various NMR methods and sophisticated spectral analysis. In this part, NMR spectra were recorded from FELIX-R&D/ CDCl_3 solution. The NMR spectral analysis was divided into four subsystems with over 13 000 000 nonzero intensity transitions. It appeared that FELIX-R&D is composed of three phenyl pyrimidine derivatives and a chiral dopant with fluorine in the asymmetric carbon atom. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5052499>

I. INTRODUCTION

Ferroelectric liquid crystals (LCs) with a wide smectic C^* (SmC^*) range are considered applicable materials for liquid crystal displays (LCDs).¹ Apart from this, the FELIX-R&D liquid crystal, used in this study, is particularly interesting because it was shown to possess a thermotropic biaxial nematic phase at temperatures near to room temperature.^{2,3} It has been proposed that biaxial nematic liquid crystals are potential candidates for LCD technology because of their fast switching times.⁴ Unfortunately, the biaxial nematic range of FELIX-R&D is narrow, only ca. 9° , restricting its use in LCD technology. The manufacturer of FELIX-R&D did not disclose its composition. Therefore, we applied a large number of NMR experiments to do it. The knowledge of the composition and the

structure of the molecules which form the FELIX-R&D liquid crystal may open new ideas for developing thermotropic biaxial nematic liquid crystals applicable within wide temperature ranges.

Often very valuable information about the properties of a physical system can be derived by introducing a spy (*aka* a probe) into the system and measuring its NMR spectrum rather than trying to use NMR of spins carried by the system itself. In studies of liquid-crystalline systems, NMR of noble gases and small molecules has appeared a very applicable means to derive information about the physicochemical properties of liquid crystals.⁵ In particular, ^{129}Xe NMR has many advantages in studies of thermotropic liquid crystals: its NMR sensitivity is good, its chemical shift, when measured over wide temperature range, provides versatile information, such as phase transitions, phase structure, sign of the diamagnetic anisotropy, density, order parameters in nematic and smectic phases, and tilt angle of the director in chiral smectic and nematic phases.^{5,6} The parallel use of ^{129}Xe and ^{131}Xe NMR can be utilized in the classification of thermotropic biaxial nematic liquid crystals.^{2,3} The NMR spectroscopy of quadrupole noble gas isotopes, ^{21}Ne (spin $3/2$), ^{83}Kr ($9/2$), and ^{131}Xe ($3/2$), reveals further information in addition to

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that available via ^{129}Xe . Namely, their NMR spectra display quadrupole splitting (QS) which is dependent on the orientational order of the liquid crystals and the size of the electric field gradient (EFG) at the nuclear site.^{5,7–10} The EFG in turn consists of two contributions: one arises from the charge distribution of the neighbouring LC molecules and the other one from the deformation of the electron cloud because of the collisions of atoms with liquid crystal (LC) molecules.^{7–10} These two contributions may possess the same sign or opposite sign.¹⁰ The challenge in recording ^{131}Xe and ^{83}Kr NMR spectra in liquid-crystalline solutions is their low gyromagnetic ratio which leads to low NMR sensitivity and to low Larmor frequency, which in turn causes a wavy background and artefacts due to acoustic ringing. In the present case, we use ^{21}Ne and ^{131}Xe NMR of the respective gases to derive the total EFG in all the liquid-crystalline phases of the ferroelectric FELIX-R&D liquid crystal as a function of temperature.

The number of studies dealing with ^{21}Ne NMR is very small. This is because the natural abundance of ^{21}Ne is only 0.27%, and its receptivity relative to ^{13}C is only 0.04, while that of ^{131}Xe is ca. 3. However, ^{21}Ne enriched gas is available and it was used to measure spin-lattice and spin-spin relaxation times in liquid and solid neon already in the early 1970s.¹¹ The chemical shift range of ^{21}Ne in solutions of isotropic liquids is about 20 ppm, while that of ^{129}Xe and ^{131}Xe is about 300 ppm meaning that ^{21}Ne shielding is remarkably less sensitive to environmental effects than that of the Xe isotopes.¹² This arises from the fact that the electron cloud of neon is less polarizable than that of xenon. Due to the quadrupole interaction, the ^{21}Ne and ^{131}Xe NMR spectra in a liquid-crystalline solution are 3:4:3 triplets (in isotropic solutions, they are singlets), and the quadrupole splitting (QS) depends on the orientational order and, in the chiral smectic C^* phase, on the tilt angle (the angle between the external magnetic field and the liquid crystal director).

The FELIX-R&D liquid crystal possesses isotropic (I), chiral nematic (N^*), smectic A (SmA), and chiral smectic C^* (SmC^*) phases in the order of lowering temperature. In the N^* phase, liquid crystal directors lie in the plane perpendicular to the helix axis, leading to a situation where the macroscopic diamagnetic anisotropy is negative, and consequently the helix axis is oriented perpendicularly to the external magnetic field of an NMR spectrometer. However, in strong enough magnetic fields, the helical structure unwinds and the N^* phase transforms into a conventional uniaxial N phase with the director along the field direction. This transformation is proved for FELIX-R&D by the ^{129}Xe self-diffusion and shielding experiments carried out as a function of temperature.¹³ During the transformation from the N phase to the SmA phase, a layered structure develops but the director remains in the magnetic field direction. On the contrary, in the SmC^* phase, directors are tilted with respect to the helix axis (and the external magnetic field) to an angle smaller than the magic angle. Thus the helix axis orients along the magnetic field direction.

II. EXPERIMENTAL

^{131}Xe NMR experiments in all the mesophases were carried out from two samples. The first sample consisted of ca. 2 g

of FELIX-R&D (product of Hoechst AG, Germany) in a thick wall (thickness 1 mm) NMR tube with the outer diameter of 10 mm. The natural xenon gas (from Messer Griesheim) pressure was ca. 5 atm. The second sample consisted of about 500 mg of FELIX-R&D in a thick wall (thickness 1 mm) 5-mm NMR tube. The final equilibrium pressure was ca. 5.2 atm. In this case, ^{131}Xe enriched gas (degree of enrichment 84%; delivered by CortecNet) was used. In both cases, a liquid crystal was first degassed in a vacuum line, and thereafter xenon gas was transferred to the tube with the aid of liquid nitrogen. The spectra were recorded on Bruker Avance DSX300WB ($B_0 = 7.05\text{ T}$; ^{131}Xe Larmor frequency 24.74 MHz) and Bruker Avance III 600 ($B_0 = 14.09\text{ T}$; ^{131}Xe Larmor frequency 49.47 MHz) NMR spectrometers. The ^{131}Xe NMR spectra were recorded either using the quadrupole echo or simple single pulse experiments. In order to get a good enough signal-to-noise ratios, typically 10^6 scans were accumulated at each temperature, the temperature stabilization time being 30 min. The ^{21}Ne NMR spectra in turn were recorded from a sample consisting of ca. 2 g of liquid crystal placed in a thick-wall 10-mm NMR tube. ^{21}Ne -enriched (degree of enrichment 95.06 at. %; from Isotec, Inc., USA) neon was introduced into the sample with the aid of liquid nitrogen, the final equilibrium pressure being ca. 0.6 atm. Finally, each glass tube was sealed with a flame. ^{21}Ne NMR spectra were recorded on the Bruker DRX500 spectrometer (^{21}Ne Larmor frequency 39.48 MHz). The temperature scale was calibrated by an 80% glycol in the dimethyl sulfoxide ($\text{DMSO}-d_6$) sample. The error in the real sample temperature is estimated to be $\pm 0.5\text{ K}$. Spectra were taken over the temperature range covering nematic (N), smectic A (SmA), and smectic C^* (SmC^*) phases. Phase transition temperatures of the pure liquid crystal are $\text{X} \rightarrow 279\text{ K} \rightarrow \text{Smectic C}^* (\text{SmC}^*) \rightarrow 327\text{ K} \rightarrow \text{Smectic A (SmA)} \rightarrow 332\text{ K} \rightarrow \text{Nematic (N}^*) \rightarrow 341\text{ K} \rightarrow \text{Isotropic (I)}$.¹⁴

FELIX-R&D is reported to be a mixture of phenyl pyrimidine derivatives. The detailed composition is not, however, disclosed by the manufacturer. Therefore, we applied various NMR techniques and the ChemAdder program¹⁵ to reveal the components and their concentrations in the mixture. In this case, FELIX-R&D was dissolved in CDCl_3 , i.e., the sample is in the isotropic phase, and it was placed in a 5-mm (o.d.) glass tube. NMR spectra were recorded on the Bruker Avance-III 600 spectrometer, equipped with a Prodigy TCI cryoprobe or on Bruker Avance-III 500 equipped with BB/ ^1H Smartprobe, which was needed to enable $^1\text{H}-\{^{19}\text{F}\}$ and $^{19}\text{F}-\{^1\text{H}\}$ experiments having ^{19}F in the BB channel. The following spectra (at room temperature) were recorded: ^1H , $^1\text{H}-\{^{19}\text{F}\}$, $^{13}\text{C}-\{^1\text{H}\}$, ^{19}F , $^{19}\text{F}-\{^1\text{H}\}$, Correlated Spectroscopy (COSY), Heteronuclear Single Quantum Coherence (HSQC), Heteronuclear Multiple Quantum Correlation (HMQC), and (several) 1D Total Correlation Spectroscopy (TOCSY). The quantitation of the spectra was performed on the ChemAdder program.¹⁵

III. RESULTS

A. Electric field gradients in FELIX-R&D

Both ^{21}Ne and ^{131}Xe are quadrupole nuclei with spin 3/2. Their electric quadrupole moments, Q , are $101.55 \times 10^{-31}\text{ m}^2$

FIG. 1. ^{21}Ne NMR spectrum of neon dissolved in the FELIX-R&D liquid crystal at 334 K.

and $-114 \times 10^{-31} \text{ m}^2$, respectively.¹⁶ Consequently, the quadrupole moment of ^{131}Xe is of the same magnitude as that of ^{21}Ne but the sign is opposite. Figure 1 shows, as an example, the ^{21}Ne NMR spectrum at 334 K, whereas Fig. 2 shows the magnitude (spectra do not reveal the sign of the splitting) of the ^{21}Ne QS and Fig. 3 shows that of ^{131}Xe as a function of temperature in the FELIX-R&D liquid crystal.

The QS is defined here as the distance between the satellite transitions (ST; transitions $-1/2 \dots -3/2$ and $+3/2 \dots +1/2$), as indicated in Fig. 1. Figure 2 shows that the magnitude of the ^{21}Ne QS varies between about 22 and 32 kHz over the temperature range from ca. 300 K to ca. 340 K. The behavior in the nematic and smectic A phases is similar to that earlier found in the NCB84 liquid crystal.¹⁰ The corresponding ^{131}Xe QS (see Fig. 3) increases from ca. 280 kHz to over 500 kHz. Thus the ^{131}Xe QS is by a factor of 12–16 larger than that of ^{21}Ne . A similar difference exists in the chemical shift range, as pointed out above. Additional factor which contributes to QS is the Sternheimer antishielding factor (SAF) $(1 - \gamma_\infty)$.¹⁷ The EFG caused by the solvent molecules induces a quadrupole moment in the electronic distribution of the noble gas atoms. This in turn induces an EFG at the investigated nucleus. This is the reason for incorporating the SAF into the equations below. For ^{21}Ne and ^{131}Xe , γ_∞ is -9.145 and -168.5 , respectively.¹⁸ The ratio of the antishielding factors, $(1 - \gamma_\infty)$, of ^{131}Xe and ^{21}Ne is 16.7, being close to the ratio of the QS's.

1. Theory

The quadrupole splitting, i.e., the separation of the satellite transitions (see Fig. 1), $|\Delta\nu_i|$, in the NMR spectrum of a nucleus i with spin I_i can be shown to be

$$|\Delta\nu_i| = \frac{3}{I_i(2I_i - 1)} |\chi_{i\parallel} P_2(\cos \theta)|, \quad (1)$$

FIG. 2. Magnitude of the ^{21}Ne quadrupole splitting in FELIX-R&D at variable temperatures. The solid line is the results of the least-squares fit of function (6) to the experimental points (see the text). The error in experimental points is estimated to be ± 0.2 kHz.

FIG. 3. Magnitude of the ^{131}Xe quadrupole splitting in FELIX-R&D at variable temperatures. The solid line is the results of the least-squares fit of function (6) to the experimental points (see the text). The error in experimental points is estimated to be ± 2 kHz.

where $\chi_{i\parallel}$ is the quadrupole coupling tensor element in the direction of the liquid crystal director and $P_2(\cos \theta) = \frac{1}{2}(3\cos^2 \theta - 1)$ is the second Legendre polynomial with θ being the tilt angle (the angle between the external magnetic field direction and the liquid crystal director). The quadrupole coupling tensor element $\chi_{i\parallel}$ is defined as

$$\chi_{i\parallel} = \frac{eQ_i \langle F_{i\parallel}^{\text{tot}} \rangle}{h}, \quad (2)$$

where e is the positive elementary charge, h is Planck's constant, Q_i is the nuclear quadrupole moment, and $\langle F_{i\parallel}^{\text{tot}} \rangle$ is the average total EFG in the direction of the liquid crystal director at the nuclear site.

As mentioned above, the total EFG at the nuclear site consists of two contributions: one arises from the distortion of the electron cloud of an atom from spherical symmetry (superscript d in the following equations) and the other one arises from the neighbouring liquid crystal molecules (ext). Consequently, we can write¹⁰

$$\langle F_{i\parallel}^{\text{tot}} \rangle = \langle F_{i\parallel}^{\text{ext}} \rangle + \langle F_{i\parallel}^d \rangle. \quad (3)$$

Experiments performed in purely nematic liquid crystals indicate that the two contributions may be either of the same sign or opposite sign, depending upon the liquid crystal solvent. If the contributions are opposite in sign, the $|\Delta\nu|$ vs. T curve displays a maximum.^{8,9} Such behavior is seen also in

the present cases within the nematic range, N (see Figs. 2 and 3).

The external EFG is very sensitive to temperature, unlike the deformational contribution. In the following, we approximate the temperature dependence of the external contribution by a linear function,¹⁰

$$\langle F_{i||}^{ext} \rangle = \langle F_{i||}^{ext} \rangle_o + \langle F_{i||}^{ext} \rangle_1 \frac{T}{T_{NI}}, \quad (4)$$

where T_{NI} is the nematic – isotropic transition temperature. Thus the total EFG can be presented in the form

$$\langle F_{i||}^{tot} \rangle = \langle F_{i||}^d \rangle + \langle F_{i||}^{ext} \rangle_o + \langle F_{i||}^{ext} \rangle_1 \frac{T}{T_{NI}}. \quad (5)$$

At the SmA-N phase transition, no abrupt jump can be observed, but a change in the curvature is obvious although in both cases, the magnitude of the QS decreases monotonically toward low temperature. At the SmC* - SmA phase transition, a clear change in the slope of the curve can be seen. This arises from the fact that in the SmC* phase, the LC director is tilted with respect to the external magnetic field while in the SmA phase the director is along the field direction. The tilt angle is dependent on temperature increasing toward low temperature.

In the case of spin-3/2 nuclei, ²¹Ne and ¹³¹Xe, we prefer to use the separation of the satellite transitions (ST) rather than that of successive peaks in the NMR spectrum (see Fig. 1). This is because the separation of the STs is independent of possible second order effects.^{2,3} Temperature dependence of the QS can now be described by a function

$$\begin{aligned} |\Delta\nu_i| &= |\chi_{i||} P_2(\cos\theta)| \\ &= \left| \frac{eQ_i \langle F_{i||}^{tot} \rangle}{h} (1 - \gamma_{\infty i}) = P_2(\cos\theta) \right| \\ &= \left| \frac{eQ_i}{h} P_2(\cos\theta) (1 - \gamma_{\infty i}) \left(A_i + B_i \frac{T}{T_{NI}} \right) \right. \\ &\quad \left. \times [S(T) + 2c\sigma_1(T)\tau_1(T)] \right|, \end{aligned} \quad (6)$$

where $i = {}^{21}\text{Ne}$ or ${}^{131}\text{Xe}$ and $|\Delta\nu_i|$ is the separation of the ST's, $A_i = \langle F_{i||}^d \rangle + \langle F_{i||}^{ext} \rangle_o$ is the sum of the temperature independent external and deformational contributions, and $B_i = \langle F_{i||}^{ext} \rangle_1$ is the coefficient of the temperature dependent part in the external contribution. Equation (6) includes now also the Sternheimer antishielding factor, $(1 - \gamma_{\infty i})$, as mentioned above. We neglect the temperature dependence of the density of the liquid crystal. In Eq. (6), $S(T)$ is the conventional second rank orientational order parameter, defined relative to the liquid crystal director, while $\sigma_1(T)$ and $\tau_1(T)$ are the mixed translational-orientational and translational order parameters, respectively. These latter two order parameters are nonzero only in the smectic phases. The coefficient c takes into account the redistribution of neon and xenon atoms during the development of the layered structure when approaching the smectic A phase from the nematic phase. The temperature dependence of the order parameters can be described by the following functions:¹⁰

$$S(T) = (1 - y_S \frac{T}{T_{NI}})^{z_S}, \quad (7)$$

$$\sigma_1(T) = (1 - y_\sigma \frac{T}{T_{NI}})^{z_\sigma}, \quad (8)$$

and

$$\tau_1(T) = \left(1 + x \frac{T}{T_{NI}} \right) \left(1 - y_\tau \frac{T}{T_{NI}} \right)^{z_\tau}. \quad (9)$$

In the above equations, T_{NI} is the N-I phase transition temperature. The constant factor in Eq. (6), $\frac{eQ_i}{h}(1 - \gamma_{\infty i})$, is equal to $2.491 \times 10^{-14} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for neon and $-4.672 \times 10^{-13} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for xenon.

2. Analyses of the quadrupole splittings

The order parameters of the liquid crystal were assumed independent of the nature of the atoms dissolved, i.e., they are the same for the ²¹Ne and ¹³¹Xe samples. The analysis of the QS's proceeds in both cases in three steps as follows:

In the *nematic* phase, due to the unwinding of the helical structure, the LC director is along the external magnetic field, meaning that $\theta = 0^\circ$ and $P_2(\cos\theta) = 1$, $S(T)$ is different from zero, but $\sigma_1(T) = \tau_1(T) = 0$.

The least-squares fit of Eq. (6) to the experimental points requires in principle 4 adjustable parameters: A_i (the two terms included in A_i cannot be determined separately), B_i , y_S , and z_S . However, in practice, the y_S value was constrained to 0.998, being the mean of the values reported for a number of liquid crystals.¹⁹

In the *smectic A* phase, the director remains in the direction of the external magnetic field. Then $\theta = 0^\circ$ and $P_2(\cos\theta) = 1$, but now $\sigma_1(T)$ and $\tau_1(T)$ are different from zero. The temperature dependence of these two order parameters are modeled with functions (8) and (9). Consequently, additional adjustable parameters are needed.

In the *smectic C** phase, the temperature dependence of the tilt angle θ was modeled by the function,²⁰

$$\theta(T) = \theta_o (1 - \frac{T}{T_{C^*A}})^\beta, \quad (10)$$

where $\theta_o = 44.27^\circ$ and $\beta = 0.2602$ and T_{C^*A} and T_{C^*A} is the SmC* - SmA phase transition temperature. The θ_o and β values were obtained by fitting the experimental results provided by Hoechst to Eq. (10).²¹

As mentioned above, the electric quadrupole moment of ¹³¹Xe is negative while that of ²¹Ne is positive. This means that the sign of the QSs is opposite provided that the nuclei experience similar EFG. However, because experiments do not reveal the sign, least-squares fits are based on the use of the absolute values of the QSs. Table I lists the EFG contributions, while the temperature dependence of the total EFG is shown in Fig. 4. Table II shows the parameters related to the temperature dependence of the order parameters.

B. Composition of FELIX-R&D

As stated above, all that is revealed by the manufacturer about FELIX-R&D is that it is a mixture of phenyl pyrimidines (see Fig. 5) and that it exists in three liquid-crystalline phases (see Sec. II). Other macroscopic properties reported are spontaneous polarization of 4.4 nC/cm^2 , optical anisotropy of 0.15, and pitch length of $>40 \text{ }\mu\text{m}$ in the chiral nematic phase.¹⁴

TABLE I. Electric field gradient factors A_i and B_i (in the units of 10^{18} V m^{-2}) in the liquid-crystalline phases of FELIX-R&D determined from the quadrupole splittings obtained from the ^{131}Xe and ^{21}Ne NMR spectra. The signs of the given factors depend on the sign of the quadrupole splittings. The analyses, however, reveal only the relative signs.

Nucleus i	Phase	A_i	B_i
^{131}Xe	Nematic	∓ 32.6	± 35.6
	Smectic A	∓ 55.0	± 58.8
	Smectic C*	∓ 8.0	± 10.2
^{21}Ne	Nematic	∓ 39.2	± 42.8
	Smectic A	∓ 30.7	± 34.2
	Smectic C*	∓ 1.1	± 3.5

There are three questions which need to be answered: (1) how many components are there in the mixture, (2) what are the lengths of the alkyl chains of the components in the mixture, i.e., what are the values of n and m , and (3) what is the chiral dopant. Key factors for finding answers to these questions are ^1H , 1D TOCSY, $^{13}\text{C}\{-^1\text{H}\}$, and ^{19}F NMR spectra.

(a)

(b)

FIG. 4. Absolute value of the total electric field gradient in the FELIX-R&D liquid crystal as a function of temperature determined from the analysis of the ^{21}Ne and ^{131}Xe quadrupole splittings. (a) $A_i + B_i \frac{T}{T_{NI}} = \text{EFG1}$ and (b) $\left| (A_i + B_i \frac{T}{T_{NI}}) [S(T) + 2c\sigma_1(T)\tau_1(T)] \right| = \text{EFG2}$. One should note that the phase transition temperatures are slightly shifted because of different amounts of gases.

TABLE II. Values of the parameters describing temperature dependence of the order parameters, $S(T)$, $\sigma_1(T)$, and $\tau_1(T)$. The given values are the same for ^{21}Ne and ^{131}Xe quadrupole splittings.

$S(T)$	$y_S = 0.998$	$z_S = 0.200$	
$\sigma_1(T)$	$y_\sigma = 0.998$	$z_\sigma = 0.098$	
$\tau_1(T)$	$y_\tau = 0.998$	$z_\tau = 0.112$	$x = 0.15$
c	-0.071		

The ChemAdder program¹⁵ plays a leading role in the quantitation of the components, i.e., in the determination of the number of components and the values of n and m . Here we display only the results of the analyses of the total ^1H spectra and 1D TOCSY spectra. Other information can be found in the [supplementary material](#).

In order to estimate the phenyl pyrimidine component ratio and the chain lengths in them, we analyzed the standard proton and 1D TOCSY spectra using quantum mechanical spectral analysis (QMSA).²² The analyses were performed with the ChemAdder/SpinAdder software,¹⁵ which was tuned for the present purposes. Without any approximations, a $(\text{CH}_2)_m\text{CH}_3$ -chain ($m = 7\text{--}9$) spin-system yields even millions of non-degenerate, non-zero intensity transitions which can be, however, packed into ca. 100 000 lines without a significant bias. The number of transitions can be greatly decreased, and the simulation can be speeded by calculation of the spin-system in parts, too. The simulation of one iteration cycle for the spin-system formed by the four (see below) chains demands ca. 25 s in a standard personal computer. The time depends much on how the spin-system is decomposed into parts. Because the extensive overlap of the 17 CH_2 -signals at around 1.3 ppm, not all the coupling constants are accurately analyzable from the spectra and there are also uncertainties in the chemical shift orders. That is why we set all the $J_{AA'}$, J_{AB} , and $J_{AB'}$ couplings (see the [supplementary material](#)) the same for the resonances in the range of 1.2–1.4 ppm, and the geminal couplings were fixed to those of heptane (-13.2 Hz).²³ The analysis of the Ph (Aryl)- $(\text{CH}_2)_n\text{CH}_3$ (with $n = 7$) 1D TOCSY spectrum yielded the chemical shifts and also some couplings with a fair confidence, which were then applied to the analysis of the total ^1H spectrum. The TOCSY analysis was performed in the normal way, except that the response factors of the CH_2 and CH_3 protons were allowed to decay from 1.0 to 0.26 in the methyl protons. The special shapes of the observed-difference spectra (at both ends of the spin-system) may arise from the TOCSY experiment. The best agreement between experimental and simulated spectra is obtained with the following composition of FELIX-R&D (note: $n = 7$ in each case):

$$\begin{aligned} m = 5, & \quad 39.30 \text{ mol. \%} \\ m = 7, & \quad 43.76 \text{ mol. \%} \\ m = 9, & \quad 19.94 \text{ mol. \%} \end{aligned}$$

FIG. 5. FELIX-R&D is a mixture of phenyl pyrimidines.

FIG. 6. Composition of FELIX-R&D.

The amount of the chiral dopant was estimated as explained in the [supplementary material](#). This results in the concentration of 5.6 mol. %.

Thus we conclude that FELIX-R&D is composed of three phenyl pyrimidines and a chiral component, as shown in Fig. 6.

IV. DISCUSSION

The analyses of the EFGs are based on the absolute values of the experimentally observed QSs, as mentioned above. The least-squares fits of the function (6) to the experimental points give, however, the relative signs of the adjustable factors A_i and B_i . Lounila and Diehl²⁴ considered the external EFG contribution and indicated that at a certain approximation it depends on the size of a cavity accommodated by a molecule or an atom. The van der Waals radii of ^{21}Ne and ^{131}Xe are 1.54, and 2.16 Å, respectively.^{25,26} If we assume that the size of the cavity is proportional to the size of a probe atom/molecule, the *external* EFG should be 2–3 times larger for ^{21}Ne than for ^{131}Xe . However, experiments do not reveal such a big difference, except at the lowest temperatures in the SmC^* phase. An earlier investigation of the total EFG in the thermotropic nematic Merck ZLI1167 liquid crystal using ^{21}Ne , ^{83}Kr , and ^{131}Xe NMR spectroscopy indicated that the magnitude of the EFG decreases in the order $\text{EFG}(^{21}\text{Ne}) > \text{EFG}(^{83}\text{Kr}) > \text{EFG}(^{131}\text{Xe})$ which is the inverse order of the van der Waals radii.⁸ Obviously the deformation of the electron cloud of xenon plays a remarkable role. An illustrative example about this is the observation of a large ^{131}Xe QS in a nematic liquid crystal mixture in which the external EFG was supposed to be small.^{7,27} Another indication of the deformational contribution is the transformation of the ^{129}Xe shielding tensor from spherical symmetry to cylindrical symmetry when moving from the isotropic phase to a liquid-crystalline phase.

The analyses of the composition and the structure of the molecules which form the FELIX-R&D liquid crystal are, in principle, rather straightforward using multinuclear NMR spectroscopy. In practice, however, this is not the case. The constituent molecules, phenyl pyrimidines with long alkyl chains, form large spin systems, whose computation requires a special tool, in the present case ChemAdder/SpinAdder program. For example, the four subsystems used in the computations (see the [supplementary material](#)) produce over 30 000 000 transitions with nonzero intensity. The ^1H spectral region of ca. 18 Hz due to methyl protons consists of 593 nondegenerate lines.

V. CONCLUSIONS

The goal of the present study was twofold: (1) determination of the electric field gradients as a function of temperature in the various liquid-crystalline phases of FELIX-R&D and (2) determination of the structure of the molecules and their concentration in the mixture which forms the FELIX-R&D liquid crystal. The item 1 was attacked using the quadrupole noble gas nuclei, ^{21}Ne and ^{131}Xe . Their NMR spectra recorded in liquid-crystalline solutions display quadrupole splittings which reveal electric field gradients. It is shown that the two nuclei experience different EFGs in ferroelectric liquid crystal FELIX-R&D, the reasons being their different sizes and the deformation of the electron cloud of xenon. It can be concluded that ^{21}Ne , for which the electron cloud deformation does not contribute significantly, is a good probe to detect electric field gradients in the various phases of liquid crystals. One should emphasize that the EFG was obtained for the first time also in the smectic C^* phase using NMR spectroscopy of quadrupolar noble gases. The second item was successfully completed with the aid of the ChemAdder/SpinAdder program.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the application of various NMR methods together with the quantum mechanical spectral analysis (QMSA) is described for the determination of the composition of the ferroelectric liquid crystals FELIX-R&D.

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