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## Probing phase transitions in a soft matter system using a single spin quantum sensor

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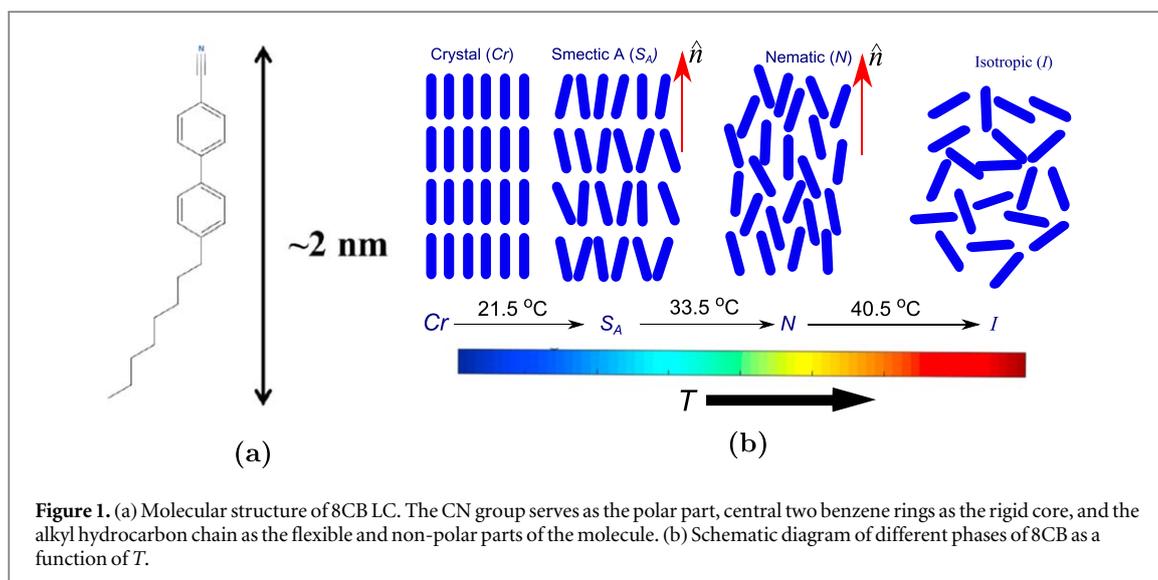
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Phase transitions in soft matter systems reveal some of the interesting structural phenomena at the levels of individual entities constituting those systems. The relevant energy scales in soft matter systems are comparable to thermal energy ( $k_B T \sim 10^{-21}$  J). This permits one to observe interesting structural dynamics even at ambient conditions. However, at the nanoscale most experimental probes currently being used to study these systems have been either plagued by low sensitivity or are invasive at molecular scales. Nitrogen-vacancy (NV) centers in diamond is emerging as a robust quantum probe for precision metrology of physical quantities (e.g. magnetic field, electric field, temperature, and stress). Here, we demonstrate by using NV sensors to probe spin-fluctuations and temperature simultaneously to obtain information about controlled phase changes in a soft matter material as a function of temperature. The soft matter system chosen for the study is a standard liquid crystalline (LC) material which shows distinct phases close to room temperature. Individual NV centers at depths of a few nm are used as a probe to detect magnetic signals emanating from a few molecular layers of sample on the surface of the diamond. The organization and collective dynamics of LC molecules in nanoscopic volumes are discussed. Our study aims to extend the areas of application of quantum sensing using NV centers to probe the soft matter systems, particularly those exhibiting mesophases and interesting interfacial properties.

**Introduction**

Some of the fascinating aspects of nature are manifested when the states of matter undergo phase transitions. Understanding the micro- and nanoscopic origins of macroscopic (bulk) phase transitions has profound impact in studying superconductivity, magnetic ordering, topological materials, ferroelectricity, superfluidity, rigidity, and fluidity of biological cell membranes etc [1–4]. In all these systems the phase transitions are often characterized by complex behaviors such as discontinuities or fluctuations in the order parameters which have their origin in the interactions between individual entities and their collective behavior at the micro or nanoscale. Soft matter systems are ubiquitous and exist as polymers, liquid crystals, gels, emulsions, colloids, surfactant self-assemblies, granular materials, and many biological materials [5]. Among them liquid crystals, owing to shape anisotropy of the constituent molecules exhibit ordering similar to crystalline solids, while still being able to flow like ordinary liquids [6]. They are used as simple model systems to understand more complex phenomena in condensed matter [5, 7], self assembly of molecules in life sciences [8, 9], and even in cosmology [10, 11]. While the bulk properties of liquid crystalline (LC) are well known, at the nanoscale however it remains a major challenge to non-invasively study structure and dynamics, nature of molecular ordering, and other properties which could be markedly distinct from their bulk counterparts.



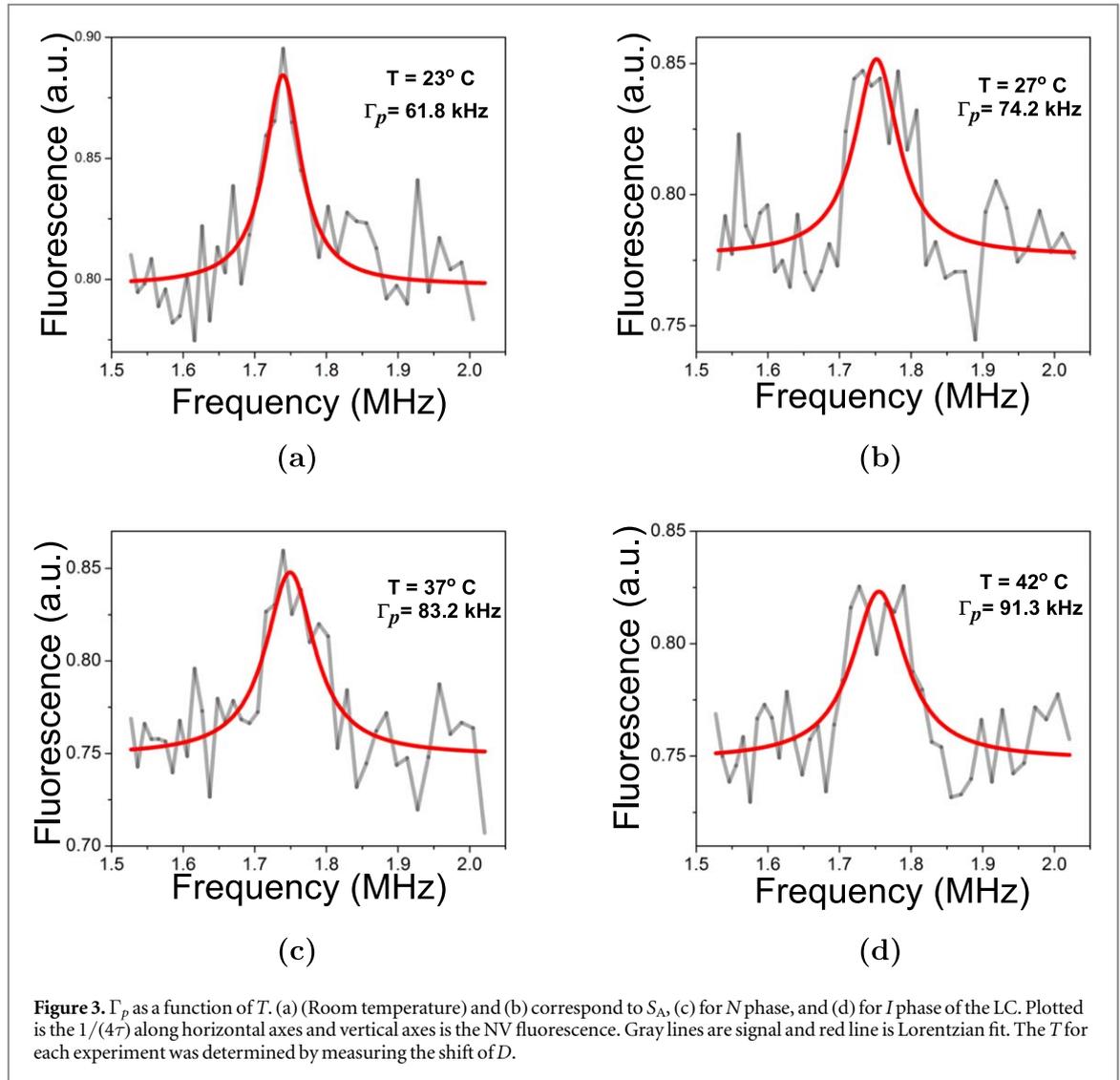
Nuclear magnetic resonance (NMR) spectroscopy, although being routinely used as a major analytical tool in several areas (including LC [12]), its extension to explore nanoscopic volumes is hindered due to large ( $>10^{15}$ ) number of spins required to generate the signal. In the recent years NV centers have been shown to be capable of obtaining NMR signal from  $\approx 10^3$  spins in nanoscopic volumes at ambient conditions [13, 14]. Besides, they are also capable of measuring temperature ( $T$ ) with  $\sim$ mK resolutions [15]. Therefore, NV sensors offer a unique advantage of probing soft matter systems at the nanoscale to precise changes in temperatures. Here, we employ NV based NMR noise spectroscopy scheme to detect phase transitions in a LC material as it undergoes transition from more ordered phase close to room temperature to disordered phases at higher temperatures. The NV center measures the NMR signals from statistically polarized proton spins from the sample volume of  $\approx (5 \text{ nm})^3$  above the diamond surface. Changes in the LC properties in this nanoscopic volume as a function of temperature imprint distinct signatures in the NMR spin-noise signals measured by the NV and this is used to infer the phase changes.

## Materials and methods

The liquid crystal we use is 4-n-octyl-4'-cyanobiphenyl ( $\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CN}$ ; molecular weight 291.43) commonly known as 8CB. It was commercially obtained from Sigma Aldrich and was used as received. The 8CB molecule has a length of about 2 nm [16] and its structure is shown in figure 1(a). 8CB LC offers a simple model system for understanding phase transitions in two dimensions [17]. There are several advantages of using 8CB as a model system. Mainly, as a standard soft matter system it offers access to study different phases close room temperature. Owing to the strong electric dipole moment (6D) of the molecules [18] they readily adsorb to hydrophilic surfaces, including diamond. The phase transition of 8CB in bulk [17] is depicted in the figure 1(b) along with the molecular ordering in various phases on an increasing temperature scale. In the crystalline ( $Cr$ ) state the molecules show long range positional and orientational order. The  $Cr$  state melts to a first LC phase known as smectic-A ( $S_A$ ) at  $T = 21.5^\circ\text{C}$ . In  $S_A$  phase the molecules are stacked into layers and in each layer the average molecular orientation is along the layer normal. This preferred direction of orientation is called as the director (denoted by a unit vector  $\hat{n}$ ) [6]. There exists no positional order within the layers and thus they behave like liquids. The  $S_A$  undergoes a transition to less ordered LC phase known as nematic ( $N$ ) at  $33.5^\circ\text{C}$ . In  $N$ , the molecules possess only an orientational order along  $\hat{n}$ . Here, the molecules flow like liquids while maintaining orientation along their long molecular axes. Upon further increase in temperature ( $T$ ), the  $N$  phase melts to isotropic liquid phase ( $I$ ) at  $40.5^\circ\text{C}$  (also known as the clearing temperature,  $T_c$ ). The  $I$  phase, which, just like ordinary liquids, possesses no order and the molecules can flow and orient randomly in all directions.

A CVD synthesized diamond with a dimension of  $2 \text{ mm} \times 2 \text{ mm} \times 100 \mu\text{m}$  containing shallow implanted NV centers was used. The NV centers were created by implantation of  $^{15}\text{N}$  ions with an energy of 2.5 keV and subsequent annealing. Based on SRIM simulation, the NV centers are estimated to be around  $d = 5 \text{ nm}$  below the surface. Prior to use, the sample was cleaned in a boiling solution of three acids ( $\text{HNO}_3 + \text{H}_2\text{SO}_4 + \text{HClO}_4$ ) for several hours. This acid treatment, apart from removing any residual impurities (organic contaminants and graphitic carbon) on the diamond surface, makes it oxygen terminated [19] and hence hydrophilic [20].





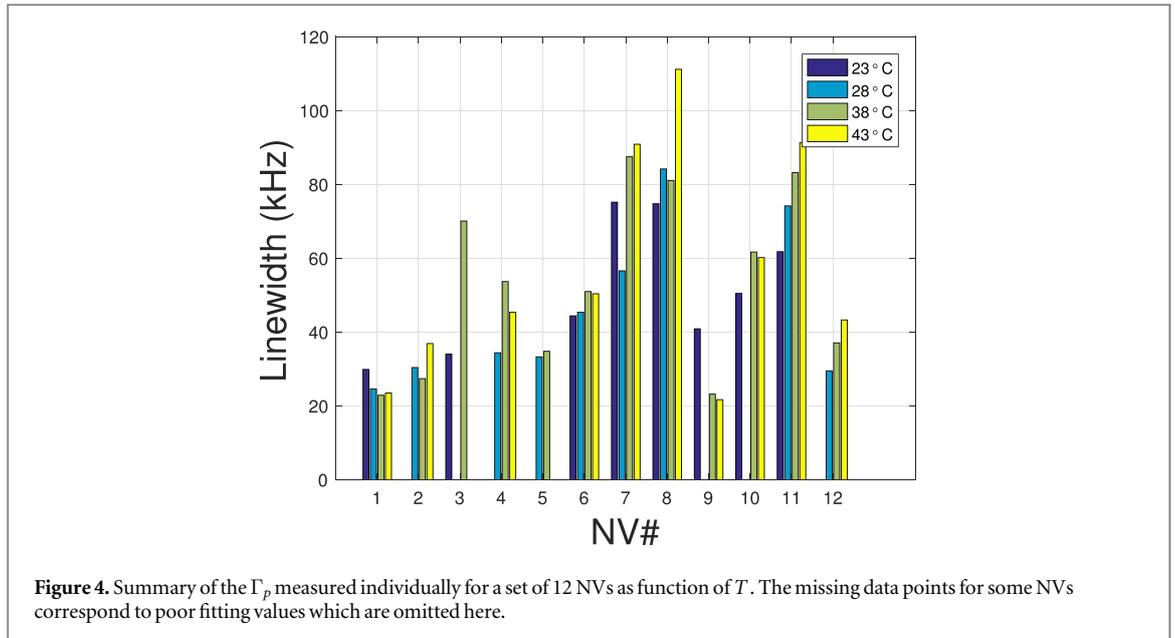
## Results

The nano-NMR method studied here is based on the  $(XY8)^n$  dynamical decoupling protocol to selectively tune the NV response to Larmor frequency of the proton spins in a given  $|B|$  in the sample, while decoupling the NV from rest of the noise frequencies [13].

A schematic of the XY8 pulse sequence and resulting proton spectrum is shown in figures 2(b) and (c), respectively. For spin manipulation we used  $m_s = 0 \leftrightarrow m_s = -1$  spin manifold in its ground state. First, a laser pulse prepares the NV spin in its  $m_s = 0$  sublevel. A MW  $\pi/2$  pulse then places the NV spin in a coherent superposition of its  $m_s = 0$  and  $-1$  sublevels. A train of alternate ( $x$  and  $y$ ) MW  $\pi$ -pulses separated by time  $2\tau$  are then applied to the NV center. Each block consisting of  $8 \pi$ -pulses are repeated  $n$  times to generate a total of  $8 \times n \pi$ -pulses. The NV spin acquires a net phase during the total interval and this phase is converted into population difference using a second  $\pi/2$  pulse. The spin state dependent contrast is finally readout by another laser pulse at the end. By sweeping the  $2\tau$  the entire spectrum of the spin noise in the NV surrounding can be recorded. The spectrum shows a Lorentzian centered at  $1/(4\tau) = f_L$ , the proton Larmor frequency given by  $\gamma_H |B|$  (where,  $\gamma_H$  is proton Gyromagnetic ratio).

Figure 3 shows the results of  $(XY8)^{64}$  proton sensing experiment in various LC phases for one NV. The four  $T$  values correspond to three different phases of the LC material: 23 °C and 27 °C for  $S_A$ , 37 °C for  $N$  and 42 °C for  $I$  phase. The temperature  $T$  values in each case were estimated by performing ODMR and measuring the shift of zero-field-splitting ( $D$ ).

A constant  $|B|$  of  $\sim 410$  G gave a peak in the signal at  $f_L \sim 1.745$  MHz. The full-width at half-maximum of the fitted curve gives the linewidth ( $\Gamma_p$ ) of the proton signal and its value in different phases indicates the local dynamics of the LC molecules in the vicinity of the NV center. Starting from an initial room temperature value of 23 °C,  $\Gamma_p$  shows clear increase and reaches a maximum in the  $I$  phase. For 23 °C and 27 °C (corresponding to



$S_A$ ), the  $\Gamma_p$  values obtained were  $61.8 \pm 14$  kHz to  $74.2 \pm 21$  kHz, respectively. These two different values for the same phase possibly arise because, as  $23^\circ$  is close to the bulk  $Cr \rightarrow S_A$  phase transition point ( $\sim 22^\circ\text{C}$ ), the complete melting of the material may not yet have happened and thus it may be still exhibiting the properties  $Cr$  phase. The  $\Gamma_p$  increases to  $83.2 \pm 20$  kHz for the  $N$  phase and a maximum value of  $91.3 \pm 24$  kHz for  $I$  phase.

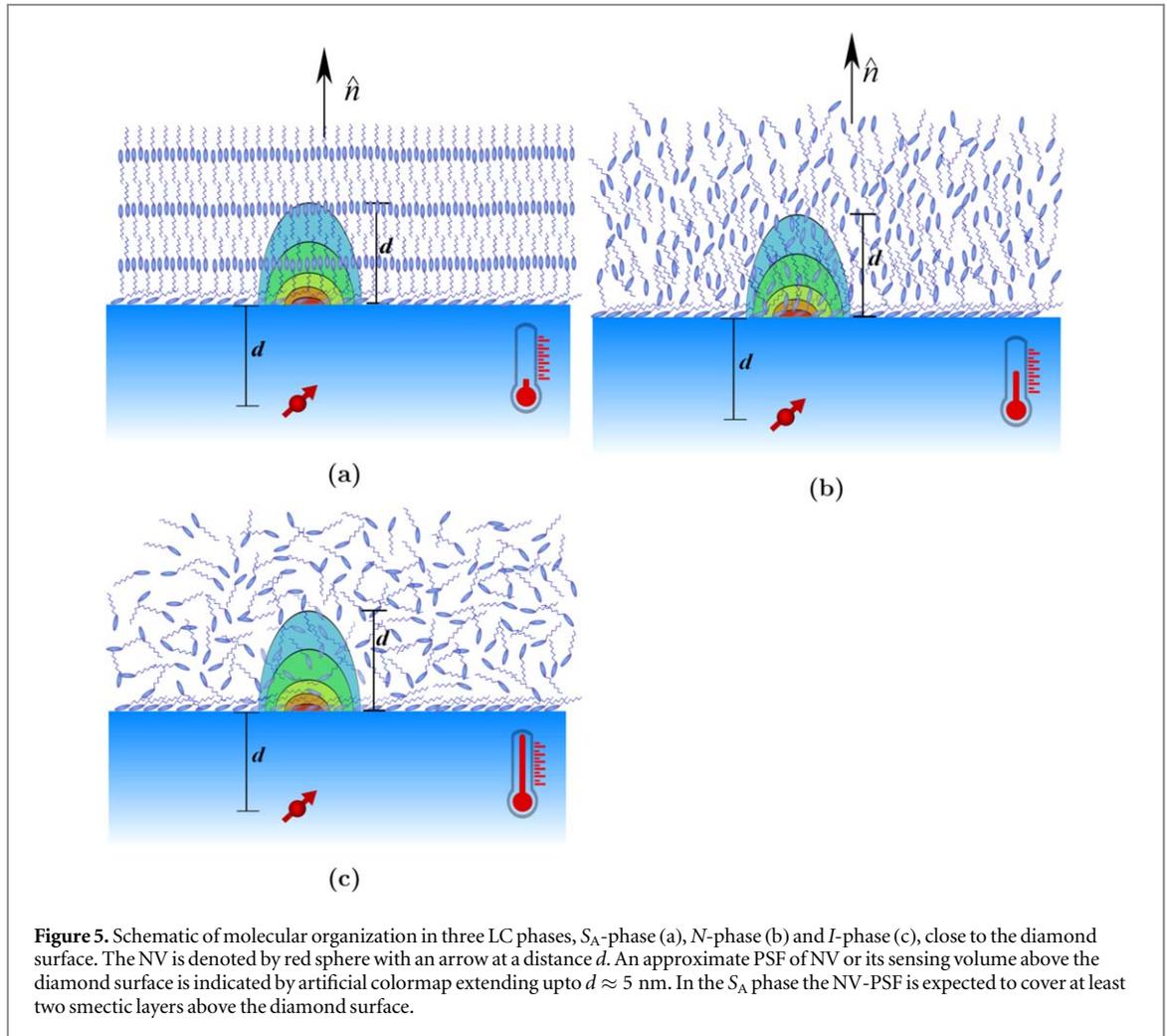
In order to see the general trend in the variation of  $\Gamma_p$  versus temperature ( $T$ ), the experiment was repeated for a total of 12 NVs. For all the experiments the  $|B|$  was kept constant around 400 G. The summary of results obtained is shown in the figure 4. For each NV the  $\Gamma_p$  obtained from the  $(XY8)^n$  experiment at four different temperatures are plotted. Note that the order ( $n$ ) of XY8 sequence for each individual NV is chosen according to its total  $T_2$  time (see *supplementary information* for  $n$  used for all NVs). But, for a given NV the  $n$  was fixed for all the four  $T$ . Longer  $T_2$  enables the higher  $n$  and hence sharper  $\Gamma_p$  at the cost of longer interrogation time. In figure 2(d) the  $f_L$  for different values of  $|B|$  are plotted and the slope ( $4.25$  kHz/G  $\approx \gamma_H$ ) of which confirms that the measured signal is coming from the proton spins in the sample.

## Discussion

The results mentioned here indicate that as LC undergoes phase transition to more liquid-like phases, the  $\Gamma_p$  increases. The results are qualitatively in agreement with the reported studies on NV based sensing of nanoscopic volumes of other systems where the line broadening was observed for more fluidic samples [21, 22].

To understand the mechanisms behind the observed changes in  $\Gamma_p$  as a function of temperature, a possible organization of LC molecules on the diamond surface is schematically drawn in figure 5. Essentially, we propose that hydrophilic nature of the diamond surface renders the same type of organization of 8CB molecules as in case of other hydrophilic surfaces such as water [17], silicon [23] or glass [24] containing thin films of 8CB on top. Essentially, the hydrophilic (polar) head groups of the molecules get anchored to the surface while the hydrophobic alkyl chains point away from it. Based on the reports in the literature there exists a prewetting monolayer [16, 25] next to the diamond surface and is tilted [17, 18]. This monolayer is assumed to be immobile for the range of temperature studied here. In the  $S_A$ , stacks of interdigitated bilayers of molecules exist on top the first monolayer [17] and constitute the layered ordering of  $S_A$  (figure 5(a)). In the  $N$ , these layers melt and molecules on average orient along the diamond surface normal (taken as  $\hat{n}$ ) (figure 5(b)). Finally, in the  $I$  phase this preferred orientation disappears and molecules are free to move randomly in all directions (figure 5(c)).

A NV center close to the surface can sense spins within its point spread function extending to distances of  $d$  (approximately equal to its depth within the diamond) [13, 14, 21, 26, 27]. This corresponds to an effective sensing volume of  $\sim(d)^3$ . As the NV centers in our case are located at about 5 nm below the surface, the sensing volume is thus about  $(5 \text{ nm})^3$ . Since an 8CB molecule has a length of  $\sim 2$  nm, in the  $S_A$  for example, the NV sensing distance extends to at least a couple of layers above the surface (figure 5(a)). It should also be noted that as our NV sensing area extends beyond the immobile monolayer (in figure 5), the sensor's overall response is mainly dictated by the dynamics of the molecules outside this monolayer. The in-plane or lateral resolving



**Figure 5.** Schematic of molecular organization in three LC phases,  $S_A$ -phase (a),  $N$ -phase (b) and  $I$ -phase (c), close to the diamond surface. The NV is denoted by red sphere with an arrow at a distance  $d$ . An approximate PSF of NV or its sensing volume above the diamond surface is indicated by artificial colormap extending upto  $d \approx 5$  nm. In the  $S_A$  phase the NV-PSF is expected to cover at least two smectic layers above the diamond surface.

power [26] in the present case is about 3.2 nm along one direction and  $\sim 5$  nm in the perpendicular direction. This is primarily governed by the depth of the NV center below the surface.

The observable  $\Gamma_p$  is related to total phase acquisition time ( $\tau$ ) as [27, 28]

$$\Gamma_p = \frac{2}{\gamma_H |B|} \cdot \frac{1}{\tau}, \quad (1)$$

where

$$\frac{1}{\tau} = \frac{1}{T_D} + \frac{1}{T_{2p}^*} + \frac{1}{T_1^{\text{NV}}}$$

with  $T_D$ -diffusion time scale of 8CB proton spins in the nanoscopic volume,  $T_{2p}^*$ -inhomogeneous dephasing time of proton spins in 8CB and  $T_1^{\text{NV}}$  is  $T_1$  time of sensing NV.

As the NV-NMR relies on measuring the spin noise from statistically polarized sample spins, fast translational diffusion of molecules in and out of the detection volumes changes the distribution of these polarized spins. This results in the randomization of polarization on fast time scale causing the broadening of  $\Gamma_p$  [21, 22, 27, 28]. This effect is more pronounced when the material is in liquid phase and termed as ‘diffusional broadening’ in contrast to ‘motional narrowing’ in bulk NMR. Similar effects play a role in the LC experiments mentioned here. In the  $S_A$  due to the orientational and quasi-positional order the molecules spend longer times ( $T_D$ ) within the NV-sensing volume. Hence the magnetization due to statistically polarized proton spins results in a narrower  $\Gamma_p$ . Further, as the  $T$  is raised, increased mobility (shorter  $T_D$ ) of the molecules contribute to broadening of  $\Gamma_p$  in  $N$  and  $I$  phases.

$T_D$  is inversely proportional to average diffusion constant  $D_{\text{avg}}$  of the LC molecules and previous NMR measurements on bulk 8CB have reported that in going from  $S_A$  to  $I$  phase the  $D_{\text{avg}}$  doubles [29]. As the recent studies on NV-NMR of other organic systems have indicated that NV can be sensitive to the doubling of diffusion constant [21], we expect that the LC phase transition studied here is indeed detectable with our method.

Although there is an overall increasing trend of  $\Gamma_p$  with  $T$ , for some NVs (e.g. NV1, NV2, and NV6,) the  $\Gamma_p$  changes were small or remained almost constant while some (NV4 and NV7) showed fluctuations in  $\Gamma_p$ . Generally the solid–liquid interfacial boundaries are quite complex [30] and in some cases the solids induce order in the liquids in contact with them [31]. In the literature it is reported that for LC on solid the solid surface induces smectic-like ordering close to it and this is even independent of  $T$  [16, 32]. However, the range of such ordering depends critically on the surface preparations [33] and strength of solid-LC interactions. We are not sure if such effects really played any role in our case causing the  $\Gamma_p$  to remain almost constant as the  $T$  was changed.

Studying electric field and charge effects could give rich understanding of liquid crystal behavior at the nanoscale and effects of surfaces. Single NV spin is an excellent quantum sensor, we can also measure the presence of charges, and electric fields etc. The LC surfaces are known to contain an electrostatic double layer which extends over the Debye screening length [34]. This screening length is reported to be about 100 nm in cyanobiphenyl based compounds [35]. Our experiments are designed to probe the magnetic signals emanating from the spins in the sample. At a typical value of  $|B| \sim 400$  G used in our experiments, in the NV Hamiltonian the electron Zeeman term dominates the transverse term  $E$  resulting from any electric field due to charges on the diamond surface. However, if the measurements are done close to zero  $|B|$  then the effects of  $E$  cannot be ignored and the presence of surface charges could be detected by the NV. Furthermore, in our measurements the proton Larmor frequency was set to  $\sim 2$  MHz. But, the Debye layer's charge relaxation rate in LC is typically in the range of kHz [36]. Therefore, due to this wide mismatch of frequencies, the dynamical decoupling method used in our experiment filters out the charge relaxation frequency components slower than MHz. If the double layer electric field induces an order close to the surface such an order could be probed using depth-calibrated shallow NV centers [37]. In such a sample, a relatively shallower NV senses only a small volume, perhaps only the nematic layer, and hence shows a constant signal linewidth over the temperature range. On the other hand a relatively deeper NV detects the larger volume and changes in the linewidth can be observed. In addition, any effects of surface charges on the transition temperature could also be probed using NV-based method. In bulk LC systems, the transition temperature ( $N - I$ ) is reported to vary about  $1^\circ\text{C}$  in the presence of double layer due to charges at the interface [38]. Since NV centers are capable of resolving milli-Kelvin temperature shifts, surface-charge induced variation in transition temperatures by  $1^\circ\text{C}$  is indeed detectable.

Here, the measured  $\Gamma_p$  of spin noise spectra was limited by the NV  $T_2$  times. By employing correlation based methods [21] one can obtain improved  $\Gamma_p$  as the interrogation time is limited by long lived NV  $T_1$  values and hence the better  $\Gamma_p$ . XY correlation experiment results on NV10 showed  $\Gamma_p$  values of 10.2, 7.9 and 9.3 kHz for  $S_A$ ,  $N$  and  $I$  phase, respectively. While the  $\Gamma_p$  for this NV has clearly improved compared to simple XY method (from  $\sim 60$  to  $\sim 10$  kHz), the changes are not clear. For example from  $S_A$  to  $N$  the value decreased and from  $N$  to  $I$  phase it shows small increase.

Finally, the amount of changes in  $\Gamma_p$  depends on the relaxation rate  $(T_1^{\text{LC}})^{-1}$  of the sample spins [39] across phase transitions. 8CB is known to exhibit an order of magnitude larger  $(T_1^{\text{LC}})^{-1}$  across phase transitions when the Larmor frequency  $f_L$  is in kHz regime than in MHz regime [40]. Thus, one way to more clearly observe the phase transitions in the present system under study is to perform experiments at low  $f_L$  (i.e.  $|B| \sim 25$  G or less) and at the limit of NV interrogation time  $(T_1^{\text{NV}})$ . In addition, using more deeper NV centers (tens of nm) below the surface would not only make the signal narrower (because  $T_D \propto \frac{d^2}{2D_c}$ ,  $D_c$ -diffusion constant) but also help probe larger sample volumes [27], possibly at correlation length scales of LC systems. This however, comes at a cost of lower sensitivities, hence polarizing the spins in LC molecules and subsequently reading the spin signals could provide a way to monitor large length scales.

NV based sensing could potentially be used to address some fundamental problems in LC. One of the long standing questions in two dimensional LC systems is the nature of  $I$  to  $N$  phase transitions. It is proposed to be first order, second order or even a Kosterlitz–Thouless type of continuous order [2, 41, 42]. But experimental confirmation of exact nature of this transition is not yet achieved, mainly due to lack of proper probes to access the information. Also, dynamics of defects in LC is suggested to be similar to those of defects that appear in very large length scales in other systems such as cosmic strings [10], for example. There is still a dearth of suitable experimental tools that can be used to study defects kinetics over a wide length scale—from individual molecules to their collective self-assemblies. Perhaps, by combining single NV based methods with ensemble NV based schemes one can bridge the gap between this wide length scale. Furthermore, NV based Nano-NMR methods could also be employed to study wetting and other interfacial phenomena in general. Particularly the finer details about molecular interactions at the solid(diamond)-liquid boundaries could be discerned non-invasively through the recently developed NV based nano-NMR methods with high spectral resolution [43–45]. The ultralong interrogation time scales offered by these methods could also enable observing the subtle molecular signatures like chemical shifts and J-coupling in ultra low sample volumes. In soft matter systems temperature plays a decisive role in determining their properties. Thus NV centers offer combined advantages of highly

sensitive magnetic and thermal field detection with nanoscale spatial resolution for studying interesting phenomena in such systems.

## Conclusions

A nano-NMR study of phase transitions in a standard room temperature LC material using atom sized sensor has been presented. Extending the NMR to nanoscale in LC could potentially allow us to access information on the molecular ordering of these systems at such length scales. Performing NV-NMR on LC at low magnetic fields and with relatively deeper NVs could help us observe the phase transitions more distinctly. The NV based non-invasive sensing method presented here provides a convenient tool to address some essential problems in surface science and soft condensed matter in general.

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