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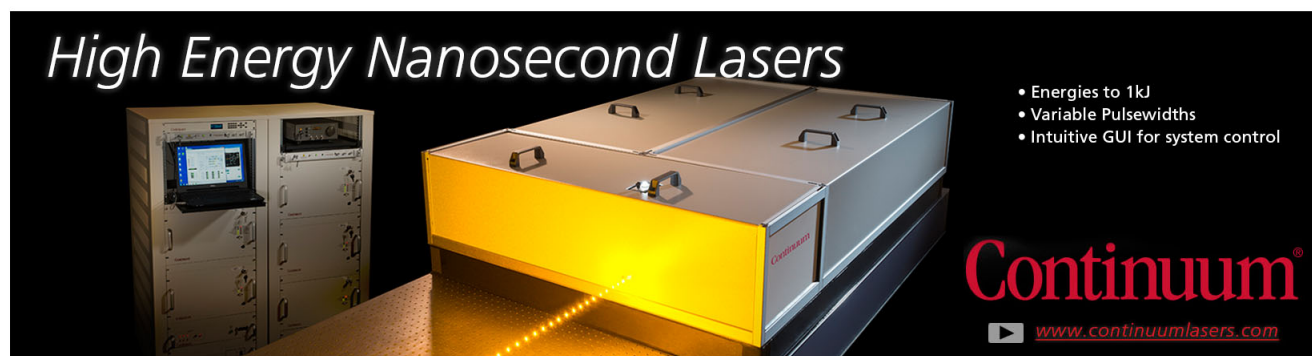
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## Nanoparticles induced multiferroicity in liquid crystal

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Soft multiferroic character has been observed in a ferroelectric liquid crystal (FLC) dispersed with nickel nanoparticles (Ni NPs). A suitable amount of ferromagnetic Ni NPs has been added into FLC material, and the co-existence of ferroelectric and ferromagnetic ordering is examined using P-E and M-H hysteresis measurements. The magnitude of ferromagnetic order is found to depend strongly on the concentration of Ni NPs. Our theoretical approach indicated a strong dependence of helical pitch of FLC on the doping concentration of Ni NPs. We proposed that the intrinsic magnetic field of Ni NPs has been coupled with that of director field of the FLC molecules to result in the observed multiferroic behavior. *Published by AIP Publishing.*

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Recently, much attention of the researchers has been on the effective utilization of various aspects of nanotechnology to manipulate/modify the electro-optical properties of liquid crystal (LC) materials.<sup>1</sup> Different kinds of nano-materials, including metallic, insulating, semiconductors, carbon based nanostructures, have been emerged as the best additives to LC materials to evolve striking features in the latter.<sup>2-8</sup> Not only the characteristics of nano-materials have been exploited to tailor the technological features of LC materials, but at the same time, the anisotropic character of the latter is utilized in imparting the order in the former.<sup>9</sup> Moreover, with the fact that most of the nanoparticles (NPs) preferably align along the director field of LCs, the investigation on the coupling between the magnetic moments of magnetic NPs and that of LC molecules is of great interest. Further, the LC materials with ferroelectric ordering, i.e., ferroelectric liquid crystals (FLCs), may be put on priority for the possible coupling between ferroelectric and ferromagnetic order to result into a composite enriched with soft multiferroicity.<sup>10,11</sup>

The investigation on the magnetization behavior of magnetic NPs shows that the magnetic NPs are always magnetized to a single domain as the formation of the flux closure configuration is energetically unfavourable.<sup>12</sup> The high value (few hundreds of Gauss) of coercive fields for such NPs is the manifestation of the fact that the magnetization reversal within the particle is not possible. The magnetic energy of these NPs has been found to depend on their size, and for a particle with diameter  $d$ , it is equal to  $M_s^2 d^3$  (where  $M_s$  is the spontaneous magnetization). These NPs are known to exhibit super-paramagnetism. The magnetic NPs strongly interact with the dipole moment of the FLC molecules, and this interaction causes the NPs to align along the LC director.<sup>13</sup> It is worth to mention that the free energy expansion (discussed later) of SmC\* consists of two order parameters: the primary order parameter is a two component tilt vector which gives the orientation of molecules with the layer plane and the secondary order parameter is the two component polarization

vector. The researchers have already probed indirectly that the orientation of magnetic nanoparticles is directly coupled to the LC director field.<sup>10,11</sup> When the magnetic NPs are included into SmC\* phase of LC, it is expected that the magnetization direction of NPs aligns along the direction of principal order parameter of the smectogen. On the basis of the crystal symmetry of the SmC\* phase, the existence of ferromagnetic LCs was proposed by Buivydas.<sup>14</sup> Spontaneous polarization and magnetization may appear in chiral smectics. Such a possibility of inducing ferromagnetic order in FLC materials has opened up a technologically exciting research field of soft multiferroic. Multiferroic materials exhibit simultaneous ferroelectric and ferromagnetic order and have promising technological relevance and fundamental scientific challenges.<sup>15,16</sup> The simultaneous magnetic and electric order made it possible to address magnetization/polarization of the material by means of magnetic and electric or both the fields.

The LC sample cells were prepared using highly conducting indium tin oxide (ITO) coated glass plates. Photolithography technique is employed to achieve the desired (squared) electrode pattern ( $0.45 \times 0.45 \text{ cm}^2$ ) of ITO on the glass plates. For the treated sample cells, the rubbed polyimide technique has been employed to align pure and Ni NPs/FLC composites. For that, the cleaned ITO substrates were first spin coated with polyimide (nylon 6/6) using spin coater, baked, and then uniformly rubbed by velvet cloth. The thickness of polyimide treated sample cells was maintained by using  $6 \mu\text{m}$  thick Mylar spacers. In fabricating untreated sample cells, coating of polyimide and rubbing was not performed. The cleaned ITO coated substrates were directly used to make the sample cells. The  $20 \mu\text{m}$  thick Mylar spacers were used to obtain thicker samples. In thick samples, having thickness much greater than that of the helical pitch of the FLC material ZLI 3654 ( $\sim 3.3 \mu\text{m}$ ), the formation of complete helicoidal structure is favorable, which may be seen in the form of dechiralization lines.

The different concentrations of highly pure Ni NPs (M/s Sigma Aldrich, USA) were added to the FLC material in the

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form of suspension. The SEM analysis of the Ni NPs revealed that they are spherical in shape and their average size is 60 nm.<sup>17</sup> In a typical process to make suspension, 1 mg powder of Ni NPs was first dispersed into 1 ml volume of acetone, and the mixture was placed in ultrasonic bath for an hour. The suitable amount of this suspension is then uniformly mixed with the FLC material in steps of 1  $\mu$ l of the NPs suspension using a micropipette. To ensure uniform mixing of NPs and evaporation of the solvent, the suitable amount (10 mg in each case) of the FLC material was first placed in the oven at the temperature just above to its isotropic transition and then taken out and the suitable amount of Ni NPs suspension is mixed uniformly till the mixture cooled to room temperature. The above step was repeated 2–3 times to ensure proper mixing and solvent evaporation.

The formation of aggregates of the nanoparticles is a well known and mostly unavoidable problem of the LC based nano-composites. Further, the tendency of forming aggregates becomes significant for higher concentrations. We have taken into account this fact and analysed (by comparing the micrographs of pure and that of Ni NPs doped FLC samples) the composites using polarising optical microscope (POM).<sup>17</sup> The dark and bright states of the samples were obtained by rotating the samples (placed on sample holder fitted with POM) under the crossed polarizers. The aggregates could be identified in the dark/bright states of the sample in the form of spots.<sup>17</sup> The appearance of different colors is due to the birefringence phenomenon possessed by LCs. The birefringence color depends on the factors such as thickness of the sample cell, angle between polarizer and the LC director, wavelength of the light used, etc.

For higher concentrations of Ni NPs, the formation of small aggregates was observed under the crossed polarisers, and the alignment of composite was greatly perturbed up to a limit (>6 wt. % in our case) where we could neither able to measure the electro-optical properties nor the M-H hysteresis behavior. However, for lower concentrations of Ni NPs, agglomeration tendency was observed to be weak enough not to hinder the multiferroic behavior as well as electro-optical switching of the composites. The pure and Ni NPs doped FLC materials were filled into the sample cells by capillary action at temperatures greater than the isotropic transition temperature of ZLI 3654 ( $\sim 86^\circ\text{C}$ ). The P-E loops were measured by using a precision workstation ferroelectric tester system (Radiant Technologies) at room temperature while the M-H loops of the samples were recorded using a SQUID magnetometer (Quantum Design MPMS XL-7).

The LC molecules in a ferroelectric phase are arranged in layers with helicoidal manner in such a way that the molecular director rotates successively from layer to layer and always lies on a hypothetical cone with a cone angle  $2\theta$  (where  $\theta$  is the tilt angle).<sup>18</sup> The symmetry ( $C_2$ ) of the FLCs permits non-zero electric polarization associated with each FLC molecule perpendicular to the director. The behavior of electric polarization on the application of an external electric field may be easily obtained in the form of the P-E hysteresis loop. It has been a promising technique to analyze the ferroelectric behavior of solids and also of the samples such as pure and nano-composites of FLC. We also observed the room temperature P-E hysteresis behavior of the pure and Ni

NPs doped FLC material ZLI 3654, which is shown in Fig. 1. Figure 1 clearly reflects the ferroelectric behavior of the pure FLC ZLI 3654, which has been one of the well studied FLC materials.<sup>19</sup> The saturation value of spontaneous polarization ( $P_s$ ) for the pure FLC material ZLI 3654 has been observed to be  $\sim 0.03 \mu\text{C}/\text{cm}^2$ , which is found in accordance with the earlier report.<sup>20</sup> Figure 1 also inferred that for the doping concentration of Ni NPs up to 0.5 wt. %, the Ni NPs/FLC composite exhibit strong ferroelectric character. However, on increasing the concentration of Ni NPs, the material ZLI 3654 almost lost its ferroelectricity that is visible from the distorted form of P-E hysteresis characteristics of 0.6 wt. % Ni NPs doped FLC ZLI 3654 [inset of Figure 1]. It can also be concluded that the ferroelectric character has been almost monotonically decreased on increasing the concentration of Ni NPs [inset of Figure 1].

Figure 2 shows the room temperature ( $\sim 27^\circ\text{C}$ ) M-H hysteresis behavior of the pure and Ni NPs doped FLC material. The majority of the LC materials possesses diamagnetic character, i.e., the LC molecular magnetic moments weakly align in the direction opposite to that of applied field upon the application of the external magnetic field.<sup>21–23</sup> The FLC material ZLI 3654 also is intrinsically a diamagnetic material which has been clearly reflected from Figure 2. However, the addition of magnetic Ni NPs into ZLI 3654 has changed the magnetic character of the latter. The presence of 0.1 wt. % Ni NPs changed the character of ZLI 3654 material from a diamagnetic to a paramagnetic one. Moreover, on further increasing the concentration of Ni NPs, the Ni NPs/FLC composite shows a strong ferromagnetic character which is clear from the M-H loops of the same (Figure 2). The saturation magnetization value of the composite is found to be increased monotonically with the concentration of Ni NPs.

The observed soft multiferroic behavior of the Ni NPs/FLC composite could be understood by taking into account the interaction between the FLC molecular magnetic moments and that of the magnetic NPs. It is well known that the application of external fields unwinds the helical

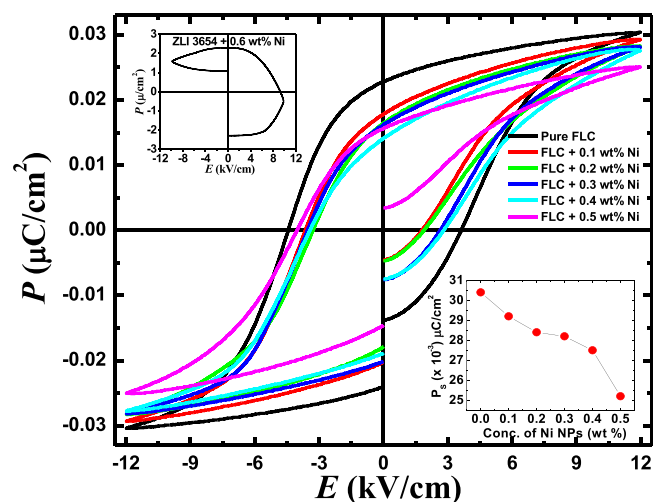


FIG. 1. Room temperature ( $\sim 27^\circ\text{C}$ ) P-E hysteresis behavior of the pure and Ni NPs doped FLC ZLI 3654. Insets of the figures show the P-E hysteresis response of 0.6 wt. % Ni NPs doped FLC ZLI 3654 (II quadrant) and behavior of saturation polarization of FLC ZLI 3654 with the concentration of Ni NPs (IV quadrant).

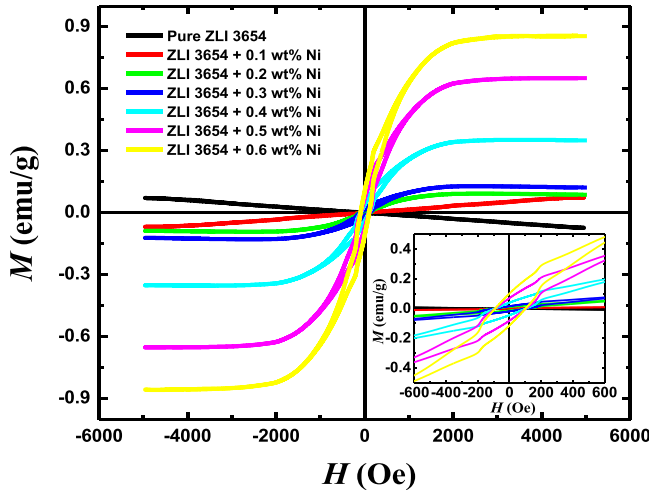


FIG. 2. M-H hysteresis behavior of pure and Ni NPs doped FLC ZLI 3654 at room temperature. The inset shows the enlarged view of the M-H hysteresis loop near the origin.

structure of the FLC molecules. The external magnetic field (critical field), required to unwind the helical structure of a FLC material, depends on the values of its elastic constant ( $K_{33}$ ), magnetic susceptibility ( $\chi_a$ ), and undistorted pitch  $P_0$ . At a particular critical field, either electric or magnetic, the helical structure gets unwound. In the presence of external magnetic and electric fields, the free energy of a SmC\* phase contains additional terms given by

$$-\frac{1}{2}\chi_a H^2 - \frac{1}{2\epsilon_a} E^2, \quad (1)$$

where  $\chi_a$  and  $\epsilon_a$  are anisotropic parts of magnetic and electric susceptibilities, respectively. It has been shown that at a certain critical field, the helical structure unwinds completely.<sup>24-26</sup>

We propose here that the addition of magnetic Ni NPs to the FLC material causes the same process of unwinding of helix and it is expected that unwinding may take place at a particular concentration of the NPs. In the presence of the external magnetic or electric field, the influence of magnetic NPs leads to the decrease in critical fields. Let the field intensity produced by each NP be  $\mathbf{h}$ . As the particles are aligned along the director, the field intensity of each NP can be resolved into two components, one along the direction of layer normal (z-direction) and the other along the plane of layers. The director rotates around the layer normal, and the net magnetic field component along the layer plane vanishes. However, the magnetic field in the z-direction produced by each NP will add up to produce some net magnetic field along the direction of the layer normal.

The magnetic field intensity produced by all the NPs in a unit volume of the sample in the z-direction can be expressed as

$$\mathbf{H}_z = \frac{1}{V} \sum_{i=1}^N \mathbf{h}_z = \frac{N}{V} \langle \mathbf{h}_z \rangle_{ave}, \quad (2)$$

where  $\langle \mathbf{h}_z \rangle_{ave}$  is the average z-component magnetic field produced by each particle. Since  $\frac{N}{V}$  is proportional to the fraction  $f$  of nano-material in FLC, we have

$$\mathbf{H}_z \propto f \langle \mathbf{h}_z \rangle_{ave}. \quad (3)$$

Let  $M_s$  be the magnitude of magnetization of the NP and  $\mathbf{m}$  is the unit vector along the direction of magnetization. Then, we write  $\langle \mathbf{h}_z \rangle_{ave} \propto M_s \mathbf{m} \cos \theta_0$ , where  $\theta_0$  is the tilt angle in the SmC\* phase and we may write  $\mathbf{H}_z$  as

$$\mathbf{H}_z \propto f M_s \mathbf{m} \cos \theta_0. \quad (4)$$

Since  $M_s$  and the tilt angle are constant for a given sample at a given temperature (here room temperature), the magnitude of  $\mathbf{H}_z$  may be written as

$$H_z = \beta f, \quad (5)$$

where  $\beta = \text{const} \times M_s \cos \theta_0$ . To study the influence of internal magnetic field on the SmC\* phase, first we consider the twist dependent part of free energy along with an external magnetic field  $\mathbf{H}$ . When the phase angle  $\phi$  is only allowed to vary with  $z$ , the free energy density of the system is written as

$$g(\phi) = -\Lambda_0 \theta_0^2 \frac{d\phi}{dz} + \frac{1}{2} K_0 \theta_0^2 \left( \frac{d\phi}{dz} \right)^2 - \frac{1}{2} \chi_a H^2 \theta_0^2 \cos^2 \phi, \quad (6)$$

where  $K_0$  is the elastic constant and  $p$  is the undistorted pitch of the helix,  $p = 2\pi/q_0$  and  $q_0 = \Lambda_0/K_0$ . Minimization of free energy  $F = \int g(z) dz$  with respect to phase angle  $\phi$  gives the Sine-Gordon equation<sup>24</sup>

$$\frac{d^2 \phi}{dz^2} = \left( \frac{\chi_a H^2}{2K_0} \right) \sin 2\phi.$$

The above equation can be solved, and it can be shown that the critical field  $H_C$  required to completely unwind the helix is

$$H_c = C q_0, \quad (7)$$

where  $C = \left( \frac{\chi_a}{2K_0} \right)^{-1/2}$ . In the case of the doped FLC, the critical field reduces because of the internal field produced by the Ni NPs. The critical field is then written as

$$H_c = H_{ext} + H_z. \quad (8)$$

Substituting  $H_z = \beta f$  gives

$$H_c = H_{ext} + \beta f. \quad (9)$$

The value of critical magnetic field depends on the material elastic constants  $K_0$ , magnetic susceptibility  $\chi_a$ , and undistorted pitch  $P_0$  and for approximate values of  $K_0 \sim 10^{-6}$  dyne,  $\chi_a \sim 10^{-7}$ , and  $P_0 \sim 10 \mu\text{m}$ , the critical field is of the order of few Tesla. To be more quantitative, the critical magnetic fields for unwinding the helix of FLCs are observed to be large, e.g., the critical field for the FLC material, namely, DOBAMBC, is found to be 12.5 T for the period of helix  $P_0 = 2 \mu\text{m}$ .<sup>27</sup> It may be assumed that for certain critical fraction of nanomaterial in the LC, the unwinding of the phase takes place without any application of the external magnetic field. In this case, the critical field is solely produced by the nano-magnetic particles in the smectogen

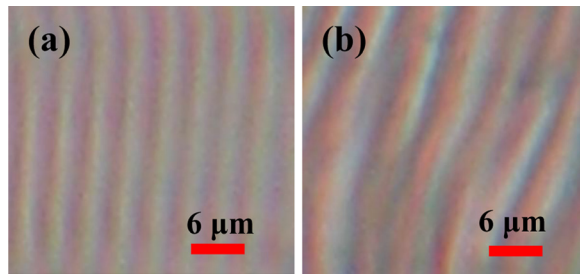


FIG. 3. Optical micrographs showing the appearance of helical lines in (a) pure and (b) 0.6 wt. % Ni NPs doped FLC ZLI 3654 at room temperature.

$$H_c = \beta f_c = Cq_0. \quad (10)$$

Generalizing this result, the helical wave vector  $q$  as a function of concentration of magnetic NPs is expressed as

$$q = q_0 - \frac{\beta}{C}f. \quad (11)$$

In the presence of external magnetic field, the above equation can be modified as

$$q = q_0 - \frac{\beta}{C}f - \frac{H_{ext}}{C}. \quad (12)$$

Thus, in the external magnetic fields, the unwinding of helix takes place at smaller values of external field.

When the external magnetic fields are absent, adding magnetic NPs to FLCs increases the helical pitch of the material and in turn the ferroelectric property of the material diminishes. However, one may expect at a particular concentration of NPs, say, a critical concentration, the ferroelectric property of the smectogen may be lost completely leading to a phase change. We measured the pitch of the pure and Ni NPs doped FLC ZLI 3654 in the absence of external field to observe the effect of Ni NPs on the same and found that the pitch increases remarkably with the doping concentration of Ni NPs. Figures 3(a) and 3(b) show the appearance of helical lines for pure and 0.6 wt. % Ni NPs doped FLC ZLI 3654 in  $\sim 20 \mu\text{m}$  thick untreated sample cells. The pitch value of pure ZLI 3654 is observed to be  $\sim 3.3 \mu\text{m}$ , and it is found to be  $\sim 6 \mu\text{m}$  for 0.6 wt. % Ni NPs. This experimental observation shows the expected unwinding of pitch and further it gives strong evidence in support of the possible interaction between Ni NPs and the FLC molecules what we proposed theoretically.

Soft multiferroicity has been observed in a potential system of FLC embedded with magnetic Ni NPs. We found that the ferromagnetic character is increased whereas ferroelectric behavior of the FLC material is decreased with the doping concentration of Ni NPs. Theoretical investigation on the system suggested the strong coupling between ferroelectric (of FLC) and that of ferromagnetic order of magnetic NPs. The reduction in the ferroelectric character on increasing the concentration of Ni NPs is observed, which is in accordance

with the theory. The multiferroic character shown by the Ni NPs/FLC composite is of great importance for its utilization in low threshold information storage, processing, and transmission.

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<sup>17</sup>See supplementary material at <http://dx.doi.org/10.1063/1.4948652> for structural characterization of Ni NPs and optical micrographs of the Ni NPs/FLC composites.

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