NMR spectrum of an icosahedral fog phase

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The NMR spectra are analyzed for various models of the blue fog phase BPIII. The NMR spectrum for a polycrystalline sample of a phase with icosahedral symmetry is shown to be qualitatively different from the NMR spectra for polycrystalline samples of phases of cubic symmetry, BPI and BPII, and also from the NMR spectrum of a system of randomly distributed "double-twist cylinders," which is an alternative model of BPIII.

The nature of the blue phases BPI and BPII of cholesteric liquid crystals has been under investigation for several years now. The structure of the phases BPI and BPII (bcc O^8 and simple cubic O^2, respectively), which has been proposed in the Landau theory of phase transitions with a tensor order parameter[1] $Q_{\alpha\beta}(\mathbf{r})$ and in the disclination model[2,3] with a locally uniaxial $Q_{\alpha\beta}(\mathbf{r})$, agrees well with the experimental results available.[4] Some recent papers[5–8] have proposed various versions of the structure for the blue fog phase, BPIII. The possible appearance of a phase with an icosahedral symmetry of the order parameter—an icosahedral quasicrystal—has been studied on the basis of Landau's theory.[5–7] The relative contributions of the first 14 harmonics of the icosahedral structure have been determined.[7] As a result, it has been shown that the significant broadening of the step in the optical transmission spectrum[9] $R(\lambda)$ and, correspondingly, of the peak in the optical scattering spectrum[10] $I(\lambda)$ for BPIII in comparison with $R(\lambda)$ and $I(\lambda)$ for BPI and BPII is not a consequence of the approximate agreement of the wave vectors of the harmonics of the icosahedral structure. This broadening occurs because the size (L) of the "quasicrystallites" of an icosahedral structure is smaller than that of the cubic BPI and BPII. The smaller size L is in turn a consequence of the fact that the anisotropy of the icosahedral phase is less than that of a cubic structure and also the effect of additional Goldstone modes: "phasons."[7] The value[10] $L \simeq 1$ μm is still quite large. Although the size L spans about eight interplanar distances[1)] $p/2 \simeq 1.3 \times 10^3$ Å, the thickness of the domain wall between crystallites is $\xi \sim \xi_- \lesssim 100$ Å (ξ is the correlation length of the order parameter below the point of the phase transition), and we have $L/\xi \gtrsim 100$.

In order to identify the structure of BPIII, we have now calculated the NMR spectra for a polycrystalline sample of a phase with an icosahedral symmetry of the order parameter and for a set of randomly distributed "double-twist cylinders," which is an alternative model of BPIII.[8] It has been found that the NMR spectrum for a "polyquasicrystal" is qualitatively different from the NMR spectra for the double-twist cylinder and for polycrystalline samples of BPI, BPII, and a biaxial cholesteric liquid crystal.

To calculate the NMR spectra of deuterated molecules of a cholestric liquid crystal, we start from the effective Hamiltonian $\mathscr{H}$ which determines the shift of a resonant line[11]:

$$\mathcal{H} = (1/2)\sum_n \{dx\rho_n(x)(x_\alpha x_\beta - x_\gamma^2\delta_{\alpha\beta}/3)\}(\partial^2 V_n(x)/\partial x_\alpha \partial x_\beta)_n , \quad (1)$$

where $\rho_n(x)$ is the charge density of deuterated nucleus n, and $V_n(x)$ is the electrostatic potential near the center ($x = x_n$) of the deuterated nucleus. Using the relation $[\partial^2 V_n(x)/\partial x_\alpha \partial x_\beta]_n \propto Q_{\alpha\beta}(x_n)$, we can write the complete effective Hamiltonian $\mathcal{H}$ in the presence of an external magnetic field $\mathbf{H}$ as follows:

$$\mathcal{H} = \sum_n \{-h\gamma I_m H + bI_m^2 Q_{\alpha\beta}(x_n)m_\alpha m_\beta\} , \quad (2)$$

where $h\gamma\mathbf{I}$ is the magnetic moment due to the spin operator ($\mathbf{I}$) of deuterated nucleus n, and $\mathbf{H} = H\mathbf{m}$. Since the operator I_m^2 can take on the values zero and one, we find an expression for the distribution of quadrupole splittings of a resonant spectra line, $N(\omega)$:

$$N(\omega) = (1/2V)\int dx_n \int (d\Omega/4\pi)\{\delta(\omega - \mathcal{H}_n) + \delta(\omega + \mathcal{H}_n)\} , \quad (3)$$

where $\mathcal{H}_n = bQ_{\alpha\beta}(x_n)m_\alpha m_\beta$, and where the average in (3) is over the position of nucleus n and the orientation of the field $\mathbf{H}$.

For a polyquasicrystal, taking an average over the position of the deuterated nuclei in the quasicrystallites, characterized by different values of the phason and phonon phases ψ_j ($j = 1,...,6$) (Ref. 7), reduces to taking an average over ψ_j. The NMR signal from the domain walls between quasicrystallites is small because the relative volume of these walls is small ($\xi/L \lesssim 10^{-2}$). Incorporating the first harmonic of the icosahedral structure (the wave vectors $\mathbf{q}_i^1$ are directed away from the center of the icosahedron to its vertices), we find the expression

$$N(\omega) = (1/16\pi^2)\int d\Omega \left\{\int_0^\infty dt \cos\omega t \prod_{k=1}^{m} J_0(b_m \sin^2\theta_k H^2 t)\right\}, \quad (4)$$

where $J_0(x)$ is the Bessel function of the first kind, θ_k is the angle between $\mathbf{q}_k^1$ and $\mathbf{H}$, $m = 6$, and $b_6 = b\mu/\sqrt{12}^2$. Expression (4) with $m = 3$ and $b_3 = b_6\sqrt{2}$ is the NMR spectrum for a polycrystallite of cubic phase BPII when one (the first) harmonic is taken into account with the wave vectors $\mathbf{q}_j^1$ corresponding to the Miller index [100].

Since the anisotropy of the icosahedral structure is slight, the process of taking an average over the directions of $\mathbf{H}$ in (4) for $m = 6$ can be replaced (with an error on the order of 1%) by an averaging in the arguments of the integrands:

$$N(\omega) = (1/4\pi)\int_0^\infty dt \cos\omega t J_0^6(2b_6 H^2 t/3).$$

The corresponding procedure would not be applicable in the case of the more highly anisotropic cubic ($m = 3$) structure. Taking account of the two remaining fundamental harmonics of the icosahedral structure, which were identified in Ref. 7 (the wave vectors are $\mathbf{q}_i^{2,3} = \mathbf{q}_i^1 + \mathbf{q}_j^1$, where $i,j = 1,...,12$), does not change the function $N(\omega)$ qualitatively. Figure 1 shows the results of a numerical integration in expression (3).

The single-peak NMR spectrum of the icosahedral fog phase is thus qualitatively different from the theoretical[1] and experimental[12] two-peak NMR spectra for polycrystalline samples of BPI, BPII, and a biaxial cholesteric liquid crystal.

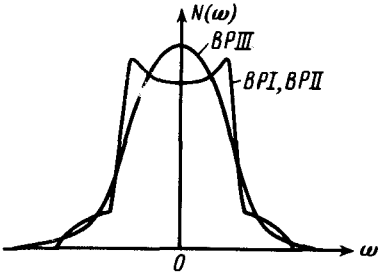

FIG. 1.

Zasadzinski *et al.*[8] studied the structure of a state of a cholesteric liquid crystal achieved by quenching BPIII. Using an electron microscope, they obtained images of the fracture surfaces of a frozen sample. As a result, they suggested[8] that BPIII is a system of randomly distributed double-twist cylinders. A double-twist cylinder is a spatially inhomogeneous configuration of the director $\mathbf{n}(\mathbf{r})$, in which the director $\mathbf{n}(\mathbf{r})$ is twisted in all radial directions from the $\mathbf{z}$ axis of the cylinder [at the axis of the cylinder, we have $\mathbf{n}(\mathbf{r}) \| [\mathbf{z}]$. In the disclination model[2,3] which derives from a "low-temperature" uniaxial asymptotic expression $Q_{\alpha\beta}(\mathbf{r}) = S[n_\alpha(\mathbf{r}) n_\beta(\mathbf{r}) - \delta_{\alpha\beta}/3]$, the cubic phases BPI and BPII are a translationally invariant packing of nonintersecting double-twist cylinders and a cubic lattice of disclination lines which pass through regions free of double-twist cylinders. Since a system of randomly distributed double-twist cylinders has also been found during the freezing of the isotropic phase (in this case we have $T - T_c \leqslant 1$–2 K, where T_c is the temperature of the transition from the isotropic phase to BPIII, and the interval in which BPIII exists is $\Delta T \simeq 0.6$ K; Ref. 8), it might be suggested that a transition might occur from BPIII to a low-temperature ($S \simeq S_{\max}$), locally uniaxial amorphous phase with a structure qualitative different from that of the high-temperature ($S \lesssim 0.2 S_{\max}$ at $T = T_c$) BPIII with a locally biaxial $Q_{\alpha\beta}(\mathbf{r})$. From the NMR spectra of BPI, BPII, and the biaxial cholesteric liquid crystal, we find the biaxial-nature parameter to be[12] $\eta \simeq 0.35$, while we have $\eta_{\max} = 1$.

Working from a double-twist-cylinder configuration of the director, $\mathbf{n}(\mathbf{r}) = \vec{\varphi} \sin q_0 \rho + \mathbf{z} \cos q_0 \rho$ (ρ, φ, and z are cylindrical coordinates; $q_0 = 4\pi/p$) and a random distribution of double-twist cylinders, we find the spectrum $N(\omega)$ for the alternative model of BPIII:

$$N(\omega) \propto \frac{1}{\sqrt{bSH^2}} \left(\frac{1}{\sqrt{-\omega + bSH^2/3}} + \frac{1}{\sqrt{\omega + bSH^2/3}} \right), \quad |\omega| < bSH^2/3.$$

This spectrum is qualitatively different from the NMR spectrum of the icosahedral fog phase.

[1)]Here p is the pitch of the cholesteric helix.
[2)]Here μ is the amplitude of the first harmonic.

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