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Effect of Pressure on the Mesomorphic Transitions in Para-Azoxyanisole (PAA)†‡

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Abstract—We report the study of the effect of hydrostatic pressure on the phase transitions in PAA up to 3 kbar. The different phases (solid, nematic and isotropic) are characterized by their NMR spectra.

The observed temperature dependences of the two transitions are:

Solid to Nematic: $T(P) = 116\,^{\circ}\mathrm{C} + 24.5 \pm 1.0\,^{\circ}\mathrm{C/kbar}$

Nematic to Isotropic: $T(P) = 133\,^{\circ}\mathrm{C} + 27.0 \pm 1.0\,^{\circ}\mathrm{C/kbar}$

The ratio of the corresponding slopes is in qualitative agreement with the existing data on latent heats and volume changes at both transitions.

On the other hand, the study of NMR spectra in the nematic phase allows the determination of the order parameter S. Our observed value of S in the nematic phase at the nematic to isotropic transition is independent of pressure within experimental error

$S(T_c) = 0.40 \pm 0.015$ from 1 bar to 3 kbar.
$N \rightarrow I$

The same is true for the solid to nematic transition

$S(T_M) = 0.55 \pm 0.015$ from 1 bar to 3 kbar.
$S \rightarrow N$

1. Introduction

The order–disorder transitions in nematic systems are commonly studied as a function of temperature. However, temperature is not the only interesting parameter in this problem. Indeed, the anisotropic intermolecular potentials, which are frequently considered as essential for nematic order in thermotropic liquid crystals, depend strongly on density. Moreover, the excluded volume effects, which

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are dominant in other nematics (larger rod-like molecules) are essentially density dependent. This suggests that a study of order (or disorder) as a function of density, in a typical nematic, might cast some light on the nature of the various effects contributing to the nematic order. We present an NMR determination of the shift with pressure of the solid–nematic and nematic–isotropic phase transition temperatures[1] (dT_M/dP, dT_c/dP)[2], and also measurements of the corresponding values of the order parameter along these transition lines ($S(T_M) = S_M$, $S(T_c) = S_c$) in PAA; the pressure range is 0–3 kbar and the temperature range 120–220 °C.

2. Experimental Techniques

We used a hydrostatic high pressure equipment, allowing to work up to 7 kbar, with purified helium gas as a pressure medium. The main advantage of using helium is that it does not interact at all with the sample; on the other hand, it requires a rather careful job to avoid leaks. The high pressure vessel is made of nonmagnetic Cu–Be and Cu–Ni alloys; the useful volume of the cavity is 6.5 cm^3 ($h = 45$ mm, $\phi = 13.5$ mm). The pressure is measured through a manganine gauge located in a part of the apparatus which is at room temperature. More details about this equipment are given in Ref. 3.

The heating filament is located inside the cavity, thermally insulated from the walls by a single thickness of pyrophyllite (1.5 mm); its winding is noninductive. The NMR coil and the sample are then placed inside the heating tube; the sample temperature is measured by a copper–constantan thermocouple whose emf is practically independent of pressure.[4] Some care must be exercised about the compensation of temperature gradients, because helium, at 3 kbar, is an extremely good heat conductor. For that reason, the sample volume was reduced down to 0.15 cm^3. Various complicated convection regimes can also develop in the helium gas, especially at high temperatures[5]; they can give rise to long term temperature instabilities. One way to cut them down is to reduce as much as possible the volume allowed to the fluid.

Finally, NMR CW measurements were made with a conventional Pound–Watkins marginal oscillator on the proton resonance at 18 MHz.