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Magnetic field dependence of the nematic-isotropic transition temperature

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The nematic-isotropic transition temperature was measured by means of an optical technique as a function of applied magnetic field for the material octyl-cyanobiphenyl. The results represent the first unambiguous demonstration of the magnetic field term in the thermodynamic equation for a liquid-crystal phase transition.

The study of liquid-crystal phase transitions in magnetic fields has long been an active area of research. Several years ago Stinson and Litster[1] measured the Cotton-Mouton coefficient near the nematic-isotropic (NI) transition in methoxybenzylidene butylaniline (MBBA). More recently Poggi and Filippini[2] and Malraison *et al.*[3] have observed the influence of high fields in quenching long-wavelength director fluctuations near the nematic–smectic-A transition. Keyes and Shane,[4] by observing the magnetic susceptibility and its derivative on the isotropic side of the NI transition, have demonstrated that this transition exhibits tricritical exponents. On the theoretical side there have also been a number of papers[5–7] dealing with various phase transition phenomena in the presence of a field. To date, however, the thermodynamic consequence of the magnetic field term on liquid-crystal phase transitions has escaped experimental scrutiny. In this article we report the first measurment of the NI transition temperature $T_{\rm NI}(H)$ as a function of magnetic field H.

We begin by writing the differential thermodynamic potential:

$$dG_i = -S_i dT - M_i dH \ , \tag{1}$$

where G_i is the Gibbs potential per unit volume, S_i the entropy per volume, T the temperature, and H magnetic field. The magnetization M_i is equal to $\chi_i H$, where χ_i is the susceptibility parallel to the field. The subscript i refers to either the nematic (N) or isotropic (I) phase. Along the NI coexistence line, the Gibbs potentials are equal in both phases. Thus, integrating Eq. (1), we obtain the Clausius-Clapeyron relation

$$\delta T = \frac{T_{\rm NI}(0)}{Q}\frac{(\chi_N - \chi_I)}{2}H^2 \ , \tag{2}$$

where δT is the small shift in the NI transition temperature, i.e., $T_{\rm NI}(H) - T_{\rm NI}(0)$, $T_{\rm NI}(0)$ and $T_{\rm NI}(H)$ the NI transition temperatures in zero field and a field H, respectively, and Q the latent heat of transition. To an excellent approximation[8] $\chi_N = \chi_I + \frac{2}{3}\Delta\chi$, where $\Delta\chi$ is the susceptibility anisotropy in the nematic phase. Making this substitution, Eq. (2) can be rewritten

$$\delta T = \frac{T_{\rm NI}(0)}{Q}\frac{\Delta\chi}{3}H^2 \ . \tag{3}$$

Since $\Delta\chi$ is positive, $\delta T > 0$ and is expected to be a few millikelvins in a field $H = 100$ kOe.

Sakamoto *et al.*[9] have used magnetic fields to observe a shift in the nematic–smectic-A transition temperature, analogous to the prediction of Eq. (2). Their results are extremely puzzling, however, in that their magnitude ($|\delta T| \simeq 1$ K for $H = 700$ Oe) and sign are in gross disagreement with the thermodynamic predictions of Eq. (2). On the other hand, Helfrich[10] has used electric fields, rather than magnetic fields, to study the NI transition. Although his results are consistent with the electric field analogy of Eq. (3), they failed to account for ohmic heating, which could have been significant in his technique. Using a typical resistivity[11] of $5\times10^8\ \Omega$ cm and sample parameters obtained from his paper (thickness of 6 μm and area of $\simeq 1$ cm^2), a 100-V potential would have resulted in approximately 30 mW being dissipated directly across the thin sample. Indeed, with electric fields it is quite difficult to quantitatively sort out ohmic heating from electric field effects.

To perform my experiment, a sample of octylcyanobiphenyl (8CB), obtained from British Drug House of Poole, England, and used without further purification, was placed between 3-mm-thick sapphire discs spaced by a 140-μm-thick copper annulus. Both the copper and sapphire were used to help improve the thermal conductivity and uniformity, essential in an experiment of this sort. The sapphire-8CB sandwich was then mounted in thermal contact with a copper holder, which in turn was mounted inside, but not in thermal contact with, a cylindrical, double can copper Dewar. Glass windows were used to permit the entry and exit of light, and the vacuum space was pumped continuously to thermally insulate the sample from the magnet. Heat was supplied by passing a current through a resistive wire affixed to the outer wall of the inner Dewar can. The entire arrangement was placed in a 5.4-cm-bore Bitter magnet capable of fields of 150 kOe, where the field was perpendicular to the plane of the sapphire discs.

To measure temperature, a small blind hole was drilled near the center of one of the sapphire discs and a thermistor thermometer[12] mounted inside; the end of the thermistor was 0.7 mm from the sample. A highly stable battery operated current source supplied a constant current of 100 μA to the thermistor, and the voltage drop across the device (and hence the temperature) was read using a Keithley 181 nanovoltmeter. The high sensitivity of the thermistor (4% K^{-1} at 40 °C) resulted in a precision of better than 0.2 mK.

The magnetoresistance of the thermistor was calibrated by supplying a constant current to the heater wire and stabilizing the temperature at the sample to 40 °C, i.e., $T_{NI}(0)$ for 8CB. The voltage drop across the thermistor was first recorded at zero field. The magnet was then swept up to a field H in 30 sec and the voltage drop recorded. The field was then brought to zero at the same rate and the voltage drop across the thermistor again recorded. This process was repeated several times with consistent results to obtain the apparent temperature change $\Delta T_M(H)$ due to magnetoresistive effects at a field H. Measurements were made at several fields. The data points ΔT_M were linear in H^2, where the slope of the line ΔT_M vs H^2 was determined by a least-squares fit to be $(1.025\pm0.015)\times10^{-3}$ mk kOe^{-2} for this thermistor.

An optical technique was used to determine the NI transition temperature $T_{NI}(H)$. A system of two lenses (an $f=82$ mm as the objective and an $f=225$ mm as the eyepiece) was used to create a microscope with a viewing distance of over 1 m and a resolution of about 10 μm. Illumination of the sample was accomplished with a white-light source from the rear, along the field direction. At zero field the sample was first brought into the nematic phase and then slowly heated at a rate between 15 and 25 mK min^{-1}. The transition temperature $T_{NI}(0)$ was taken as the temperature at which the entire region was seen to become isotropic. (The sample was observed to have a two-phase region of approximately 18 mK around the NI transition. A likely source of the two-phase region was impurities; based upon the work of Martire *et al.*[13] we can estimate from the size of this two-phase region that the sample purity was about 99.95%, consistent with the manufacturer's specifications using gas-liquid chromatography. Because of the high sample purity, the width of the two-phase region was not expected to depend upon magnetic field.)

A small temperature gradient of less than 1 mK mm^{-1} was present in the sample, with the coldest region being adjacent to the thermistor and the warmest at the far end from the thermistor. Thus, the final transition to isotropic always occured adjacent to the thermistor, minimizing the temperature differential between the thermistor and point of transition and thereby assuring an accurate determination of T_{NI}. The process of heating the sample through T_{NI} was performed several times in zero field, with reproducibility of T_{NI} of approximately 0.3 mK. The transition temperature was always recorded on heating because superheating effects are, in practice, much smaller than supercooling effects.[14]

After recording $T_{NI}(0)$, the sample was cooled to approximately 30 mK below $T_{NI}(0)$, then slowly heated again. Approximately 45 sec before the transition was to have occured, I began a 30-sec sweep of the field from zero to a value H. Thus, within 15 sec of the transition, the field reached a steady-state value H and $T_{NI}(H)$ was then recorded. The field was then brought back to zero, the sample cooled into the nematic phase, and the process repeated to obtain another reading of $T_{NI}(0)$. (In all cases it was observed that the transition temperature was independent of the temperature at which heating first began.) The apparent shift ΔT_{tot} in T_{NI} (including the magnetoresistance ΔT_M) was the difference between $T_{NI}(H)$ and the average of $T_{NI}(0)$ before and after the high-field

measurement. The true shift $\delta T(H)$ in transition temperature was therefore $\delta\, T(H) = \Delta T_{\text{tot}}(H) - \Delta\, T_M(H)$. Although the magnetoresistive term was considerably larger than $\delta T(H)$, it was nevertheless measured with great accuracy. Therefore, uncertainty in $\Delta T_M(H)$ represents only a few percent error in $\delta T(H)$.

Measurements of $\delta T(H)$ were made for fields between 73 and 148 kOe and are plotted versus H^2 in Fig. 1. The error bar includes the uncertainty in magnetoresistance, uncertainty in the temperature measurements, and the small uncertainty in precisely locating T_{NI}. A least-squares fit of δT vs H^2 produced a slope of $(2.5\pm0.3)\times10^{-4}$ mK kOe^{-2}. Comparing this result to the thermodynamic prediction of Eq. (3), we take $T_{\text{NI}}(0)=313$ K and for Q a value[15] of 6.12×10^9 erg mol^{-1} $\cong 2\times10^7$ erg cm^{-3}. A value $\Delta\chi = 5\times10^{-8}$ cgs was obtained by extrapolating available data[3] in the nematic phase to T_{NI}. Equation (3) then gives a slope of 2.6×10^{-4} mk kOe^{-2}, in excellent agreement with experiment.

In summary, these results represent the first unambiguous observation of the magnetic field term [cf. Eq. (1)] in the thermodynamics of a liquid-crystal phase transition.

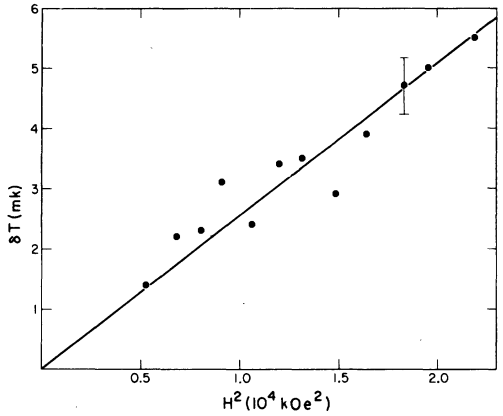

FIG. 1. Increase in NI phase transition temperature δT (over the zero field case) vs H^2. The solid line represents a least-squares fit to the data and has a slope $(2.5\pm0.3)\times10^{-4}$ mK kOe^{-2}, as compared to a theoretical value of 2.6×10^{-4} mK kOe^{-2} from thermodynamic data. A typical error bar is shown.

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