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# Ultrasonic Investigation of the Cholesteric-Nematic Transition

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# Ultrasonic Investigation of the Cholesteric–Nematic Transition

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**Abstract**—The magnetic field-induced cholesteric to nematic transition has been monitored via ultrasonic pulse–echo attentuation measurements in two liquid crystalline materials. In particular, the kinetics of the transition have been investigated in one of these materials. The activation energy for " twisting-back " to the cholesteric state from the nematic state is some 0.3 eV.

## 1. Introduction

The cholesteric–nematic liquid crystal field-induced transition has been treated theoretically,(1,2) and has been observed with NMR(3) and optical techniques.(4,5,6,7) We have found that the magnetic field-induced cholesteric–nematic transition can also be monitored by means of ultrasonic attenuation measurements. Standard pulse–echo measurement techniques were employed. They have been described in an earlier paper.(8) In the present work the attenuation was determined automatically with a MATEC AARU unit and recorded continuously during measurements. All measurements were at 3MHz.

## 2. Results

Figure 1 shows the ultrasonic attenuation as a function of magnetic field, at various concentrations (by weight) of cholesteryl chloride (CC) in *p*-azoxianisole (PAA) at 122 °C. (All measurements in the CC/PAA mixtures were at 122 ± 0.5 °C). In this case, the magnetic field ($H$) is in the same direction as the direction of propagation of the sound wave ($k$). The general nature of this field dependent attenuation is independent of the angle between $H$ and $k$. For example, Fig. 2 shows the variation when $H$ is perpendicular to $k$,

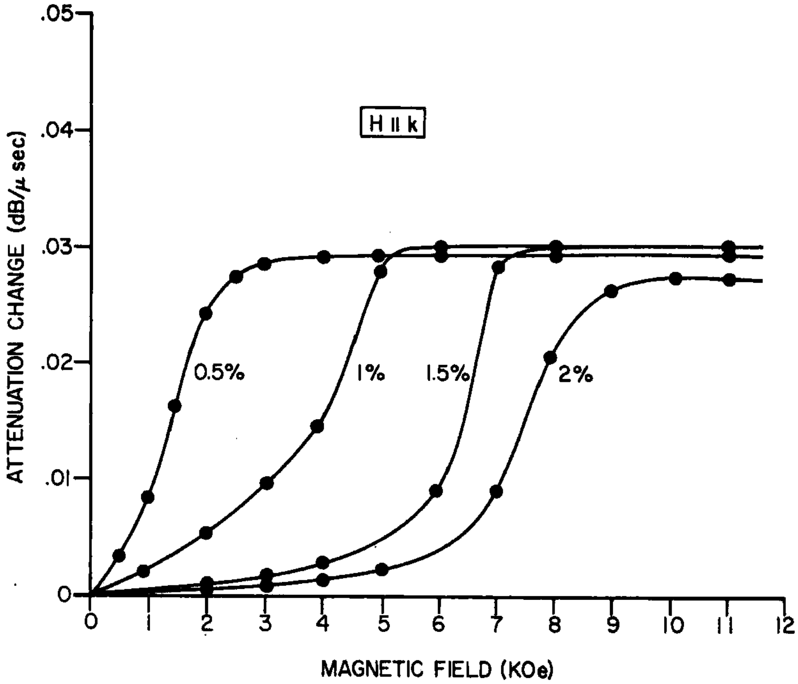

Figure 1. Ultrasonic attentuation versus magnetic field in the cholesteryl chloride–*p*-azoxianisole (CC/PAA) system for various concentrations of (CC), at 122 °C. The magnetic field (*H*) is directed parallel to the propagation vector (*k*) of the sound wave.

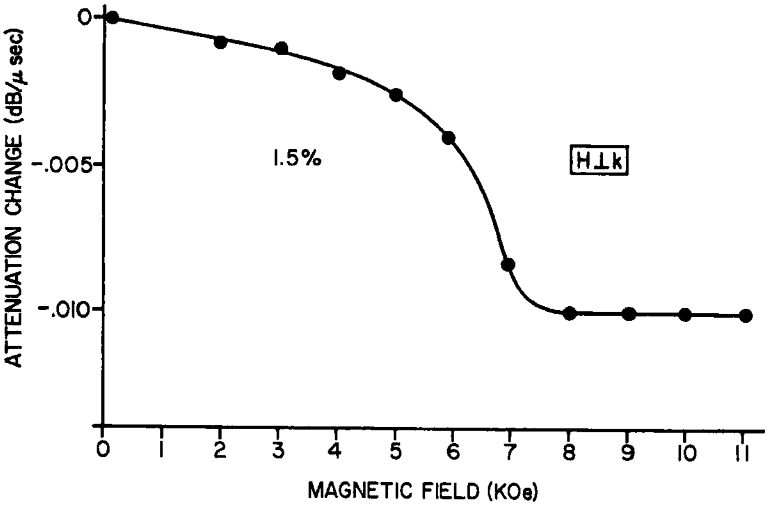

Figure 2. Ultrasonic attenuation versus magnetic field in (CC/PAA) system for $H \perp k$, at 122 °C.

where even though the attenuation change is smaller and in the opposite sense as Fig. 1, the same basic form is evident.

The critical field is that value of field where the cholesteric structure is destroyed completely and the molecules are lined up in the nematic state. Judging from our previous work in nematics,(8) once the oriented nematic states are achieved, higher values of field will cause no further change in attenuation. Thus the critical field is that value where the attenuation levels off. For example, we determine the critical field for 2% (CC) to be 9.6 KOe; this is exactly the same as that given from optical techniques.(4) As shown in Fig. 3, the critical fields determined here vary in a linear manner with concentration of (CC); this was also found optically in Ref. 4.

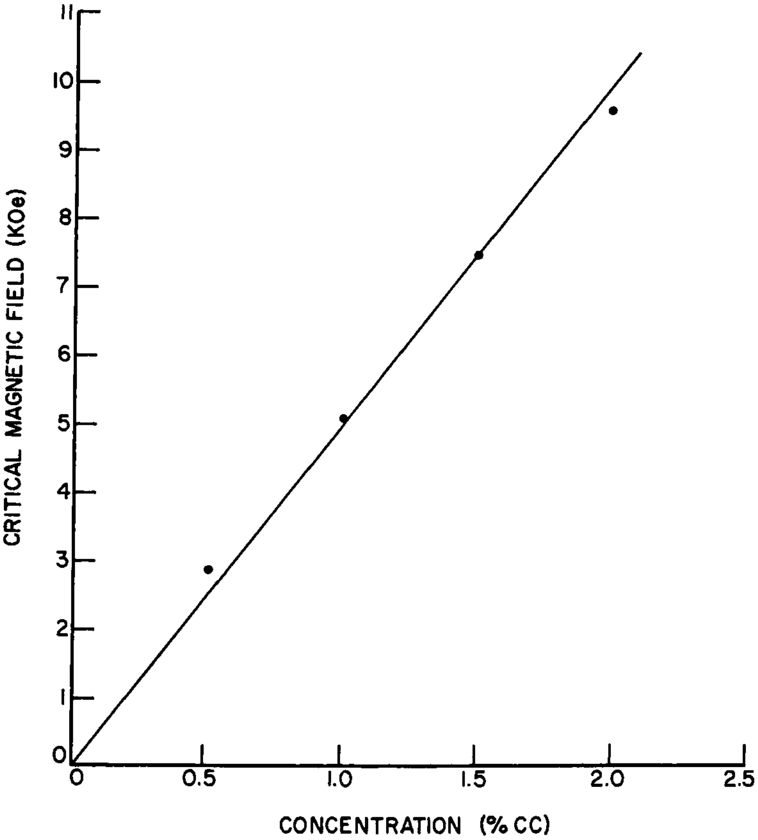

Figure 3. Critical magnetic field versus concentration in (CC/PAA) system at 122 °C.

There seems little doubt therefore that attenuation measurements in the bulk can be used to monitor the cholesteric to nematic transition.

There is significant hysteresis in attenuation versus field curves. The changes which occur when increasing the field take place quite rapidly (in a few seconds at most), whereas the changes upon decreasing the field can be quite sluggish. Figure 4 shows some times needed for transformation from the nematic to cholesteric state at different field values for various concentrations. In each case the material was placed in the nematic state with a large field. Then the field was reduced as quickly as possible to the indicated value and the attenuation was monitored until it reached a constant value, at which point it was assumed that the transformation was complete for that value of magnetic field.

It was desired to learn more about the kinetics of the transformation. The (CC/PAA) system has severe limitations in this regard because of its narrow liquid crystal state temperature range. For this reason we used a nematic with a wider liquid crystalline range; it was ($p$-ethoxyphenylazo) phenyl heptanoate which has a nematic range from 60–119 °C. This material was doped with a small amount of (CC), 0.75% proving convenient for preliminary work. (Figure 5

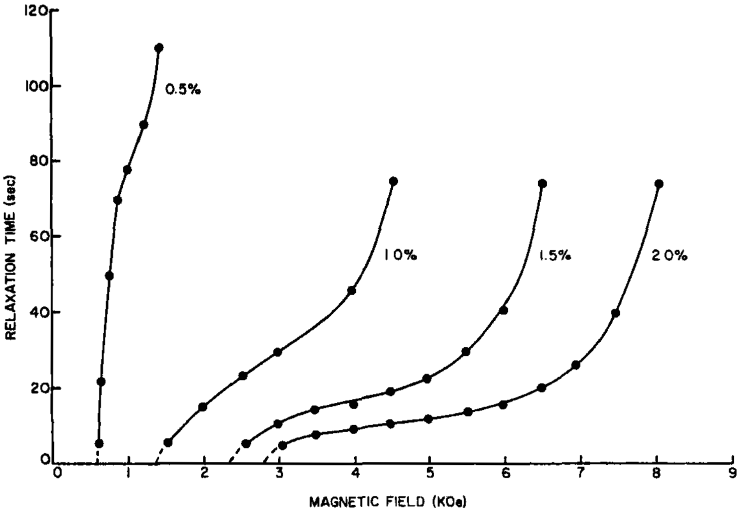

Figure 4. The relaxation time for the nematic to cholesteric transition versus magnetic field in the (CC/PAA) system for various concentrations of (CC), at 122 °C.

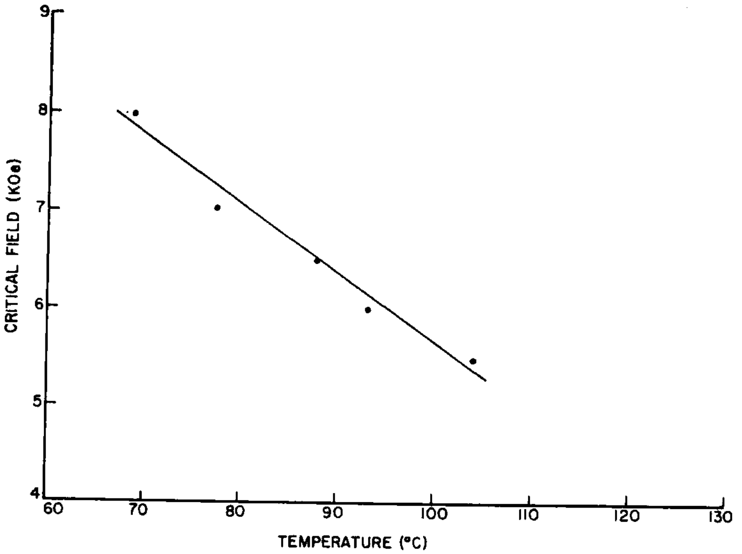

Figure 5. The critical field versus temperature in the CC/(60–119 °C) system for 0.75% CC.

shows the critical field, determined from attenuation measurements, as a function of temperature. This is the first report of critical field variation over a wide temperature range, as far as the author is aware.) Curves similar to Fig. 4 were obtained for this system at different temperatures. A question arises as to which relaxation times one should compare at the different temperatures, due to the fact that the critical field changes with temperature. Also the magnitude of the field-induced attenuation changes slightly with temperature. The most consistent approach seemed to be to take the times corresponding to the same relative attenuation change, $\Delta\alpha/\alpha_0$, where $\alpha_0$ is the total attenuation change induced by the $H$-field and $\Delta\alpha$ is the change at some field lower than the critical field. Figure 6 shows the results of determining the relaxation time as a function of temperature. The top line is for $\Delta\alpha/\alpha_0 = 0.115$ and the bottom line for $\Delta\alpha/\alpha_0 = 0.213$. Assuming a simple activated process, the following law should hold between the relaxation time $\tau$ and the absolute temperature $T$,

$$\tau = \tau_0 \exp\,[\Delta H/RT],$$

where $\Delta H$ is the activation energy and $R$ the gas constant. A least

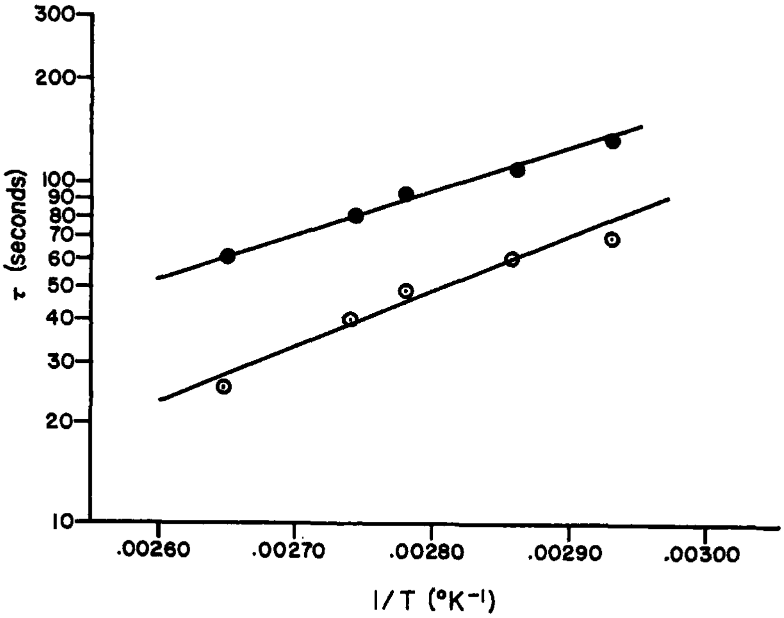

Figure 6. Relaxation time versus temperature in the CC/(60–119 °C) system.

squares fit of the top curve gives

$$\tau = \exp[2.85(10^3)/T],$$

and the bottom curve is given by

$$\tau = \exp[3.64(10^3)/T],$$

which correspond to activation energies of 0.246 eV/molecule and 0.313 eV/molecule, respectively. Although we have not made a complete study, the kinetics appear to be independent of the initial preferred direction of the nematic state with respect to the *k*-vector. At this preliminary state it does not seem appropriate to ascribe much significance to the difference in the values of these two activation energies.

## 3. Discussion

Our results confirm the fact that the cholesteric–nematic transformation is identical in many respects in both thin film and bulk specimens.

No theory exists at present for the field dependent attenuation in cholesteric liquid crystals, although a theory is available for nematics.(9) It is hoped that our work here will serve as incentive for such a theoretical development, and in this regard we offer a few additional observations. It would appear from our preliminary work that most of the field dependent attenuation comes from helix destruction and not very much from the lining up of the helical axis.† We derived this information from attenuation versus field measurements in a 1.75 : 1 weight mixture of (CC) and cholesteryl myristate. This material has a negative magnetic anisotropy ($\Delta\chi < 0$) which should preclude helix destruction.(11) The material undergoes helical inversion at about 43 °C. A very small change in attenuation with field was observed in the vicinity of the inversion temperature. This change was no more than one-sixth that seen in the (CC/PAA) system ($\Delta\chi > 0$). We attribute this small change to the lining-up of all the individual helical axes.

We are aware of only one other study concerned with the kinetics of the transformation, and that was done by the Xerox liquid crystal group.(12) They used thin films and drove the transformation with an $E$-field. There are numbers of similarities in their work and ours. One of the main differences is that when they reduce their bias field to zero, the relaxation times are still many seconds. Although it is not possible for us to reduce the field to zero very quickly, it is obvious that our relaxation times are considerably below theirs for low fields. This difference is probably due to a much larger surface effect acting in the thin film work.

At this preliminary stage we can only say that the activation energy for "coiling-back" to the cholesteric state is some 0.3 eV. This seems to be the first report of an actual value for the activation energy for the nematic–cholesteric transition. If indeed there is a true difference between the two activation energies reported here, it may be possible with further work, to derive some significant information concerning the variation of free energy of the cholesteric state with magnetic field.

† There is no indication of conical helical perturbation(2,10) in our results. There should be none in (PAA) because $k_{33} > k_{22}$ (Ref. 2).

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