[9]L. J. Lanzerotti, A. Hasegawa, and N. A. Tartaglia, J. Geophys. Res. 77, 6731 (1972).

[10]J. A. Jacobs and K. Sinno, Geophys. J. Roy. Astron. Soc. 3, 333 (1960).

[11]N. C. Maynard and D. P. Cauffman, J. Geophys. Res. 78, 4745 (1973); N. C. Maynard, private communications.

[12]C. R. Chappell, Rev. Geophys. Space Phys. 10, 951 (1972).

[13]C. Uberoi, Phys. Fluids 15, 1673 (1972).

[14]$\nabla \cdot \vec{\xi} = 0$ is used here for simplicity and is not essen-

tial to present results. If we assume adiabatic compression, Eq. (2) remains essentially the same so long as $|k_x^2| \gg |k_z^2|$.

[15]Z. Sedláček, J. Plasma Phys. 5, 239 (1971).

[16]R. K. Burton, C. T. Russel, and C. R. Chappell, J. Geophys. Res. 75, 5582 (1970).

[17]C. R. Chappell, K. K. Harris, and G. W. Sharp, J. Geophys. Res. 75, 50 (1970).

[18]Damped surface eigenmodes have been identified in laboratory θ-pinch experiments (W. Grossman and J. A. Tataronis, to be published).

Tricritical Behavior in a Liquid-Crystal System*

P. H. Keyes, H. T. Weston, and W. B. Daniels
Department of Physics, University of Delaware, Newark, Delaware 19711
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The isotropic–cholesteric and cholesteric–smectic-A phase transitions in cholesteryl oleyl carbonate have been studied for pressures up to 7 kbar. The latter transition possesses a tricritical point at 2.66 kbar and 60.3°C, where the behavior changes from first to second order.

Recently, there has been considerable interest in the study of the tricritical point, where a line of phase transitions changes from first to second order. This interest is largely motivated by the fact that the conventional scaling approach, which has been so highly successful in describing second-order transitions, breaks down near a tricritical point.[1]

Examples of systems having tricritical points include the metamagnetic-antiferromagnetic transitions in dysprosium aluminum garnet,[2] $FeCl_2$,[3] and $Ni(No_3)_2 \cdot 2H_2O$,[4] the λ transition in He^3-He^4 mixtures,[5] and the orientational order-disorder transitions in NH_4Cl[6] and ND_4Cl[7] crystals. It is the primary purpose of this Letter to report the discovery of a new type of tricritical point which occurs at higher pressures for the transition between the smectic-A and cholesteric liquid-crystalline phases of cholesteryl oleyl carbonate (COC).

Until recently, all liquid-crystal transitions were believed to be first order. It was originally suggested by McMillan,[8] based upon mean-field calculations for a specific interaction model, that the transition between the smectic-A and the nematic or cholesteric phases might be second order under certain conditions. In particular, he predicted that for a homologous series of liquid crystals, the discontinuity in the order parameter at the transition should decrease with chain length and eventually vanish for sufficiently short

molecules, thus rendering the transition second order. This trend was subsequently verified experimentally by Doane et al.,[9] who found one instance of a nematic–smectic-A transition which was second order or at least very nearly second order.

It seemed quite plausible that the behavior observed by varying chain length could also be induced for molecules of a given size through changes in the density. Therefore, we began an investigation of the phase transitions of the liquid crystal COC at elevated pressures. This substance was chosen primarily because of its ready availability and convenient temperature ranges for the smectic-A and cholesteric phases. To the best of our knowledge, the only other liquid crystal which has been investigated at high pressures is p-azoxyanisole,[10] which exhibits only the nematic mesophase.

The COC used in this study was obtained from Eastman Organic Chemicals and was not further purified. A sample of approximately $\frac{1}{2}$ mm thickness was sandwiched between two cylindrical glass windows and contained at the perimeter by a tightly stretched piece of fluran tubing. This arrangement was placed in a high-pressure optical cell filled with Octoil S, which was used as the pressurizing fluid. High pressures were generated by means of a reciprocating hand pump and measured with a Bourdon gauge having an accuracy of 100 lb/in.^{2} The temperature of the cell

was controlled to better than 0.01°C. The beam
from a Spectra-Physics model 165 argon-ion la-
ser tuned to the 4545-Å wavelength was passed
through the windows of the high-pressure cell and
the sample holder.

The location of a phase transition was observed
by slowly varying either the pressure or the tem-
perature until there occurred a sudden change in
the intensity of the transmitted light as measured
by a photocell. In this manner the phase diagram
shown in Fig. 1 was constructed. The melting
and vaporization curves were not investigated in
this study.

Particular attention was focused on the choles-
teric–smectic-A transition where a tricritical
point was anticipated. At a given pressure the
smectic phase was approached from the choles-
teric by slowly lowering the temperature in equal
steps of approximately 0.3°C. The transmitted
intensity decreased as the transition was ap-
proached, reaching a minimum just above the
transition temperature. This behavior is very
much like that found in systems having critical
points.

Below the transition two quite different types
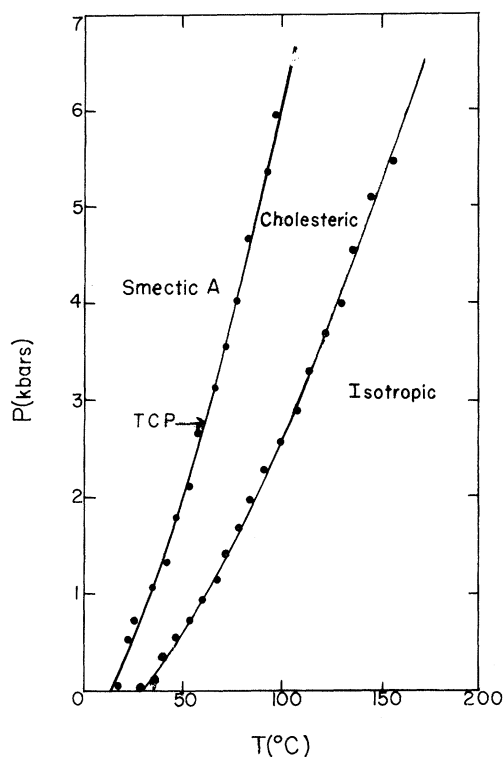of behavior were found. At higher pressures,

the intensity increased smoothly as the sample
was lowered further below the transition temper-
ature, signifying a continuous variation of the or-
der parameter and, hence, a second-order tran-
sition. The equilibration times after each tem-
perature change were comparable to those found
above the transition and of the order of 5–10 min.

At lower pressures the intensity was not a con-
tinuous function of temperature, indicating first-
order behavior. Immediately after the sample
crossed through the transition, the transmitted
intensity began to rise steadily and continued to
do so for several hours with no sign of saturating.
As a practical matter, then, it was difficult to
obtain a full measure of the discontinuity since
the sample was never observed to reach equilib-
rium. It was decided that by adopting a standard
waiting period of four hours, the resulting dis-
continuities would be large enough to differenti-
ate clearly between the regions of first- and sec-
ond-order transitions, while, at the same time,
the constancy of the temperature and pressure of
the sample could be guaranteed.

The discontinuities in the transmitted intensity
measured in this manner have an estimated re-
producibility of 20% and are shown in Fig. 2 as a
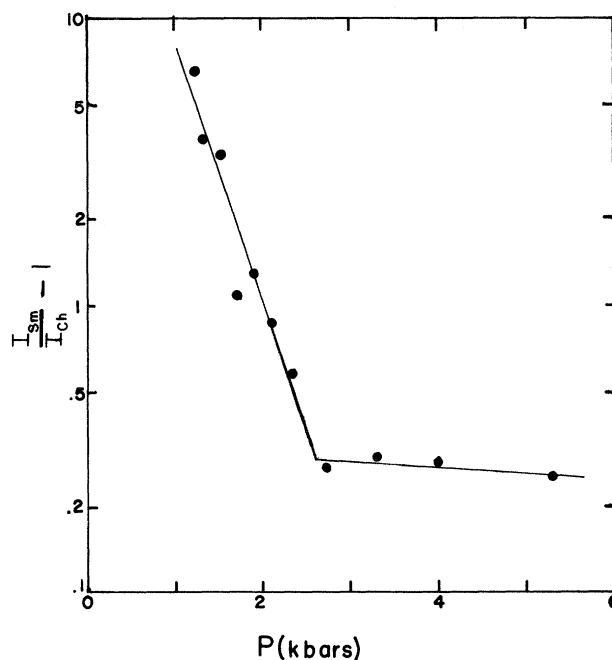function of the transition pressure. The straight

FIG. 1. The P-T phase diagram for cholesteryl oleyl
carbonate. "TCP" denotes the tricritical point.

FIG. 2. The discontinuity in the transmitted light in-
tensity as a function of transition pressure. I_{Ch} and
I_{Sm} denote the intensity on the two sides of the choles-
teric-smectic phase boundary.

line segments are linear least-squares fits to the two distinct portions of the data. The tricritical point is identified by the intersection of these two lines at a pressure of 2.66 ± 0.12 kbar, corresponding to a tricritical transition temperature of $60.3 \pm 1.5°C$. The apparent discontinuity for the region above the tricritical point reflects the fact that, even though the transition here is continuous, the intensity one step below the transition temperature is higher than at the transition itself, where it is a minimum.

Ideally, the pretransitional intensity data could also be used to calculate the excess turbidity near the transition and, therefore, certain critical and tricritical exponents. While this should be relatively straightforward for a nematic-smectic transition, it is a complicated proposition for a cholesteric-smectic transition, at least when visible light is used. This is because the ordering of the molecules into the planar arrangement of the smectic phase is accompanied by the untwisting of the cholesteric helix, thereby leading to interference effects which are responsible for the well-known pretransitional color bands. These bands are superimposed on the critical scattering behavior and, unfortunately, there is no known way of accurately assessing the individual contributions of these two effects. As we have determined through the use of a 6328-Å helium-neon laser, the interference effects seem to be greater for longer wavelengths, suggesting that these problems could be surmounted by probing this transition with x rays. Alternatively, one could discover and study the analogous tricritical phenomena for a nematic–smectic-A transition, where such interference effects would be absent.

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[1]R. B. Griffiths, Phys. Rev. Lett. 24, 715 (1970), and Phys. Rev. B 7, 545 (1973); E. K. Riedel, Phys. Rev. Lett. 28, 675 (1972); F. Harbus and H. E. Stanley, Phys. Rev. Lett. 29, 58 (1972).

[2]B. E. Keen, D. Landau, B. Schneider, and W. P. Wolf, J. Appl. Phys. 37, 1120 (1966); D. Landau, B. E. Keen, B. Schneider, and W. P. Wolf, Phys. Rev. B 3, 2310 (1971); W. P. Wolf, B. Schneider, D. Landau, and B. E. Keen, Phys. Rev. B 5, 4472 (1972).

[3]I. S. Jacobs and P. E. Lawrence, Phys. Rev. 164, 866 (1967).

[4]V. A. Schmidt and S. A. Friedberg, Phys. Rev. B 1, 2250 (1970).

[5]E. H. Graf, M. Lee, and J. D. Reppy, Phys. Rev. Lett. 19, 417 (1967); G. Goellner and H. Meyer, Phys. Rev. Lett. 26, 1543 (1971).

[6]D. W. Garland and B. B. Weiner, Phys. Rev. B 3, 1634 (1971); I. J. Fritz and H. Z. Cummins, Phys. Rev. Lett. 28, 96 (1972).

[7]W. B. Yelon, D. E. Cox, P. J. Kortman, and W. B. Daniels, to be published.

[8]W. L. McMillan, Phys. Rev. A 4, 1238 (1971).

[9]J. W. Doane, R. S. Parker, B. Cvikl, D. L. Johnson, and D. L. Fishel, Phys. Rev. Lett. 28, 1694 (1972).

[10]G. A. Hulett, Z. Phys. Chem. Stoechiom. Verwandschaftslehre 28, 629 (1899); A. Puschin and W. Grebenschtschikow, Z. Phys. Chem. Stoechiom. Verwandschaftslehre 124, 270 (1926); J. Robberecht, Bull. Soc. Chim. Belg. 47, 597 (1936); B. Deloche, B. Cabane, and D. Jerome, Mol. Cryst. Liquid Cryst. 15, 197 (1971); J. R. McColl, Phys. Lett. 38A, 55 (1972); J. R. McColl and C. S. Shih, Phys. Rev. Lett. 29, 85 (1972).