for an excitation energy close to 33.614 cm^{-1} (corresponding to an energy located between the $40p$ and $41p$ levels for an unperturbed atom) is shown in Fig. 1, which also gives the best fit to the Fano theoretical formula. The corresponding parameters are

$$\Gamma = 0.13 \text{ GHz and } q = 3.3.$$

Of course, before entering upon a quantitative interpretation of such parameters, a more extensive study on a broader spectral range and for many different values of the applied field must be carried out. However, our present results already demonstrate unambigously the validity of the process suggested by Littman, Kash, and Kleppner and show that it is possible to obtain experimentally precise values of the parameters which characterize the interaction between a quasistable Stark level and the underlying ionization continua. In addition, it must be noticed that the resonances are superimposed to strong oscillations of the continuum, the period being approximately 13 GHz. We have not yet found a definite explanation of such oscillations but it must be emphasized that the phenomenon exhibits some similarities with the broad resonances observed by Freeman *et al.*[10]

Further experiments are certainly needed.

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[1] For references see, for example, Proceedings of a Conference on Atomic and Molecular States Coupled to a Continuum, Colloq. Int. CNRS No. 273, pp. 55–317.

[2] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).

[3] W. Cooke and T. Gallagher, Phys. Rev. A 17, 1226 (1978).

[4] S. Feneuille, S. Liberman, J. Pinard, and P. Jacquinot, C. R. Acad. Sci., Ser. B 284, 291 (1977); P. Jacquinot, S. Liberman, and J. Pinard, Colloq. Int. CNRS 273, 215–226 (1977); S. Liberman and J. Pinard, Phys. Rev. A (to be published).

[5] M. G. Littman, M. M. Kash, and D. Kleppner, Phys. Rev. Lett. 41, 103 (1978).

[6] See, for example, R. J. Damburg and V. V. Kolosov, J. Phys. B 9, 3149 (1976), and Phys. Lett. 61A, 233 (1977), and Opt. Commun. 24, 211 (1978).

[7] U. Fano, Phys. Rev. 124, 1866 (1961).

[8] S. Feneuille and P. Jacquinot, Atomic Physics-6 (Plenum, to be published).

[9] J. Pinard and S. Liberman, Opt. Commun. 20, 344 (1977).

[10] R. R. Freeman, N. P. Economou, G. G. Bjorklund, and K. T. Lu, Phys. Rev. Lett. 41, 1463 (1978).

Polymorphism in a Lamellar Liquid-Crystal Bilayer System

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The lamellar liquid-crystal phase, L_α, of the potassium-palmitate–water system is shown to be actually polymorphic. Using deuterium magnetic resonance as well as birefringence observations, two sharp phase transitions are observed in the simple neat soap bilayers. Optical conoscopy shows the high-temperature phase to be uniaxial and the other two to be biaxial. Deuteron magnetic resonance shows that each phase transition is accompanied by a change in orientational order.

The lamellar liquid-crystal phase, L_α, in bilayer systems has not generally been regarded as being polymorphic[1] although polymorphism in membrane bilayers has been observed[2] and peculiar behavior suggestive of phase transitions has been observed in nuclear magnetic resonance (NMR) measurements of self-diffusion,[3] spin-lattice relaxation,[4] and quadrupolar splitting[5] in some simple soap systems. In this Letter, we wish to show both NMR and optical evidence for two distinct phase transitions within the lamellar L_α (soap boilers' neat soap) region of the potassium-palmitate–water system as the temperature is varied. This region is at temperatures above the gel phase and below the superneat phase of this system. The NMR studies were made from perdeuterated samples of potassium palmitate and the optical studies from nondeuterated sam-

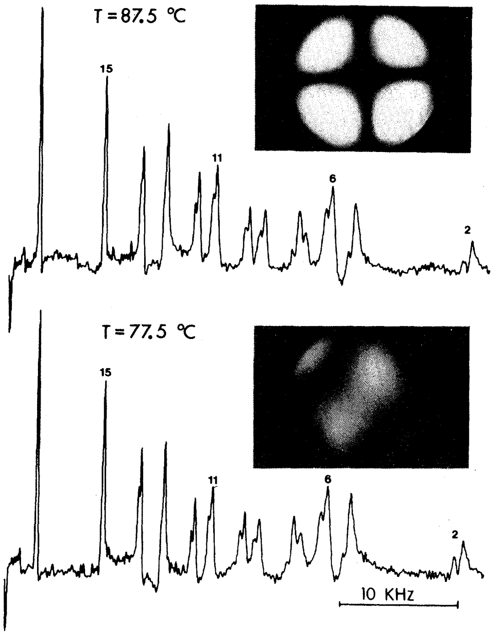

FIG. 1. Deuterium spectra at 9.2 MHz of perdeuterated potassium palmitate from homeotropically aligned samples with the bilayer normal parallel to the magnetic field. The samples contained a (72% potassium plamitate)-(28% water) mixture. One-half of the spectrum in two different L_α phases after 4000 and 8000 sweeps, respectively, are shown. Insets show the optical conoscopic patterns observed in each phase.

ples. Both the deuterated and nondeuterated samples were shown to exhibit the phase transitions.

Potassium palmitate d_{31} was prepared by heating a mixture of palmitic acid d_{31} (Merck, 2.0 g, 7.4 mM), KOH (475 mg), and H_2O (1.1 g) at 60° with stirring for 5 min. Purification was achieved by recrystallization from absolute ethanol to give 1.58 g (69.6%) of the salt. Nondeuterated potassium palmitate was prepared in an identical manner from palmitic acid.

Aligned samples for the NMR studies were prepared from a stack of ~30 thin glass slides with no spacers between the slides other than the potassium-palmitate–water mixture. The aligned samples for the optical studies were prepared in flat rectangular microslides (Vitro Dynamics, Inc.) of thicknesses 200, 300, and 400 μm. The glass surfaces in both cases were prepared in the usual fashion for homeotropic alignment[6] and the samples sealed.

Figure 1 shows typical DMR (deuteron magnetic resonance) spectra obtained from a macroscopically aligned sample of 72% (by weight) potassium palmitate and 28% water mixture. Each spectrum was taken at a different temperature well above the gel transition and belong to a different phase which we label as phase I and II, the insets show the corresponding observed conoscopic figures which are typical of uniaxial and biaxial phases.[7]

Each spectral line (some lines partially overlap) corresponds to a deuterion pair from a segment of the alkyl chain. The assignment of the lines is well understood in terms of progressive disorder along the chain.[8] Each resolved spectral line appears as a doublet (actually an unresolved triplet) attributed to the dipole-dipole interaction between deuterium spins on each segment.[9] Theoretically each splitting $\delta\nu_i$ is a triplet with $\delta\nu_i^{(1)} = \delta\nu_i^Q - \frac{3}{2}D$, $\delta\nu_i^{(2)} = \delta\nu_i^Q + \frac{1}{2}D$, and $\delta\nu_i^{(3)} = \delta\nu_i^Q + \frac{3}{2}D$, where D is the strength of the dipole interaction[9] and $\delta\nu_Q$ is the quadrupole splitting. $\delta\nu_i^{(1)}$ and $\delta\nu_i^{(2)}$ are the lines of strongest intensity and can be identified in most of the spectral lines in Fig. 1 with the effect becoming more pronounced on the larger quadrupole splittings corresponding to the more highly ordered segments of the chain. The observed values of $\delta\nu_i^{(1)}$ and $\delta\nu_i^{(2)}$ are consistent with that expected for a separation distance of 1.59 Å between the segmental deuterons and for a flexible chain which prefers, on the average, the all-*trans* conformation. This feature did not appear to change throughout the temperature range of the L_α region, indicating that the all-*trans* conformation is the most preferred conformation in all three phases.

Figure 2 shows the temperature dependence of four of the splittings $\delta\nu_i^{(2)}$ obtained from selected spectra.

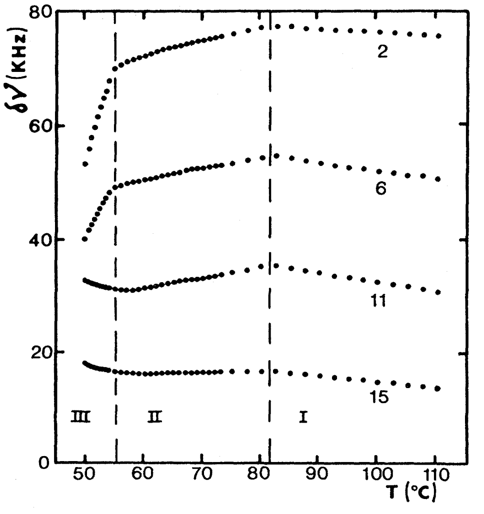

FIG. 2. Temperature dependence of four selected spectral splittings.

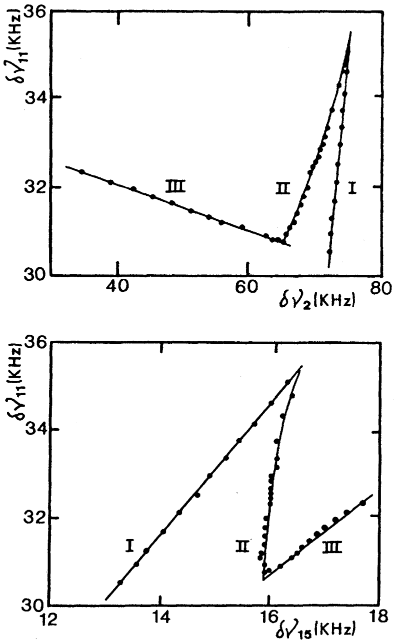

FIG. 3. Plots of one quadrupole splitting vs another where each point corresponds to a different temperature. Solid lines are drawn to aid the eye.

These plots are not as enlightening as plots of one splitting versus another as shown in Fig. 3 where we have removed the dipolar contribution from $\delta\nu_i^{(2)}$, using the expression $\delta\nu_i^{Q}=\frac{1}{4}(\delta\nu_i^{(1)}+3\delta\nu_i^{(2)})$. Similar plots using $\delta\nu_i^{(1)}$ or $\delta\nu_i^{(2)}$ show the same features.

The phase transitions involving orientational order or molecular conformations are easily observed in these plots.[10] This follows from the nature of the time-averaged quadrupole interaction of the deuterium spins and its dependence on the molecular and conformational order. For an experimental arrangement in which the director (bilayer normal) is parallel to the magnetic field direction, the quadrupole splitting for a spin $I=1$ can be written[10-12]

$$\delta\nu_i^{Q}=\tfrac{3}{2}\nu_Q^{i}[\langle\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2})(\tfrac{3}{2}\cos^2\beta_i-\tfrac{1}{2}\rangle+\tfrac{4}{3}\langle\sin^2\theta\cos2\psi\sin^2\beta_i\cos2\alpha_i\rangle+\tfrac{4}{3}\langle\sin2\theta\sin\psi\sin2\beta_i\sin\alpha_i\rangle], \quad (1)$$

where ν_Q^{i} is the quadrupole coupling constant for the ith site in the molecule. The instantaneous orientation of the C-D$_i$ bond at the ith site in the molecule relative to a common molecular frame is defined by the polar angle β_i and azimuthal angle α_i. Since the lipid molecule is flexible, these angles are modulated by fluctuations in the conformation of the molecule. The instantaneous orientation of the molecular frame relative to the space-fixed bilayer normal is given by the polar angle θ and azimuthal angle ψ. These angles are also time dependent but modulated by thermal fluctuations in the orientation of the molecular frame relative to the bilayer normal. In Eq. (1) we have used the fact that the liquid crystalline phases under consideration are, on the average, apolar. This requires diffusion of the molecules across the bilayer on the time scale of the NMR measurement.[13] Removing the apolar feature of the phase would simply add two more terms to Eq. (1) and in no way alter the arguments in this Letter.

The linearity of the plots in Fig. 3 for phases I and III indicates that the temperature dependence of one of the terms in Eq. (1) dominates that of the others for these phases. This follows in that for such a case we can write

$$\delta\nu_i^{Q}=a_{ij}\delta\nu_j^{Q}+b_i, \quad (2)$$

where a_{ij} and b_i are constants. The discontinuities in Fig. 3 therefore characterize phase transitions in which there is either an onset of a different orientational order or an abrupt change in the preferred comformation of the molecule. The coefficients a_{ij} and b_i are different for phases I and III suggesting that the dominant temperature-dependent term in Eq. (1) and hence the molecular or conformational orientational order is different for each of these phases. The plot in Fig. 3 for phase II is not linear, indicating that more than one temperature-dependent term in Eq. (1) is involved.

The identification of the terms in Eq. (1) involved in the discontinuities of Fig. 3 and hence the specific changes in orientational or conformational order occurring at each of the phase transitions is beyond the scope of this Letter.

There are several other features of the DMR spectra worth pointing out. One is that the spectra in all three phases show that the chains are in a flexible "liquid" state characteristic of the α variety of lamellar phases. Another is that the time-averaged quadrupole interaction of all deuterium spins share the same principal axis which is parallel to the glass slides in all three phases. This is evidenced by the $P_2(\cos\theta_0)$ angular dependence of the quadrupole splittings where θ_0 is the angle between the direction of the magnetic field and the direction normal to the glass slides. The lines become broader at angles $0° < \theta_0 < 90°$ but we were unable to distinguish between the misalignment of the director and biaxiality in their contribution to the broadening effect. Finally, we should point out that the variation of the spectral lines with temperature in Fig. 2 are continuous across the phase transitions. Similar data reported by Davis and Jeffrey[5] on the same compound show a discontinuity near the temperature we report here as the II-III transition temperature. This could indicate that the character of this particular phase transition is concentration or purity dependent.

Both phase transitions could also be observed by changes in texture and conoscopic figures under a polarizing microscope in aligned samples. From the optical studies it was found that both of these transition temperatures, as well as the gel-phase transition temperature, increased with decreasing water content.

The optical studies of the homeotropically aligned samples showed, furthermore, that upon increasing the temperature in phase I an instability would form and persist up to 300°C, the limiting temperature of the heating stage. Upon cooling, the instability vanished at about the same temperature of its onset. The instability appeared to be of the type described by Rosenblatt *et al.*[14] A DMR study of D_2O spectra showed a surprising increase in the orientational order of the water in the region of the instability. This increase in the splitting of the D_2O spectra was not accompanied by a broadening of the spectral lines nor was a similar increase observed in the spectral lines of the lipids. Further studies are required to fully understand this behavior.

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[1] P. Ekwall, in *Advances in Liquid Crystals*, edited by G. H. Brown (Academic, New York, 1975), Vol. 1, pp. 1–142.

[2] L. Powers and P. S. Pershan, Biophys. J. 20, 137 (1977).

[3] R. Blinc, K. Easwaran, J. Pirš, M. Volfan, and I. Zupančič, Phys. Rev. Lett. 25, 1327 (1970).

[4] J. H. Davis, K. R. Jeffrey, and M. Bloom, J. Magn. Reson. 29, 191 (1978).

[5] J. H. Davis and K. R. Jeffrey, Chem. Phys. Lipids 20, 87 (1977).

[6] F. J. Kahn, Appl. Phys. Lett. 22, 386 (1973).

[7] T. Taylor, J. L. Fergason, and S. L. Arora, Phys. Rev. Lett. 24, 359 (1970).

[8] B. Mely, J. Charvolin, and P. Keller, Chem. Phys. Lipids 15, 161 (1975).

[9] Z. Luz, R. C. Hewitt, and S. Meiboom, J. Chem. Phys. 61, 1758 (1974).

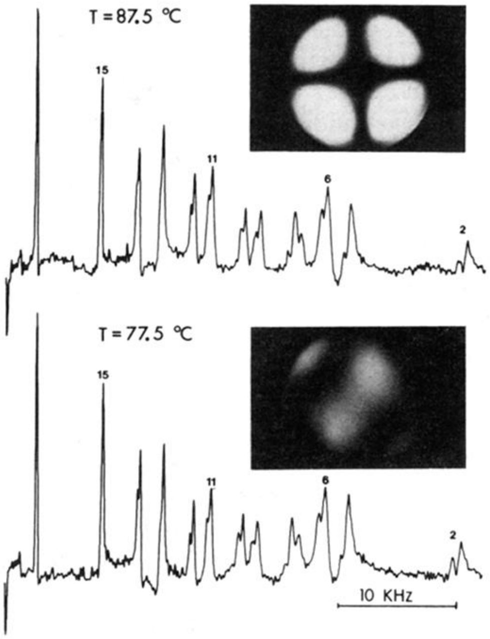
[10] P. J. Bos and J. W. Doane, Phys. Rev. Lett. 40, 1030 (1978).

[11] P. J. Bos, M. Neubert, and J. W. Doane, to be published.

[12] J. W. Doane, in *Magnetic Resonance Studies of Phase Transitions*, edited by F. J. Owens, C. P. Poole, and H. A. Farach (Academic, New York, to be published).

[13] By using pulsed gradient techniques, diffusion parallel to the bilayer normal in the potassium-palmitate–water system was measured to be $\sim 10^{-9}$ cm^2/sec by P. Ukleja and J. W. Doane, to be published.

[14] C. S. Rosenblatt, R. Pindak, N. A. Clark, and R. Meyer, J. Phys. (Paris) 38, 1105 (1977).



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