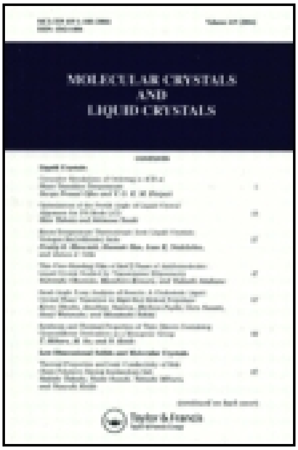

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Highly Curved Defects in Lyotropic Lamellar Phases

Manuel Allain [a] [b] & Jean-Marc Di Meglio [c]

[a] DTech/SESI-CEN, B. P. 6,92260 Fontenay-aux-Roses, France

[b] Laboratoire de Physique des Solides, Univ. Paris-Sud, 91405, Orsay, France

[c] Laboratoire de Physique de la Matière Condensée, Collège de France, 11 Place Marcelin Berthelot, 75231, Paris, Cédex 05 France

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Highly Curved Defects in Lyotropic Lamellar Phases†

MANUEL ALLAIN

DTech/SESI-CEN, B.P. 6,92260 Fontenay-aux-Roses France,
and Laboratoire de Physique des Solides, Univ. Paris-Sud, 91405 Orsay France

and

JEAN-MARC DI MEGLIO

Laboratoire de Physique de la Matière Condensée, Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cédex 05 France

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Lamellar phases of non ionic surfactant/water systems were investigated by two different experimental methods:

(i) Spin labelling, which revealed the existence of highly curved defects, precursors of the high temperature phase, whose concentration increased with temperature.

(ii) Electron microscopy of replicas of freeze-fractured samples which showed the existence of screw dislocations, whose concentration increased with temperature. These screws are the components of dislocation loops crossing the layers.

Parts of the highly curved areas indicated by ESR are attributed to the cores of these dislocations.

ESR EXPERIMENTS

Introduction

The spin labelling method is very suitable for the study of lyotropic systems[1] since its characteristic frequency is of the same order as that of molecular motion. In particular, when a surfactant molecule diffuses over a curved surface, its mean axis undergoes a disorientation[2]

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and if R is the radius of curvature and $D_{\ell at}$ the lateral diffusion constant, we observe modifications of the ESR spectra (*i.e.* line broadening and shifting of peak positions) when

$$\frac{R^2}{4D_{\ell at}} < 10^{-6} s \quad \text{(see ref. 3).}$$

Observations of defects

As reported in a recent publication,[4] the spectra of the 73% $C_{12}E_5$ and the 73% $C_{12}E_6$ aqueous solutions were found to be the superposition of two different spectra: one with a very long angular correlation time ($\tau_R \rightarrow \infty$) which corresponds to the flat areas (lamellae) and the other with a short correlation time ($\tau_R \simeq 10^{-8}$s) which coresponds to highly curved areas ($R \simeq 15$ Å).

We attribute this to the presence of highly curved defects inside the layers, as layer edges (Figure 1). The exact structure of such defects, however, cannot be determined by the spin labelling method.

Figure 2 represents a typical spectrum for an oriented $C_{12}E_5$ sample. Spectral lines $L_1L_2L_3$ correspond to the flat regions and the lines M_1M_3 to the defects. The line shapes are very close to Lorentzian and we can thus determine the number of defects (more precisely the ratio of curved surface/total surface) by the following formula

$$N = \frac{h_M \Delta_M^2}{h_M \Delta_M^2 + h_3 \Delta_3^2} \quad (1) \quad \text{(see notation on Figure 2).}$$

Study of the numbers of defects with respect to temperature

The spectra of the two systems ($C_{12}E_5$ and $C_{12}E_6$) were recorded between 26 and 60°C.

Figure 3 represents the number of defects N as a function of temperature. N first increases slowly and then changes abruptly a few

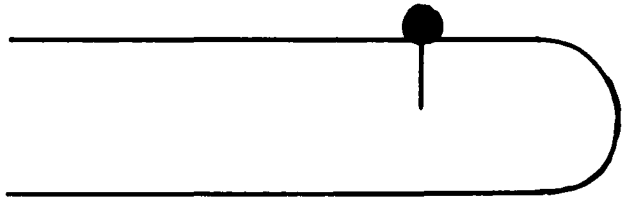

FIGURE 1 Schematic representation of an edge of lamella.

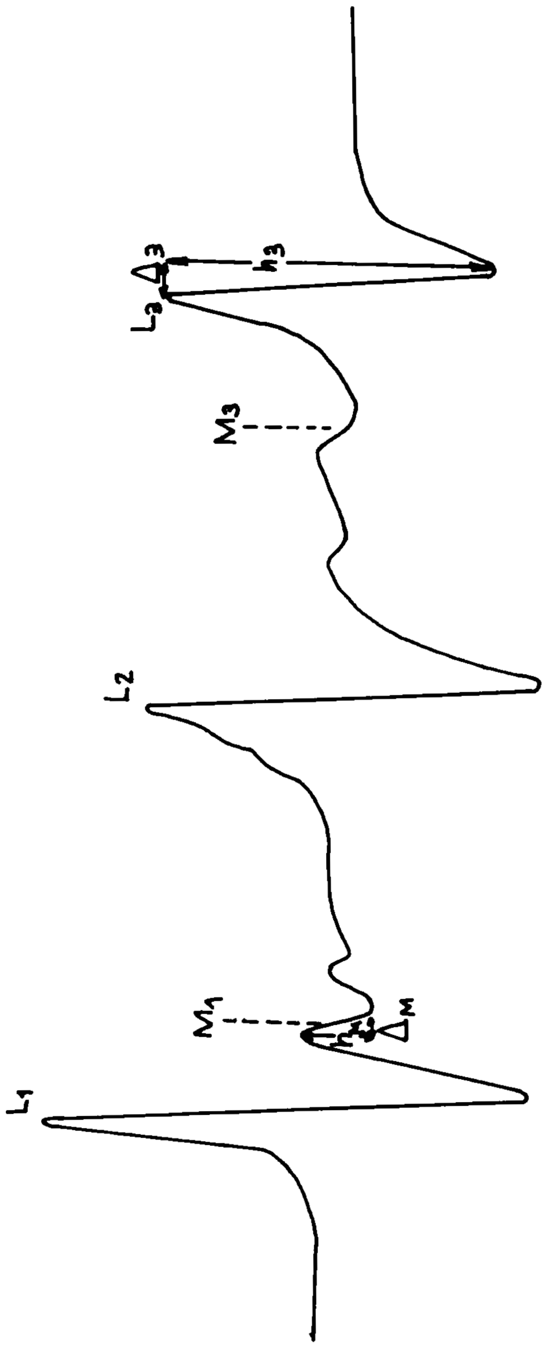

FIGURE 2 Typical spectrum of an oriented sample of lamellar $C_{12}E_5$.

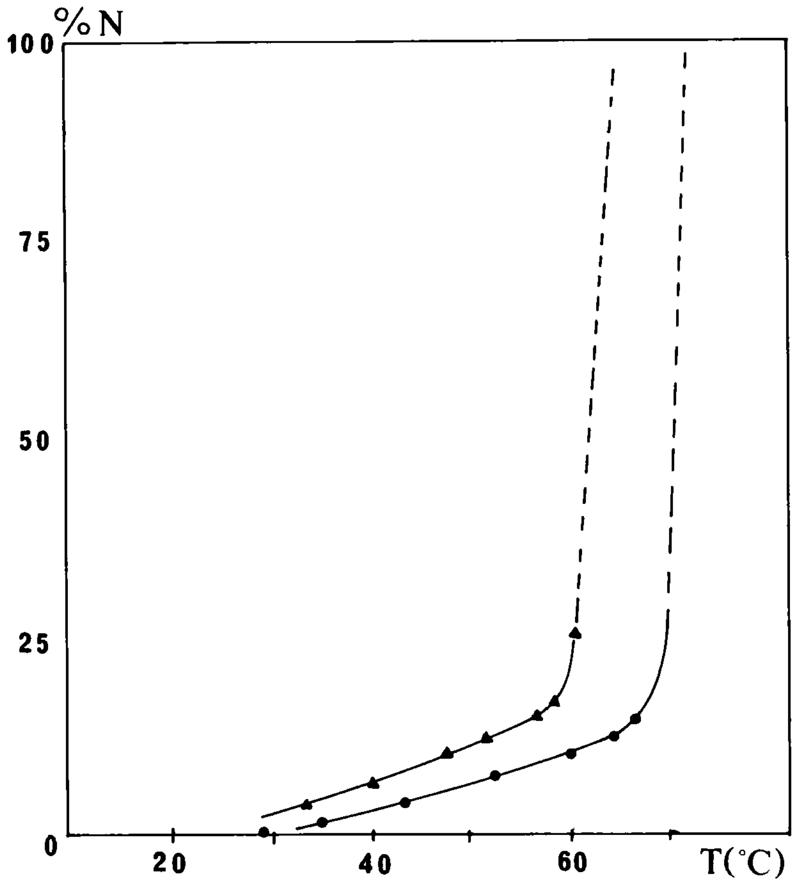

FIGURE 3 Number of defects with respect to the temperature.

● $C_{12}E_5$ system
▲ $C_{12}E_6$ system

degrees before the transition from the L_α phase towards the high temperature phase. The activation energy for the creation of defects may be computed from the slopes of Arrhenius plots. We found: $W = 6500$ K for $C_{12}E_5$ and $W = 5500$ K for $C_{12}E_6$.

ELECTRON MICROSCOPY STUDY

Introduction

The same systems have been observed by electron microscopy: samples, quenched from various temperatures (between 20°C and 60°C), were replicated after freeze fracture.

As reported in a recent publication,[5] each replica shows lamellar fracture faces as would be expected from the phase diagrams. Screw dislocations emerging from the fracture face are revealed by a step which ends in the middle of a smooth area. The Burgers vector of the observed screws is always equal to one repeat distance of the L_α phase.

Influence of temperature

At low temperature (20°C), a few screw dislocations intersect the fracture face. They are either isolated or gathered in twist walls (Figure 4). As the temperature rises from 20°C to 60°C the disorder increases (Figure 5), due to the increasing number of screw dislocations.

Screw dislocations organize as follows:

(i) screws of the same sign gather in walls made of up to 100 screws

(ii) screws of opposite sign gather two by two, connected by a step (Figure 5)

(iii) concentration of intersections of screws with the fracture face increases very abruptly near the transition (Figure 6).

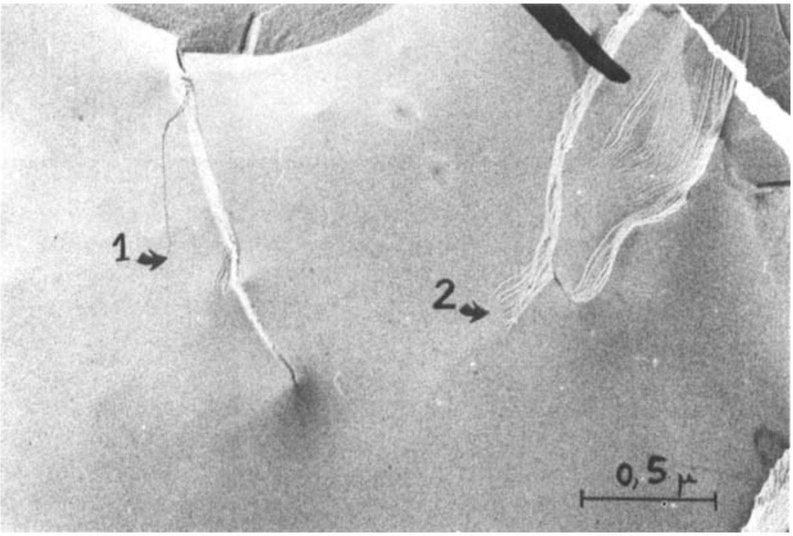

FIGURE 4 $C_{12}E_5$ 20°C. Arrow 1 shows isolated screw dislocation. Arrow 2 shows a wall.

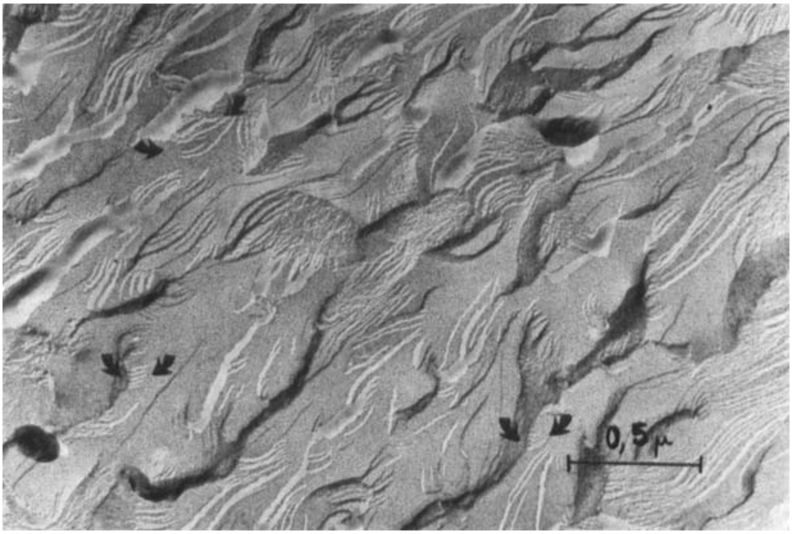

FIGURE 5 $C_{12}E_5$ 60°C. Disorder had increased with the occurrence of numerous screw dislocations. Arrows show pairs of screw dislocation of opposite sign linked by a step.

The Arrhenius plot yields a value of 6500 ± 1000 K for the activation temperature of formation in $C_{12}E_5$ and 5500 ± 1000 K in $C_{12}E_6$. At a given temperature there are more screws in $C_{12}E_6$ than in $C_{12}E_5$.

DISCUSSION

Comparison of ESR and electron microscopy

The first obvious point, if we compare the two previous experiments (see Figure 3 and 6) is a striking analogy between the increase of "curvature" and the increase of dislocation concentration as the temperature increases. This analogy appears also in the close similarity between the activation temperatures, for both systems, in the two experiments.

If we wish to make this qualitative evidence more quantitative, we are faced to the difficult problem of transforming a quantity of curved area into a dislocation concentration. According to a simple model (see Figure 7) we assume the core of the dislocations to be made of edges of lamellae of semicircular section. We may then calculate the curved area due to a concentration of infinite screw dislocations.

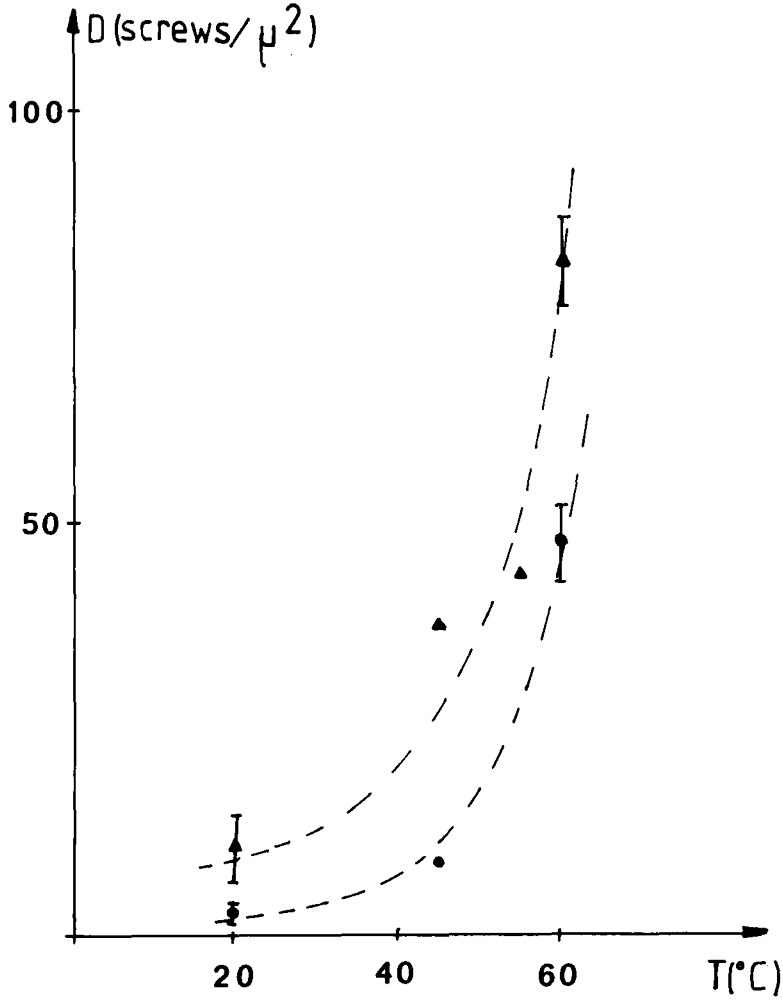

FIGURE 6 Concentration of intersections of screws with the fracture face as a function of temperature.

● $C_{12}E_5$ system
▲ $C_{12}E_6$ system

Assuming that screws are the only source of curvature, we find 50 times more "curvature" in the ESR experiment than with electron microscopy.

This large discrepancy may have three major origins:

(i) Defects observed by electron microscopy are defects remaining

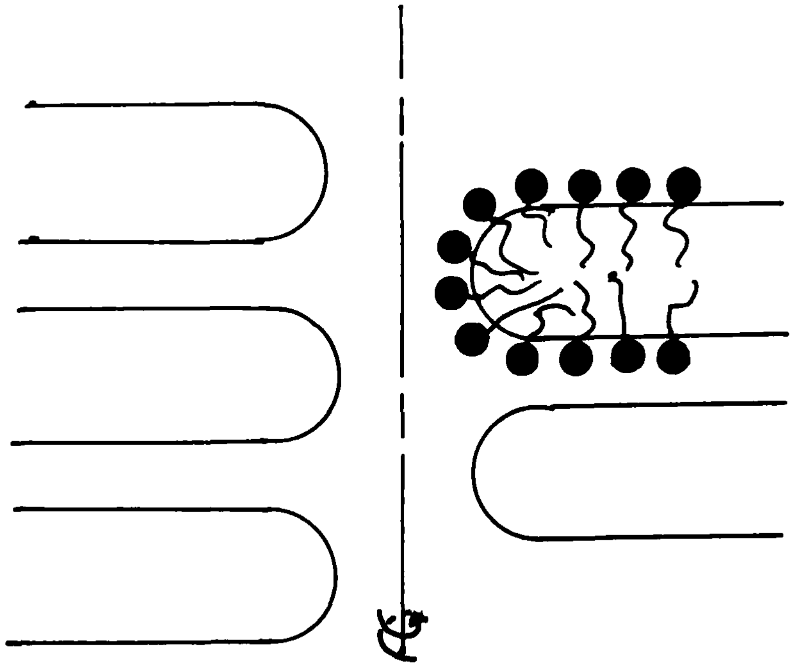

FIGURE 7 Simple model of the core of a screw dislocation.

after quench. Partial recovery during the quench itself could lead to an underestimate of the concentration measured by electron microscopy.

(ii) On the other hand, the ESR experiment is not a direct measure of curvature and the interpretation of ESR spectra in terms of curvature depends on a model.

(iii) The main source of error is due to the difficulty of linking quantitatively the two different sets of measurements. The present tentative attempt to relate ESR measured curvature to dislocation density is probably very crude. Screw dislocations may not be the only source of curvature: one can also visualize the presence of small dynamical pores, involving no transport of matter and so having a low energy, which could either disappear during quenching or be too small to be seen (diameter less than 40 Å). Points (i) and (iii) are expected to give rise to an underestimate of curvature in quenching experiments as compared to ESR experiments, which is what we actually find.

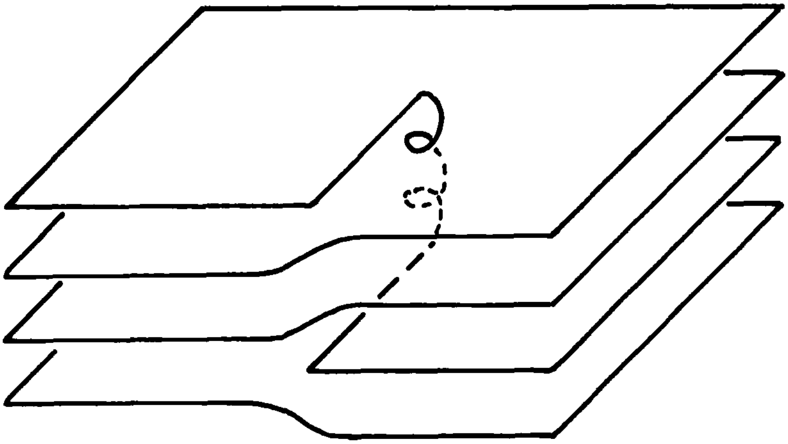

FIGURE 8 A model loop, made of two screw dislocations linked at their end by two edge dislocations, cut by a mediator plane.

Loop picture

In this paragraph we shall try to explain how screws organize. We shall use the second item of our observations: two screws of opposite sign are linked by a step. We then postulate that these screws belong to a dislocation loop crossing lamellae. Such a loop would be made of pieces of screw dislocations and edge dislocations linked together (Figure 8). Loops would pile up and screws of the same sign would build walls. On micrographs, we cannot measure the length of screw dislocations (which cross lamellae and are rarely parallel to the fracture face). We can, however, estimate the length of edge dislocations in a loop by measuring the length of the step linking two screws of opposite sign. Knowing the concentration of defects and of curved area we then deduce the length needed for screws, but this calculation gives an unrealistic result (l = 0.3 repeat distance) and again shows that the core of these defects cannot be the only source of curvature.

This description does not change the quantitative aspect of the problem, in fact for the same reasons which we gave in paragraph 3.1, it fits observations better than an "infinite screw picture."

CONCLUSION

Highly curved defects have been revealed by ESR in lamellar phases of $C_{12}E_5/H_2O$ and $C_{12}E_6/H_2O$ systems. The concentration of these defects increases with temperature, very abruptly near the transition. At a given temperature, more defects are present in $C_{12}E_6$ system than in $C_{12}E_5$ system.

Electron microscopy of replicas of the same systems, showed the existence of defects whose concentration increases with temperature and which are more numerous in $C_{12}E_6$ than in $C_{12}E_5$. These defects are described as dislocation loops crossing lamellae, made of pieces of screw dislocations linked by pieces of edge dislocations.

Qualitatively, the cores of these defects exhibit curved interfaces as revealed by ESR. Quantitatively there is a discrepancy between measured values of concentration of defects and concentration of curved area.

We attribute part of this discrepancy, to experimental uncertainties, e.g. the partial recovery of defects in freeze fracture experiments and difficulties in the interpretation of ESR spectra. But the main factor is the difficulty of matching two measurements not directly related: we must take into account other possible sources of curvature.

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