

**22.1-03** SUB-GRAIN BOUNDARY SELF-DIFFUSION IN THE ORIENTATIONALLY DISORDERED PHASE OF SUCCINONITRILE. By M. Brissaud-Lancin, C. Mahric, A. Riviere, J. Philibert, Physique des Matériaux Department, CNRS, Meudon, France.

Sub-grain boundary self-diffusion has been studied in only two orientationally disordered or so-called plastic crystals, adamantane (J. Bleay, Phil. Mag. (1977) 36, 885) and pivalic acid (M. Brissaud-Lancin, Phil. Mag. (1981) to be published). Sub-grain boundary self-diffusion speed is much higher in pivalic acid than in adamantane (roughly 500 times higher at  $0.91 T_m$  ( $T_m$ , melting temperature)) whereas lattice self-diffusion speed is of the same order of magnitude. Adamantane and pivalic acid give FCC crystals which differ by several properties such as plasticity and degree of orientational disorder (formation entropy  $\Delta S_f = 2.5R$  and  $0.8R$  respectively for adamantane and pivalic acid). So we performed a study in succinonitrile which gives highly plastic crystals of a high degree of orientational disorder ( $\Delta S_f = 1.35R$ ). Its plastic phase is BCC and stable from the transition point  $T_t = 233K$  to  $T_m = 351K$ .

Material containing less than 0.05% of impurities as determined by gas-liquid chromatography was used to grow crystals by the Bridgman technique. A convenient sub-structure was introduced by compression creep. The average grain size was about 200  $\mu m$ . Thin layer of succinonitrile labelled with  $^{14}C$  was deposited on samples' surfaces. Suzuoka solution (T. Suzuoka, Trans. Jap. Inst. Met. (1961) 2, 25) was used to determine the sub-grain boundary self-diffusion coefficients  $D'$ .  $D'$  were measured from 250 to 280K. Results are compared with those obtained previously. As in pivalic acid,  $D'$  is much higher than  $D$  ( $D$ , lattice self-diffusion coefficient (H. Hawthorne, Trans. Farad. Soc., (1970) 66, 1792)).

**22.1-04** X-RAY STUDY OF THE ROTATOR PHASE OF N-ALKANES. By J. Doucet, Laboratoire de Physique des Solides Université Paris-Sud, 91405 Orsay, France, I. Denicoló, Departamento de Física, UFSC, Brazil, and A.F. Craievich, Departamento de Física, IFQSC, USP, Brazil.

We present here a study of the "rotator" phase(s) displayed by the odd-numbered n-alkanes  $C_n H_{2n+2}$  with n ranging from 17 to 25. A structural model is derived from X-ray experiments performed both on single domains and on powder samples. The structure of the rotator phase(s) which appear(s) between the crystalline and isotropic liquid phases closely resembles the crystalline structure, i.e. the molecules are packed within layers forming a bilayer structure with the molecular axes orientated perpendicular to the layer planes. For compounds n = 17, 19 and 21 the space group of the rotator phase (RI) is C<sub>2</sub>cm. It implies the appearance of an orientational disorder of the molecules around their long axes which is the main characteristic of the crystalline  $\rightarrow$  rotator phase transition. Before melting, the RI phases of compounds n = 23 and 25 transform into another rotator phase (R II) the symmetry of which is hexagonal. This transition RI  $\rightarrow$  RII which is detected for the first time is a very weak first-order one.

**22.1-05** THE GEL PHASE OF A TYPE II LYOMESOPHASE-PHASE SYSTEM. L.Q. Amaral, Instituto de Física, Universidade de São Paulo, C.P. 20516, São Paulo, SP, Brasil.

The quaternary system SDS (Na decyl sulfate/water/decanol/Na sulfate, with wt% composition 37/53/5/5) at room temperature forms a type II lyomesophase, which orients in presence of magnetic fields with the optical axis perpendicular to the field. From small angle X-ray diffraction (SAX) in oriented samples, a model of finite planar bilayered micelles (platelets) surrounded by water was proposed (Amaral et al, J. Chem. Phys. 71, 2940, 1979). The characteristic inner band at 80-140 Å and outer ring at 38 Å have relative intensities which are strongly dependent on the sample container and on the degree of sample orientation (Amaral & Tavares, Mol. Cryst. Liq. Cryst. Let. 56, 203, 1980); these results have been explained with the hypothesis that the platelets aggregate, keeping only solvation water between them, while the excess water is segregated.

This paper presents the study of the same system at lower temperatures, when it is in an apparently solid phase. SAX results at 18°C evidenced a lamellar structure with repetition distance  $d = 31.4$  Å. The first three orders only are present, with intensities respectively VS-M-M. Higher angle diffraction showed two sharp rings at 4.0 and 4.2 Å. These results indicate a gel phase with extended carbon chains.

The observed d value is incompatible with extended chains perpendicular to the lamellar plane ( $\theta = 0^\circ$ ) together with homogeneous distribution of amphiphilic (A) and water (W) layers, since this would require  $d = 100$  Å for bilayers ( $d_a = 37.5$  Å) or  $d = 50$  Å for monolayers.

Tilted monolayers with  $\theta \approx 30^\circ$  would be the only model compatible with homogeneous distribution of A and W layers. The other possibility would be inhomogeneous distribution of A and W, with large multilayer aggregates intercalated with the excess water. Since these two possibilities correspond to different electronic distributions  $R(x)$  along the normal to the lamellar plane, a calculation of the structure factors for various models for  $R(x)$  was performed.

The observed intensities of the three reflections rule out models with small  $d_a$  values and without  $CH_3$  at the middle of the  $A^a$  layer and therefore don't give support to the tilted monolayer model with homogeneous A and W distribution. A model with  $CH_3$  at the middle of the A bilayer and  $d_a = 30$  Å explain the observed intensities.

Therefore, SAX results in the gel phase indicate the formation of large aggregates of multibilayers slightly swollen, separated by the excess water, in agreement with our proposed model for the type II lyomesophase at room temperature.

DSC thermal analysis of the same system showed three phase transitions at 0°C, 12°C and 22°C. The lower transition is probably associated with melting of the bulk water and the last one with breaking of the large multibilayer aggregates and change in the conformation of the carbon chains.

Transmission electron micrographs of replicas obtained by freeze-etching starting at 25°C and 18°C sample temperatures gave different results, which confirmed the lamellar phase at the lower temperature and the separation of A and W regions at the higher temperature. (FINEP, CNPq and FAPESP support).