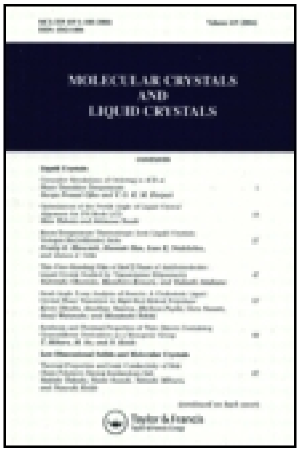


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

An X-Ray and Microscopic Investigation of the Thermotropic Phases of Lead(II)Decanoate

H. A. Ellis [a]

[a] Department of Chemistry, University of the West Indies, Mona, Kingston, Jamaica

To cite this article: H. A. Ellis (1997): An X-Ray and Microscopic Investigation of the Thermotropic Phases of Lead(II)Decanoate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 308:1, 111-120

To link to this article: http://dx.doi.org/10.1080/10587259708045099

Mol. Cryst. Liq. Cryst., 1997, Vol. 308, pp. 111–120
Reprints available directly from the publisher
Photocopying permitted by license only

An X-Ray and Microscopic Investigation of the Thermotropic Phases of Lead(II)Decanoate

HENRY A. ELLIS

Department of Chemistry, University of the West Indies,
Mona, Kingston, Jamaica

(Received 22 July 1996; In final form 12 March 1997)

The phase textures observed on heating lead(II)decanoate, $(CH_3(CH_2)_8COO)_2Pb$, from the room temperature crystalline solid to isotropic liquid melt are characterised by polarising light microscopy and X-ray diffraction. The results suggest a phase sequence:

$$\begin{array}{c}\text{Lamellar Crystal}\\ \text{(+ ve biaxial)}\end{array} \underset{347\,\text{K}}{\overset{360\,\text{K}}{\rightleftharpoons}} \begin{array}{c}\text{Lamellar}\\ \text{Crystal}\end{array} \underset{367\,\text{K}}{\overset{372\,\text{K}}{\rightleftharpoons}} \text{Smectic C} \underset{384\,\text{K}}{\overset{384\,\text{K}}{\rightleftharpoons}} \begin{array}{c}\text{Isotropic}\\ \text{Liquid}\end{array}$$

Though the phase assignments are consistent with conoscopic observations, molecular modelling and other calculations, they disagree somewhat with the assignments previously proposed by other workers. However, unlike previous work, the effects of thermal expansion and orientational disordering in the long axes of carboxylate chains are quantified as a function of temperature, and the phase sequence assigned in the light of these considerations in conjunction with the microscopic and X-ray data.

Keywords: Lead(II)decanoate; mesophase; smectic C; X-ray diffraction; light microscopy

INTRODUCTION

Lead(II)decanoate exhibits two thermotropic phases between the solid and isotropic liquid [1–3]. However, there has been no agreed classification of the two phases in the literature. For example, the low temperature phase (~ 360 K) was reported to have a crystalline structure [2], one intermediate between a solid and a liquid crystal [3] and more recently, a structure similar to a gel phase [4]. In the case of the intermediate phase at ~ 372 K, an ordered smectic of type S_E has been proposed [3] in contradiction to an earlier suggestion that the phase was crystalline [2]. Contrary proposals have also been presented for the high temperature phase (~ 384 K). For example, whilst Burrows and co-workers [3, 4] have presented microscopic, ^{207}Pb N.M.R., X-ray and other data in support of a smectic S_A phase a different interpretation of the data supports a disordered smectic S_C phase [2, 5]. These differ by having hydrocarbon chains either orthogonal (S_A) or tilted with respect to the phases containing Pb^{2+} ions (S_C). Nevertheless, there is general agreement on a lamellar structure for all the thermotropic phases exhibited by this compound [2, 3]. Unfortunately, the effects of thermal expansion and orientational disordering of carboxylate chains during heating, were ignored in arriving at the phase structures. For instance, comparisons were made between the layer thickness measured at temperatures well in excess of room temperature, and molecular lengths calculated from data obtained at room temperature. Clearly any definitive characterisation of thermotropic phases must consider both these factors.

In this paper the effects of thermal expansion and orientational disordering, as a function of temperature, are quantified and the results used, in conjunction with microscopic observation, to propose structures for the room temperature crystal and thermotropic phases of lead(II)decanoate.

EXPERIMENTAL

The preparation and purification of lead(II)decanoate, $(CH_3(CH_2)_8COO)_2Pb$, have been described previously [6, 7]. The purity of the compound was checked by I.R. spectroscopy and elemental analysis. The recrystallised and vacuum dried compound was free from water and acid (a common contaminant). Additionally, the percentage C and H were in excellent agreement with expected values.

Differential scanning calorimetry (D.S.C.) measurements were performed on a Mettler TA 3000 system. Samples in the weight range of 2–10 mg. were sealed in aluminium crucibles and scanned at 1.0 K min^{-1}. Phase transition data were collected from triplicate runs on fresh samples.

Phase structures were determined with an Olympus polarising light microscope fitted with a Kofler micro heating stage. For conoscopic studies a Swift petrological microscope was used.

X-ray data were collected from samples sealed in glass capillaries of 0.7 mm diameter. A sample was introduced into the capillary by a vacuum melt technique after which the capillary was sealed to minimise any effects of humidity. The sample tube was then fitted into a temperature controlled copper block, which also served as a collimator for the X-ray beam, and irradiated for one hour with a Ni-filtered Cu kα radiation ($\lambda = 1.5418$ Å). Diffraction patterns were recorded on flat polaroid films (type 57) perpendicular to the incident beam at a sample to film distance of 80.03 mm. A room temperature diffraction pattern was also obtained on a Siemens D500 diffractometer from a powered sample.

RESULTS

Phase transition temperatures are collected in Table I and show excellent agreement between values obtained from differential thermal analysis (DTA) [1] and DSC [2, 3]. All the phases exhibit enantiotropic behavior. Additionally, considerable supercooling (5–13 K) was observed (value in parenthesis in Table I) on cooling into the 360 K and 372 K phases though not for the 384 K phase. The 360 K phase was optically anisotropic, when viewed under cross polarisers, and highly viscous. A fine mosaic texture (Fig. 1(a)) was observed on cooling into the phase. The 372 K phase was also optically anisotropic and viscous. However, on cooling into this phase, needle like crystals appeared first (Fig. 1(b)) followed, fairly quickly, by conversion to a fine mosaic texture (Fig. 1(c)). Both phases demonstrate some resistance to a sheer stress applied to the microsccope coverslip, as expected for crystalline phases. A highly viscous phase is formed at ~ 384 K. Cooling into this phase producted fan textures [2, 3] typical of a S_A or S_C phase.

The X-ray pattern from the room temperature, 360 K and 372 K phase (Fig. 2) consisted of many sharp reflections, are indicative of diffraction from an ordered lamellar structure, as previously agreed [2, 3], and allows

TABLE I Phase transition temperatures for lead(II)decanoate

Transition temperatures/K			*References*
354.9	367.4	385.2	1
359	371	384	2
357	369	387	3
360 (347)	372 (367)	384 (384)	this work

( )-values obtained on cooling. Errors in values are quoted to within ± 2%.

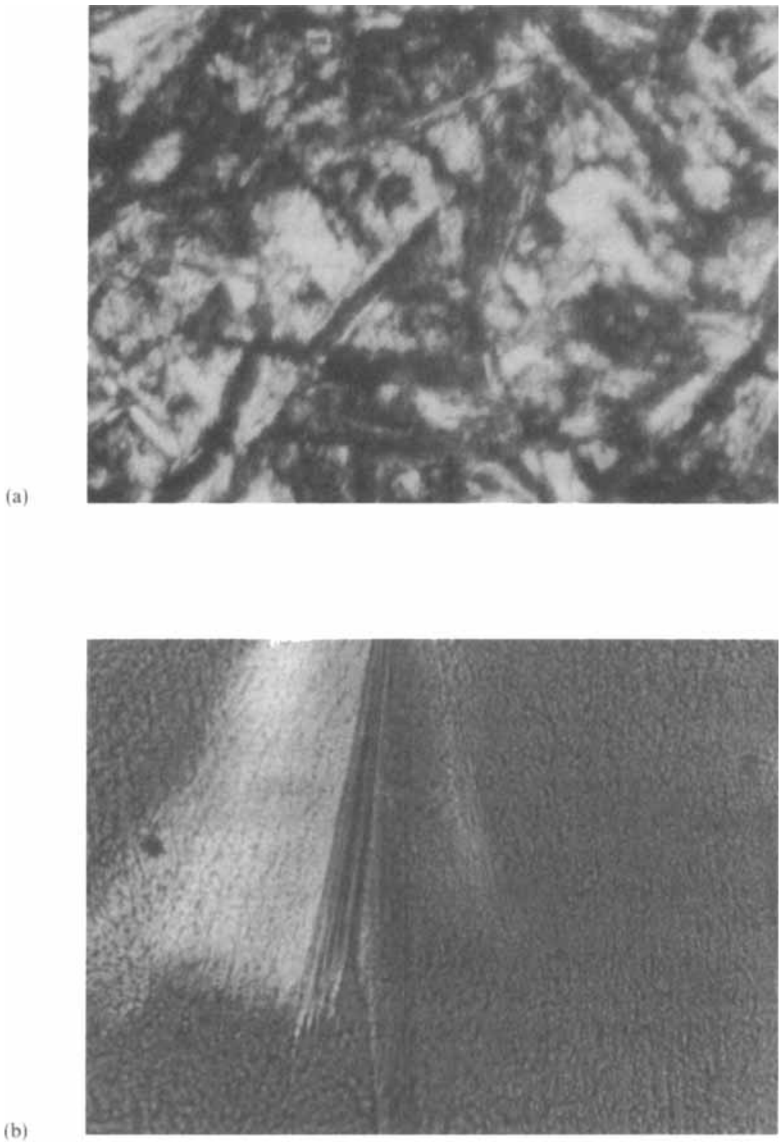
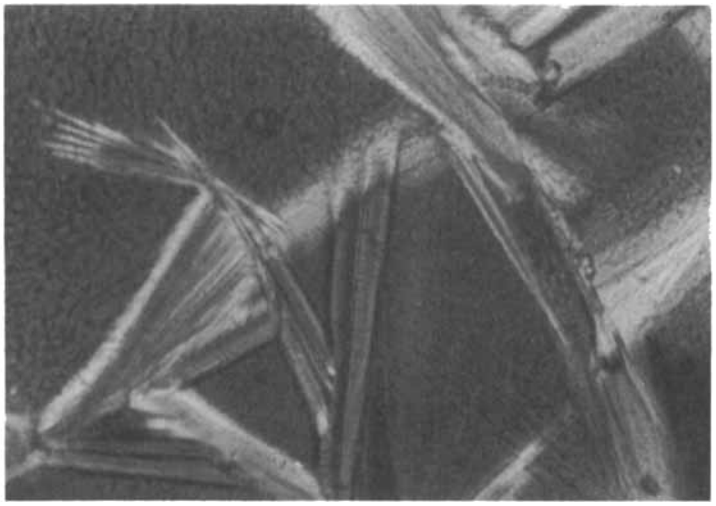


FIGURE 1 (a) 360 K Mosaic phase. (b) 372 K Crystal phase. (c) Mosaic crystal phase. (See Color Plate IV).

calculation of the lamellar spacing, d. These are calculated from the diameter of the inner diffraction ring using the Bragg relation:

$$n\lambda = 2d \sin\theta$$



(c)

FIGURE 1 (Continued).

where n is the order of diffraction, λ is the wavelength of radiation used (1.5418 Å) and θ the diffraction angle. The d spacings, at various temperatures between ambient and 382.4 K are collected in Table II.

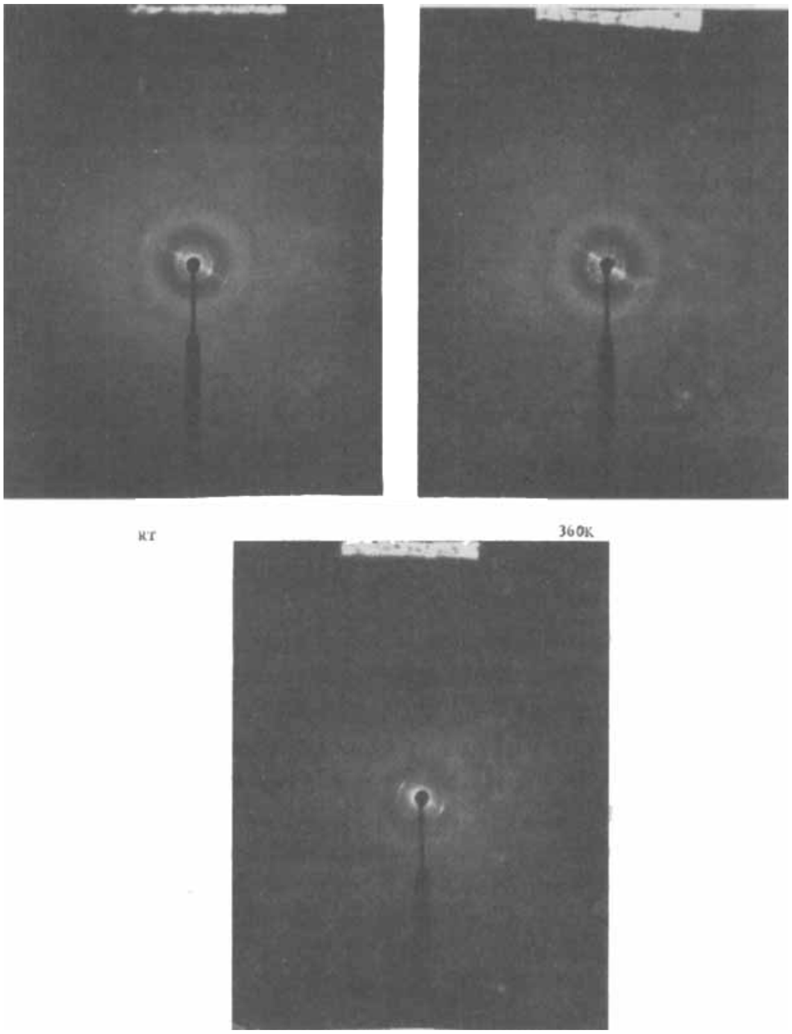
The spacings decrease with increasing temperature from a value of 30.9 Å at 298 K to ~22 Å in the region of 382 K. The molecular length, l, was calculated at 298 K assuming an all-trans conformation for carboxylate chains, standard bond lengths and angles and 2.4 Å as the ionic radius of Pb^{2+} ion [8, 9]. Additionally, all the d values at the various temperatures are corrected for thermal expansion by the relation:

$$l(T) = l + \Delta l(T),$$

Where $l(T)$ is the molecular length at a temperature T and $\Delta l = l \times \alpha \times \Delta T$; ΔT is $(T - 298\ \text{K})$ and α is the average thermal linear expansion. The linear expansion at each temperature is calculated from corresponding coefficient of volume expansion β, assuming that [10]:

$$\alpha = \beta/3$$

The β values reported by Burrows and coworkers [3] are used in conjunction with present data to calculate the $l(T)$ values presented in Table II. As expected $l(T)$ increase with increasing temperature. A further correction


RT

360K

FIGURE 2 X-ray photographs of lead(II)decanoate at various temperatures.

was made for orientational disordering in the long axes of the carboxylate chains as a function of temperature. The degree of parallelism of the long axes of the molecule to the layer planes is given by the orientational order parameter, S.

$$S = 1/2\langle 3\cos^2\theta' - l\rangle,$$

TABLE II X-ray data

T/K	$d/Å$	$l(T)/Å$	$d_{cal}/Å(S_c model)$
298.0	30.9(26.3) ± 1	30.6 ± 2	
352.1	28.4	30.8	
365.1	26.9	30.9	
372.9	22.5	31.2	27.9
377.2	22.5	31.2	27.9
381.5	22.1	31.3	28.0
382.4	22.0	31.3	28.0

where θ' is the angle between the molecular long axes and the average direction of these long axes. For example, when the long axes of the molecules are orthogonal to the planes, $S = 1$. Accordingly, the influence of S on d is calculated from the relation:

$$d_{\text{cal}} = l(T)\langle\cos\theta'\rangle$$

where d_{cal} is d corrected for orientational disorder. The choice of a value for $\langle\cos\theta'\rangle$ depends on the type of mesophase present. For instance, deVries and coworkers [11] have successfully used models of the S_A and S_C mesophases to calculate the effect of orientational disordering as a function of temperature for four different compounds. For a type S_A mesophase, 0.8 and 0.927 were chosen as the values for S and $\langle\cos\theta'\rangle$ respectively; for the S_C mesophases the corresponding values were 0.7 and 0.894. These values are used to calculated d_{cal} for the S_C mesophase (Tab. II). However, no d_{cal} values are presented for the 360 K and 370 K phases since orientational disordering is only significant at temperatures in excess of 372 K [3, 12]. The S_C model suggests that orientational disordering accounts for ~ 8–10 percent reduction in chain length. The larger reduction is quite possibly due to transition from all-trans to disordered chains [5]. The results are not very different which ever model for the mesophase is chosen.

DISCUSSION

Low symmetry and difficulties in preparing single crystals make structural analysis of the room temperature solid difficult. Nevertheless, useful structural information can be obtained from X-ray diffraction patterns of powder samples. These support a lamellar structures [2, 3, 5]. Additionally, model calculations [2, 3] and other data [13–16] indicate that the hydrocarbon chains are in the fully extended all-trans configuration and are packed into a layer with the two carboxylate chains on opposite sides of the lead ions. Bearing this in mind, a comparison of d (30.9 Å) and l (30.6 Å) at 298 K suggests an orthogonal arrangement of the carboxylate chains to planes containing lead ions. However, the expected optical uniaxial interference figure, in support of that structure, was not seen. Rather, a biaxially positive interference figure was observed. This was confirmed when, on rotating the microscope stage, the diffuse cross interference figure rapidly broke up into two hyperbolic isogyres.

For a uniaxial or orthogonal arrangement of carboxylate chains to the layer normal, the diffuse cross would remain unchanged on rotation of the stage [17]. Clearly then, in the room temperature structure, carboxylate chains are tilted with respect to the layer normal. This implies that the value of d is somewhat closer to 26.3 Å, the Siemens D5000 derived value, than 30.9 Å.

For the 360 K phase, the X-ray diffraction pattern is almost identical to that obtained from the room temperature solid. Additionally, an $l(T)$ value of ~ 31 Å compared to a value of ~ 27 Å for d at the same temperature suggests that the carboxylate chains are also tilted with respect to the layer normal. Such a conclusion is supported by ^{207}Pb NMR^3 and a.c. impedance data [18] which indicate that the metal ion is restricted in motion in this phase and that the three dimensional lamellar structure of the room temperature solid is maintained. Furthermore, on cooling into the phase, a typically mosaic crystalline texture [19] (Fig. 1(a)) was observed to deposit as thin plates on the preceeding phase texture. The phase was further characterised by its resistance to a sheer stress applied to the microscope coverslip and by the considerable supercooling (~ 13 K) observed on cooling into it. Since mesophases are mobile and tend not to supercool [19], the data support a crystalline structure for the 360 K phase.

On cooling into the 372 K phase, fibrous radiating aggregates were first observed which then changed, on further cooling, to give an optically anisotropic texture typical of a crystalline phase [19, 20] (Fig. 1(b)). Additional support for a crystalline phase was provided by the ≈ 5 K supercooling oserved on forming the phase. Furthermore, the contraction in d to ~ 23 Å compared to d_{cal} of ~ 28 Å, at the same temperature, suggests that this phase might also be biaxial. The contraction in d can be ascribed to orientational disordering of the direction of the long axes of the molecule ($\sim 10\%$) in conjunction with possibly a larger effect resulting from the transition from all-trans to partially disordered chain [3, 5]; though with an overall biaxial order. Evidence is support of disordered chains comes from thermodynamic studies which show a marked increase in entropy ($\sim 50\,\mathrm{JK}^{-1}\mathrm{mol}^{-1}$) on transition from the preceeding phase [2] and the introduction of gauche bonds into the carboxylate chains [3]. Clearly the evidence points to a crystal-like structure with biaxial order, for this phase, and not a mesophase as suggested by others [3,4,13].

In contrast, the 384 K phase was formed without supercooling, typical of an enantiotropic mesophase. On cooling into the phase, from the isotropic liquid, fan textures appeared (Fig. 3), identical to those described for a smectic mesophase of type S_A or S_C [3]. The appearance of a liquid crystalline phase at this temperature is evidence for some degree of molecular order resulting, possibly, from ionic interactions between Pb ions. This would allow for the formation of a two dimensional layer structure within which are partially disordered alkyl chains. Furthermore, a comparison of d (~ 22 Å) and d_{cal} (~ 28 Å) suggests that the alkyl chains are either interdigitated or tilted within layers. However, there is no evidence for interdigitation. Moreover, it seems unreasonable to expect a biaxial starting material, on disordering under the influence of increasing temperature, to give a uniaxial mesophase; that is the more thermodynamically ordered S_A structure. Therefore, the model for partially disordered carboxylate chains with the average direction of the molecular long axis tilted with respect to the layer normal seems more plausible and is here proposed. A revised

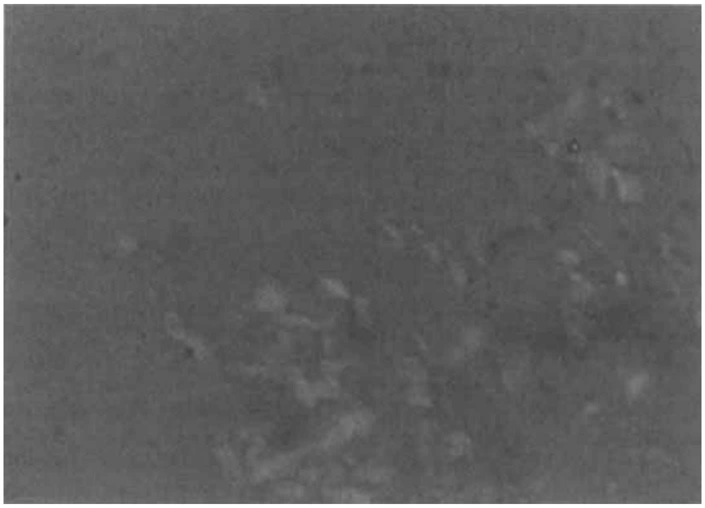


FIGURE 3 Smectic phase showing broken fan textures. (See Color Plate V).

phase sequence is:

$$\begin{array}{c}\text{Lamellar Crystal}\\ \text{(biaxially + ve)}\end{array} \underset{347\,\mathrm{K}}{\overset{360\,\mathrm{K}}{\rightleftharpoons}} \begin{array}{c}\text{Lamellar}\\ \text{Crystal}\end{array} \underset{367\,\mathrm{K}}{\overset{372\,\mathrm{K}}{\rightleftharpoons}} S_C \underset{384\,\mathrm{K}}{\overset{384\,\mathrm{K}}{\rightleftharpoons}} \begin{array}{c}\text{Isotropic}\\ \text{Liquid}\end{array}$$

Acknowledgement

Special thanks are expressed to Dr. R. Ahmad of the Geology Department for help with the conoscopic studies. Also the co-operation of Dr. A. de-Vries of the liquid Crystal Institute, Kent State University, Ohio, in the X-ray measurements is gratefully acknowledged. Sincere thanks to Alcan Jamaica Ltd., for a grant to purchase the DSC instrument.

References

[1] S. O. Adeosun and S. J. Sime, *Thermochim. Acta*, **17**, 351 (1976).
[2] H. A. Ellis, *Mol. Cryst. Liq. Cryst.*, **139**, 281 (1986).
[3] A. M. Amorim Da Costa, H. D. Burrows, C. F. G. C. Geraldes, J. J. C. Teixeira-Dias, C. G. Bazuin, D. Gullion, A. Skoulios, E. Blackmore, G. J. T. Tiddy and D. L. Turner, *Liquid Crystals*, **1**, 215 (1986).
[4] H. D. Burrows, *Acta Bioguin*, **2**, 11 (1989).
[5] H. A. Ellis and Adrian de Vries, *Mol. Cryst. Liq. Cryst.*, **163**, 133 (1988).
[6] M. E. Ekwunife, M. U. Nwachukwu, F. P. Rinehart and S. J. Sime, *J. Chem. Soc.*, Faraday, 1, **71**, 1432 (1974).
[7] H. A. Ellis, *Thermochim. Acta*, **47**, 261 (1981).
[8] T. R. Lomer and K. Perera, *Acta Cryst.*, **B30**, 2912 (1974).
[9] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, London, 309 (1972).
[10] F. W. Sears, M. W. Zemansky and H. D. Young, "College Physics", Addision-Wesley Publishing Company, sixth edition, 291 (1981).
[11] A. de Vries, A. Ekachai and N. Spielberg, *Mol. Cryst. Liq. Cryst.*, **49**, 143 (1979). A. de Vries in A. C. Griffin and J. F. Johnson (Eds.), "Liquid Crystals and Ordered Fluids", **4**, Plenum Press, New York, 137 (1984).
[12] H. D. Burrows in D. M. Bloor and E. Wyn-Jones (Eds.) "The Structure, Dynamics and Equilibrium properties of colloidal systems", Kluwer Academic Publishers, Netherlands, 415 (1990).
[13] C. G. Bazuin, D. Guillion, A. Skoulios, A. M. Amorim da Costa, H. D. Burrows, C. F. G. C. Geraldes, J. J. C. Teixeira-Dias, E. Blackmore and G. J. T. Tiddy, *Liquid Crystals*, **3**, 1655 (1988).
[14] G. Feio, H. D. Burrows, C. F. G. C. Geraldes and T. J. T. Pinherio, *Liquid Crystals*, **9**, 417 (1991).
[15] H. D. Burrows, C. F. G. C. Geraldes, M. G. M. Miguel, T. J. T. Pinherio and J. J. C. Cruz-Pinto, *Thermochim. Acta*, **206**, 203 (1992).
[16] H. D. Burrows, C. F. G. C. Geraldes, T. J. T. Pinherio, R. K. Harris and A. Sebald, *Liquid Crystals*, **3**, 853 (1988).
[17] N. H. Hartshorne and A. Stuart, "Practical Optical Crystallography", Edward Arnold Publishers Ltd., 82 (1971).
[18] S. O. Adeosun and S. J. Sime, *J. Chem. Soc.* Faraday, **1**, 75, 953 (1979).
[19] M. E. Neubert, "Identification of Liquid Crystal Textures", Liquid Crystal Institute, Kent State University, USA, unpublished monograph.