This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Molecular dynamics in liquid crystals by dielectric relaxation and neutron scattering

L. Bata[a]; G. Pépy[b]; L. Rosta[ab]
[a] Central Research Institute for Physics, Budapest, Hungary [b] Laboratoire Léon Brillouin, CEN-Saclay, Gif sur Yvette Cedex, France

To cite this Article Bata, L. , Pépy, G. and Rosta, L.(1988) 'Molecular dynamics in liquid crystals by dielectric relaxation and neutron scattering', Liquid Crystals, 3: 6, 893 — 900
To link to this Article: DOI: 10.1080/02678298808086546
URL: http://dx.doi.org/10.1080/02678298808086546

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1988, VOL. 3, NOS. 6 AND 7, 893–900

Molecular dynamics in liquid crystals by dielectric relaxation and neutron scattering

by L. BATA†, G. PÉPY‡ and L. ROSTA†‡

†Central Research Institute for Physics H-1525 Budapest, P.O. Box. 49, Hungary
‡Laboratoire Léon Brillouin, CEN-Saclay 91191 Gif sur Yvette Cedex, France

Detailed dielectric permittivity and relaxation investigations have been performed on compounds having different liquid-crystalline phases. At the smectic B–smectic A as well as the smectic G–smectic B transitions definite jumps were found in the dielectric relaxation times associated with rotation of the molecules around their short axis. For the interpretation of the large jumps in the relaxation times the change of the phonon spectra at the two dimensional crystal–two dimensional liquid phase transition was assumed. To verify this idea an inelastic neutron scattering study was performed. The measurements have proved the good orientation of the smectic A and smectic B phases. The values of the layer spacing, and the appearance of libron peaks for the smectic B phase at different momentum transfer were determined.

Downloaded At: 16:10 26 January 2011

1. Introduction

The molecular dynamical processes in liquid crystals have been the target of N.M.R., neutron scattering and dielectric relaxation investigations for a long time. By N.M.R. and neutron scattering studies we obtain information about many types of dynamical processes, the difficulty is how to separate the different types of motion. The situation is similar for the interpretation of high frequency dielectric dispersion measurements, while at low frequency dielectric relaxation, which is very characteristic in liquid crystals, the situation is quite different. We know that this dispersion is associated with molecular rotation around the short axis. We have found in many experiments [1] that there is an order of magnitude jump in critical frequency at the two dimensional crystal–two dimensional liquid, i.e. S_A–S_B etc. phase transition. In this paper we describe the use of both the dielectric and the neutron scattering technique to investigate and interpret this effect.

2. Dielectric relaxation experiment

By dielectric relaxation we study the dipole–dipole correlation function which generally has the form

$$\gamma(t) = \sum_i a_i \exp(-t/\tau_i). \tag{1}$$

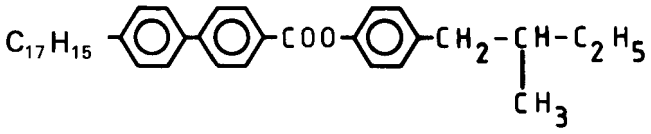
In experiments we investigate the frequency dependence of the dielectric permittivity, which is the Fourier transform of the dipole–dipole correlation function, the dielectric permittivity can be written as

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) \sum_i \frac{b_i}{1 + i\omega\tau_i}. \tag{2}$$

When there are only two equivalent positions of the molecules during their rotational motion (this is the case for rotational motion around the short axis in a liquid-crystalline phase) then only one relaxation time characterises the motion ($i = 1$). ε_0 is the dielectric permittivity below the frequency at which the dispersion starts, ε_∞ is the value after the relaxation process has finished.

By different type of bridges we can measure the real $\varepsilon'(\omega)$ and the imaginary $\varepsilon''(\omega)$ parts of $\varepsilon^*(\omega)$. For liquid crystal phases we orient the director of the system by a magnetic field in the nematic phase and perform the dielectric dispersion measurements both parallel $\varepsilon_\parallel$ and perpendicular $\varepsilon_\perp$ to the field direction. By using the Cole–Cole plot (i.e. $\varepsilon'_\parallel$ versus $\varepsilon''_\parallel$) we can discover whether one relaxation time characterizes the motion. This was found to be so in low frequency region for many compounds [1, 2].

For the detailed study of the phase transitions the compound 4-(2-methyl-butyl)-4′-*n*-heptyl-biphenyl-4-carboxylate (7BEF5), that is



was chosen, which possesses the phases

C–40°C–S_G–57°C–S_B–68°C–S_A–138·5°C–N–148°C–I.

The temperature dependence of the critical frequency ($f_c'' = 1/2\pi\tau_\parallel$) is shown in figure 1. In parentheses the activation energies are given in kJ/mole.

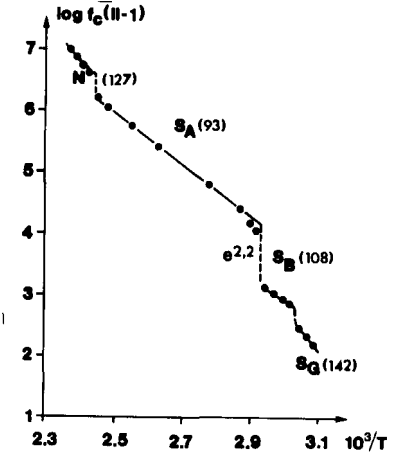


Figure 1. The critical frequency of 7BEF5 versus $1/T$ in different liquid-crystalline phases, measured by dielectric relaxation methods.

In accordance with the results found for other compounds [1] the order of magnitude change can be seen at the S_B–S_A phase transition. (For other compound breaks were found only at the S–N transition). It was supposed [1] that this effect is due to the step like change of the librational frequency at the two dimensional crystal–two dimensional liquid transition. The building up of the two dimensional ordering of the centres of gravity enables the system to establish collective modes, to produce synchronized librational motion. The libron mode makes the individual

Downloaded At: 16:10 26 January 2011

molecular libration more stable, the molecules need more thermal energy to remove this collective motion, which is why the jumps are found at this phase transition.

Our task is now to provide experimental evidence from this hypothesis. First we try to determine approximately the frequency of the libron mode from the dielectric data. We can do it only with the aid of an analogy. For uniaxial smectic (S_A, S_B) phases the single particle is taken to have potential the form

$$U(\cos\theta, x, y, z) = -u_0 \left\{ \left(S_\theta + S_{\theta d}\alpha^{\parallel} \cos\frac{2\pi z}{d} \right. \right.$$
$$+ 2S_{\theta ab}\alpha^{\perp}\left(\cos\frac{2\pi x}{a} + \cos\frac{2\pi y}{b}\right) P_2(\cos\theta) + S_d\delta^{\parallel}\cos\frac{2\pi z}{d}$$
$$\left. \left. + 2S_{ab}\delta^{\perp}\left(\cos\frac{2\pi x}{a} + \cos\frac{2\pi y}{b}\right)\right\}. \tag{3}$$

The first term agrees with the Maier–Saupe potential the second and fourth are the McMillan terms [3], the others characterise the smectic B phase. S_θ, $S_{\theta ab}$ and $S_{\theta d}$, S_d are the order parameters and $\alpha^{\parallel}$, $\delta^{\parallel}$, $\alpha^{\perp}$, $\delta^{\perp}$ are constants of the potential determined from the behaviour of the thermodynamic functions (e.g. the energy and enthalpy) at the phase transitions [4].

Using this potential with some approximation [4] we can calculate the critical frequency in the smectic A and smectic B phases. In the smectic A phase the relaxation time has the form

$$\tau_{\parallel}^{A} = \tau_{\parallel}^{N} \exp\left[\frac{u}{kT}(\Delta S_\theta + \tfrac{4}{5}\alpha^{\parallel}S_\theta)\right], \tag{4}$$

where

$$u = \tfrac{9}{8}u_0,$$

and ΔS_θ is the change of the orientational order parameter at the smectic A nematic transition.

In the smectic B phase the relaxation time can be written as

$$\tau_{\parallel}^{B} = \tau_{\parallel}^{A} \exp\left[\frac{\mu}{kT}\left(\Delta S\,\frac{B}{\theta} + \tfrac{4}{5}\sigma^{\parallel}\Delta S_{\theta d} + \tfrac{16}{5}\alpha^{\perp}S_{ab}\right)\right]. \tag{5}$$

From studies of molecular crystals [5] we know that if the interaction potential has the form

$$V(\theta_{ij}) = -u_1 P_2(\cos\theta_{ij}) \tag{6}$$

then the collective librational mode is

$$\omega_l^2 = \frac{6u_1}{I}, \tag{7}$$

here I is the moment of inertia of the molecules. If we compare equations (3) and (7) we find

$$u_1 = 2u_0\alpha^{\perp}S_{\theta ab} \tag{8}$$

and

$$\omega_l^2 = 12u\,\frac{\alpha^{\perp}}{I}\,S_{\theta ab}. \tag{9}$$

Downloaded At: 16:10 26 January 2011

This equation enables us to calculate the librational frequency from dielectric relaxation measurements. From the experimental data we can determine the libration frequency by the equation

$$\frac{\tau_B}{\tau_A} = \exp\left(\frac{3\omega_l^2 I}{10kT}\right); \tag{10}$$

i.e. if we write the relaxation time ratio in exponential form the value can easily be calculated. From this equation we obtain $\omega_l \approx 0{\cdot}25\,\text{meV}$. That is if this type of motion exists, we should be able to find it by neutron inelastic coherent scattering as intensity peaks between the quasi-elastic scattering and the phonon peaks.

3. Neutron scattering experiments

3.1. *Sample preparation and instrumentation*

The 7BEF5 sample was placed in a quartz cell with dimensions $0{\cdot}1 \times 1 \times 4\,\text{cm}^3$ and a thin Al–Gd alloy grating was introduced into the container to reduce multiple scattering. To avoid a temperature gradient around the quartz cell, it was put into an aluminium box filled with helium. The temperature of the sample in the oven for the scattering experiments was controlled with a precision of 0·5 K. To orient the sample an electromagnet was used which produced a horizontal field of 0·7 T.

Two kinds of neutron scattering measurements were carried out. Prior to the spectroscopic studies the structure and the orientational behaviour of the sample has to be characterized by diffraction type experiments. This was performed partly on the 4F2 cold neutron triple axis spectrometer and partly on the PAXY small angle scattering instrument at the Saclay Orphée reactor. Inealstic scattering measurements were performed on the 4F2 triple axis spectrometer.

Downloaded At: 16:10 26 January 2011

3.2. *Diffraction*

In order to provide a monodomain the sample was cooled very slowly from the isotropic phase in a magnetic field. Especially from the S_A–N transition into the smectic B phase the cooling took about 8 hours. The small q (scattering vector) range was analyzed by the XY patterns from the coordinate detector of the small angle scattering spectrometer at 3·7 Å incident neutron wavelength. As shown in figure 2 a small peak has appeared in the nematic phase corresponding to the molecular form factor at 28·42 Å ($T = 413\,\text{K}$). When transforming into the smectic A phase the intensity increased about ten times and the peak became sharper. The appearance of this very intense and narrow Bragg-reflection from the smectic layer planes indicates the very good orientation, the quasi-monocrystal quality of the sample. The mozaicity of the monodomain sample was characterized with a full width at half maximum of 2·5° from the rocking curve. In the S_B phase a similar peak was recorded (not shown in figure 2.). At about 332·5 K the next phase transition occurs and after the completion of this transformation a complete splitting of the smectic peak is observed (see figure 2) indicating the existence of a tilted smectic phase with a tilt angle of 16·1°. No higher order reflections were observed in any phases.

The transition kinetics were also studied by q-scans perpendicular to the magnetic field direction on the 4F2 spectrometer at 4 Å incident neutron wavelength. By lowering the temperature from the S_B phase the spitting of the smectic speak can be followed. This transition is nearly reversible, since on reheating (in the magnetic field) the single peak appears in the smectic B phase, further heating, however, into the S_A

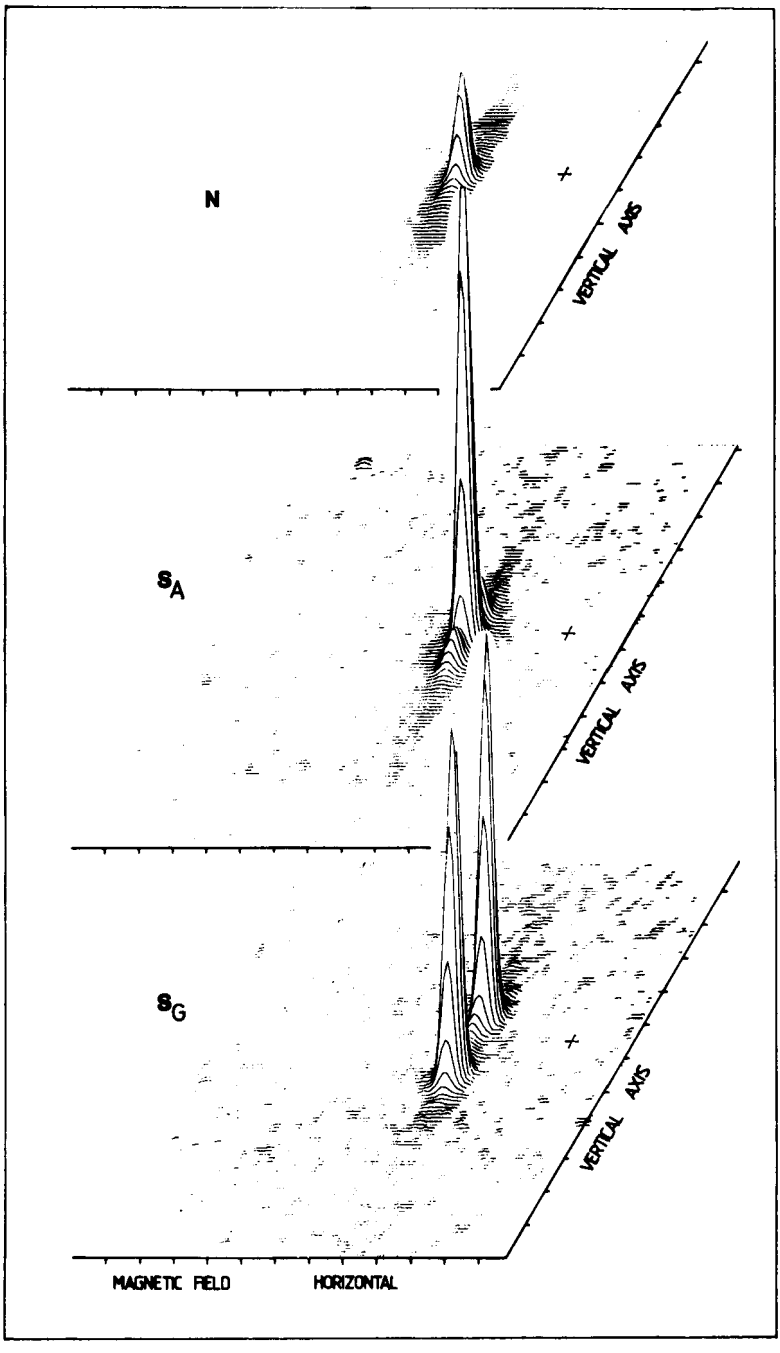


Figure 2. Elastic coherent neutron scattering intensities (Bragg-reflections) for N, S_A and S_G phases, measured with the PAXY small angle scattering instrument.

Downloaded At: 16:10 26 January 2011

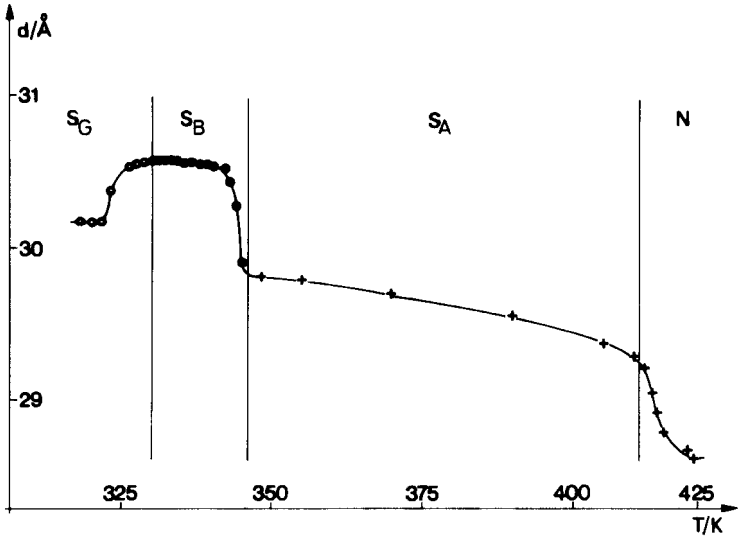


Figure 3. The layer spacing of 7BEF5 in different liquid-crystalline phases.

Downloaded At: 16:10 26 January 2011

phase destroys the ordering, meaning that the S_B to S_A transition is not reversible from the point of view of the macroscopic orientation.

As a result of the diffraction studies, the smectic layer spacing could also be determined as a function of temperature (see figure 3). It can be seen that the layer distance parameter can be determined with a high precision and phases can be well distinguished by the discontinuities in this curve, however the temperature values are somewhat different from the literature data.

3.3. *Inelastic scattering*

To observe eventually collective excitations in the low energy range triple axis spectrometer measurements were made on the characterised, magnetic field oriented sample. Constant q momentum transfer scans were made on the S_A, S_B and S_G phases at $q = 0{\cdot}66$ and $1\,\text{Å}^{-1}$ values. A typical inelastic scan is shown in figure 4 measured with an incident neutron wavelength of 4·18 Å. For geometrical reasons only the $-3{\cdot}2$ to 2·2 meV range has been covered including the quasielastic part. The sample-holder background has been subtracted for each scan.

The measured points were analysed by fitting the following function:

$$F(\omega) = \delta + L_1 + L_2 + \text{Ph}_1 + \text{Ph}_2 + \text{C},$$

where $\delta(I)$ is a Dirac delta corresponding to elastic scattering, $L_1(I, \eta)$ and $L_2(I, \eta)$ are lorentzians describing the quasielastic part, $\text{Ph}_1(I, \omega, \eta)$ and $\text{Ph}_2(I, \omega, \eta)$ are damped harmonic oscillators and C represents the spectrometer background correlated with the resolution function. I, ω, η are the fitting variables as the intensity, position and full width at half maximum, respectively.

In the table results for the inelastic scattering parameters are shown (the fitting quality is indicated by the χ^2 values). It can be seen from figure 4 and the table that, despite the poor statistics, it is reasonable to attribute on the measured curves to the systematically appearing enhancements in the 1·5–2·5 meV region collective excitations. For the $q = 1\,\text{Å}^{-1}$ scans better fits could be achieved by supposing two

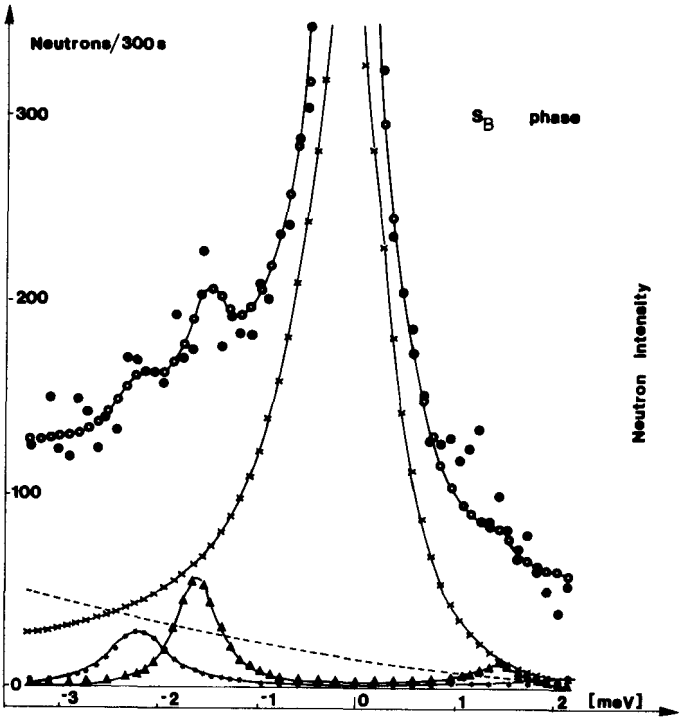


Figure 4. The measured neutron intensities (●) at constant ($q = 0{\cdot}66\,\text{Å}^{-1}$) momentum transfer as a function of energy changes. ⊙ denotes the calculated curves with × quasielastic, ▲ and * inealstic intensities. – – – denotes the background.

Inelastic neutron scattering parameters

Phase	Q/Å^{-1}	Parameters	δ	L_1	L_2	Ph_1	Ph_2	C	χ^2
S_A (396 K)		Int/a.u.	6876	601	–	63	44	62	2·87
	0·66	POS/THz	0	0	–	0·39	0·62		
		FWHM/THz	0	0·10		0·2	0·2		
		Int/a.u.	4857	894	94	29	22	–	2·15
	1	POS/THz	0	0	0	0·46	0·78		
		FWHM/THz	0	0·08	0·67	0·25	0·25		
S_B (339 K)		Int/a.u.	8055	371	–	55	29	51	4.12
	0·66	POS/THz	0	0	–	0·39	0·57		
		FWHM/THz	0	0·13	–	0·10	0·14		
		Int/a.u.	6822	603	91	30	22	–	2·48
	1	POS/THz	0	0	0	0·39	0·65		
		FWHM/THz	0	0·10	0·78	0·21	0·29		
S_G (323 K)		Int/a.u.	8413	311	–	29	27	52	4·73
	0·66	POS/THz	0	0	–	0·40	0·54		
		FWHM/THz	0	0·15	–	0·12	0·12		
		Int/a.u.	7324	431	85	31	23	–	2·43
	1	POS/THz	0	0	0	0·36	0·72		
		FWHM/THz	0	0·10	0·69	0·33	0·34		

Downloaded At: 16:10 26 January 2011

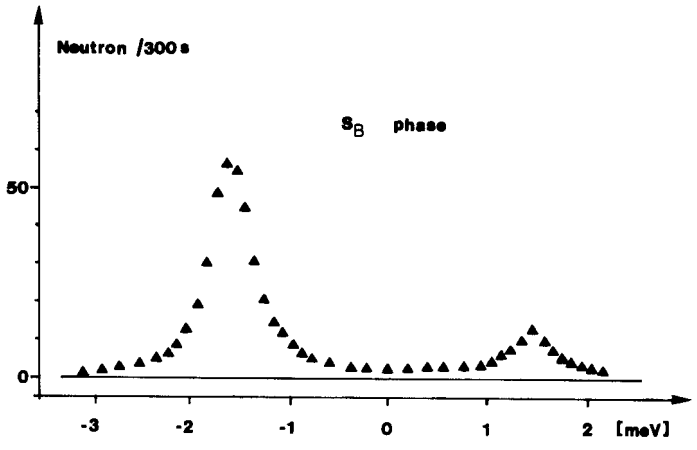


Figure 5. The measured libron peaks as a function energy changes.

lorentzians without the background term. The pure coherent inelastic neutron scattering peaks demonstrating the existence of the collective librational mode is shown in figure 5 we should point out that by using a deuteriated sample for this coherent inelastic type scattering measurement much better results could have been achieved by decreasing the incoherent background resulting from the H atoms.

4. Conclusion

From coherent inelastic neutron scattering measurements we can conclude that collective librational motion exists in smectic liquid crystals (especially S_B and S_G phases), the frequency of this mode is in the range, which can explain the jumps of the dielectric critical frequency measured at smectic B–smectic A phase transition.

References

[1] Bata, L., and Buka, Á., 1981, *Molec. Crystals liq. Crystals*, **63**, 391.
[2] Buka, Á., Bata, L., and Pintér, K., 1984, *Molec. Crystals liq. Crystal*, **108**, 211. Kresse, H., and Buka, Á., 1982, *Cryst. Res. Tech.*, **17**, 1123.
[3] McMillan, W. L., 1971, *Phys. Rev.* A, **4**, 1238; 1972, *Ibid.* **6**, 136.
[4] Bata, L., 1986, *Z. Chem.*, **26**, 27.
[5] Raich, I. C., 1971, *J. chem. Phys.*, **55**, 3901.

Downloaded At: 16:10 26 January 2011