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MÖSSBAUER SPECTROSCOPY OF THE FERROCENE-CONTAINING THERMOTROPIC LIQUID CRYSTALS

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Abstract The ^{57}Fe Mössbauer spectroscopy has been used to study the liquid crystalline disubstituted derivatives of ferrocene (FLCn). Characteristic Debye temperatures, order parameters, intramolecular and lattice contributions to the nuclear vibrational anisotropy have been obtained for these compounds and 7% (weight) solution FLC10 in the nematic LC H8.

INTRODUCTION

Recently a great interest in liquid crystals (LC), containing a metal atom inside the molecule has increased both from fundamental point of view and possible applications. Several new disubstituted derivatives of ferrocene (F) with mesomorphic behaviour have been synthesized [1]. The compounds are a Shiff base of F and exhibit nematic phase above 140°C. In this work we report the Mössbauer results for some of these compounds: 1,1'-bis(alkyloxybenzoyloxybenzylydene-p-acetylhydrazone)ferrocene with general formula $Fe(C_5H_4C(CH_3)=N-N=CHC_6H_4COOC_6H_4OC_nH_{2n+1})_2$, where n = 8, 10, 12 (abbreviated as FLCn, n = 8, 10, 12).

EXPERIMENTAL

The studied solution was prepared by dissolving 7% (weight) FLC10 into the nematic liquid crystal (NLC) H8. The sample was heated in vacuum to temperature of isotropic liquid and maintained at this temperature for

two hours. The ordered glasses of FLCn's and prepared solution were formed by rapid cooling the samples from NLC-phase to liquid nitrogen temperature in the presence of 0.67 T magnetic field. The angle of alignment, θ, was defined as the angle between the prefered direction determined by the magnetic field and the gamma-rays direction and it was altered from 0° to 90°.

The Mössbauer spectra were taken over the range of 90 - 350 K. Standard constant acceleration Mössbauer spectrometer with source of $^{57}Co(Cr)$ was used.

RESULTS AND DISCUSSION

The Mössbauer spectra of the studied compounds were quadrupole doublets of Lorentzian lines with Mössbauer parameters close to those for the F and its derivatives[2].

The Figure 1 shows the plots of the logarithm of the Mössbauer effect probability (f') vs temperature for some of studied compounds. The effective Debye temperatures Θ_D^*, characterizing the dynamics of molecules in the compounds were estimated from these depen-

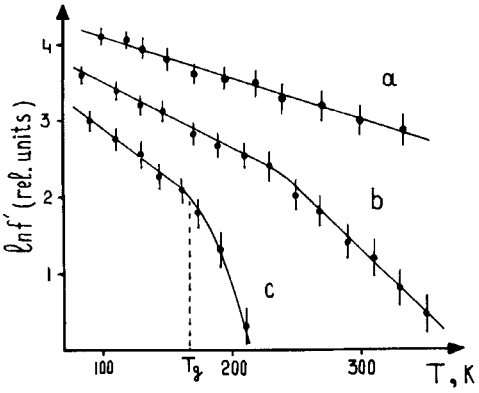

Figure 1. Plots of the ln f' vs T for polycrystalline F (a), FLC10 (b) and frozen solution FLC10 in H8 (c).

TABLE I Characteristic Debye temperatures for different types of LC's

LC-phase	Θ_D^*, K		References
	Solid	Glass	
Smectic B,H	70 - 75	53 - 60	4 - 5
Smectic A,C	60 - 65	45 - 60	--"--
Nematic	60 - 62	40 - 50	--"--
Cholesteric	20 - 30	---	3
Discotic	52	47	7
LC-polymers: a) main chain	---	59	8
b) mesogenic regions	---	78	--"--
FLCn (nematic)	21 - 29	21 - 29	This work

dences. The calculated values of Θ_D^* lie in the range of 21 - 29 K both for solid and glass phases of FLCn which are considerably less than those for F (Θ_D = = 80 ± 6 K) and diacetylferrocene (DAF, Θ_D^* = 90 ± 7 K)[3]. It means apparently that intramolecular bonds in FLCn's are essentially weaker than those for F and its non-mesomorphic derivatives. One can see from the Table 1, that Θ_D^* values for FLCn's are also the smallest among the different types of LC's studied by Mössbauer spectroscopy both in solid and glassy LC phases.

The value of Θ_D^* obtained for LC matrix H8 in this work (Θ_D^* = 45 ± 3 K) is closer to the true value than one reported in [6] (Θ_D^* = 39 ± 2 K), where H8 has been studied with F as Mossbauer label, because the geometrical form of FLCn molecules is closer to one of LC studied. Indeed, in [6] has been shown that F-labels are localized in the end-chain regions of the H8 molecules.

As the Figure 1 shows, the deviation of ln f'(T) dependence from linear behaviour was observed above 250 K for polycrystalline FLCn's. For such "long-chain" LC-compounds this fact can be explained apparently due to the "defreezing" of the hydrocarbon chains mobility above 250 K.

It was found that orientation of the FLCn's by external magnetic field results in the appearance of considerable lines asymmetry A of quadrupole doublet, indicating alignment of FLCn molecules in the NLC phase. From the analysis of angular dependences of $A(\theta)$ and $f'(\theta)$ according to [9] we obtained the order parameters S, intramolecular E_M and lattice E_L contributions to the nuclear vibrational anisotropy for studied compounds in the ordered glassy NLC phases. Table II compares these data with those for some other LC-systems.

TABLE II Parameters obtained from MS of NLC-compounds oriented by magnetic field

NLC	Label	S ±0.07	E_M ±0.04	E_L ±0.05
FLC8	-	0.27	0.11	-0.04
FLC10	-	0.21	0.04	-0.07
H8	FLC10	0.36	-0.02	-0.10
MBBA*	DAF	0	0.15	-0.15
H8 **	SnTBC	0.05	-0.80	-0.09
H8 **	SnTBL	0.09	-0.80	-0.14

* - from[10]; ** - from [12]; SnTBC - tin tributyl capronate ; SnTBL - tin tributyl laurinate.

As follows from these data the FLCn's are well aligned by magnetic field in the nematic phase. The small values of E_M implie that intramolecular vibra-

tions are isotropic, which is typical for disubstituted derivatives of F [9]. Previously, DAF was found not to order in the LC-materials [10,11]. One can see from the Table II that the Sn-bearing labels have a poor alignment in NLC's. The value of S = 0.36 obtained in this work for studied solution is the greatest among all NLC-materials investgated by the Mössbauer spectroscopy, as far as we know.

CONCLUSIONS

Analysis of the f' vs T shows that FLCn's have the weak intermolecular bonds, which results in the appearance of the additional degrees of freedom for FLCn molecules above 250 K. It is shown that these compounds, used as Mössbauer labels, give the most adequate information about the structural, dynamic and orientational properties of the studied NLC systems.

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