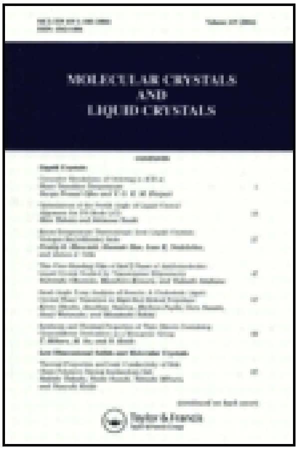

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RELAXATION MODES IN A FERROELECTRIC LIQUID CRYSTAL UNDER PRESSURE

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Relaxation Modes in a Ferroelectric Liquid Crystal under Pressure

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The complex dielectric constant of a ferroelectric liquid crystal was measured under pressures up to 350MPa. The chiral smectic C (SmC*)- smectic A (SmA) transition temperature, T_C, increases with an initial slope of dT_C/dp=0.19 K/MPa. The real part of the complex dielectric constant in the SmC* phase decreases as the pressure increases. The dielectric strength, $\Delta \varepsilon_G$, of the Goldstone mode shows an initial decline for pressures of up to about 100MPa, and then approaches a constant value, and the relaxation frequency, f_G, of the mode decreases steadily. Taking into account of the phenomenological relations of $\Delta \varepsilon_G \propto 1/K$ and $f_G \propto K/\gamma$ (K: elastic constant, γ: rotational viscosity), we conclude that the reduction of the dielectric constant in the SmC* phase is mainly caused by a decrease in the relaxation frequency due to an increase in the rotational viscosity.

Keywords: ferroelectric liquid crystal; relaxation mode; pressure effect

INTRODUCTION

Liquid crystals undergo a phase transition with changing temperature or pressure.

The application of pressure decreases the intermolecular distance and changes the intermolecular interaction, and then leads to a shift in the transition temperatures or the appearance of some new phases. Therefore, high-pressure investigation of these liquid crystals helps us to understand the physical properties of the materials [1-5].

It has been reported that the dielectric constant of p-decyloxybenzilidene-p'-amino 2-methyl butyl cinnamate (abbreviated DOBAMBC) decreases with increasing pressure, and that the chiral smectic C (SmC*) - smectic A (SmA) transition temperature, T_C, increases linearly with a pressure coefficient of dT_C/dp = 12.5 K/kbar [1]. Prasad *et al.* have reported that the relaxation frequencies of the Goldstone mode and the soft mode in a ferroelectric liquid crystal (abbreviated FLC) decrease as the pressure increases [2]. However, they do not mention the dielectric strength of the Goldstone mode. In the present study, the complex dielectric constant ε^* of an FLC was measured under pressure, and the pressure dependence of the relaxation frequency and the dielectric strength are discussed.

EXPERIMENTAL

The FLC sample used is CS-1017(Chisso), and the phase sequence at atmospheric pressure is as follows: SmC*-(55℃)-SmA-(64℃)-N*-(68℃)-Iso., where N* and Iso. are chiral nematic and isotropic phases, respectively. A homogeneously aligned cell was prepared by rubbing two ITO glass plates with polymide. The cell thickness is about 30 μm at atmospheric pressure and changes with increasing pressure. However, the increase of the sample capacitance due to the change in the cell thickness have been disregarded at the present stage. The sample cell was sealed with an epoxy resin so that a pressure-transmitting fluid(Shinetsu Silicone, KF-96-50CS) could not enter into the cell. The applied pressure in the high-pressure vessel was measured by a calibrated pressure converter (Minebea, STD-5000K). The temperature of the sample was monitored with a clomel-alumel thermocouple close to the sample. The complex dielectric constant was measured with impedance analyzers (Solartron SI-1260, HP4194A) in the frequency range between 10Hz and 100kHz.

RESULTS AND DISCUSSION

The complex dielectric constant, ε *, of CS-1017 was measured at various temperatures and pressures. Figure 1 shows the temperature variation of the real part of the complex dielectric constant, ε ', at a frequency of 560Hz. At atmospheric pressure, ε ' changes abruptly at the SmC*-SmA transition temperature, T_C. As the pressure increases, ε ' in the SmC* phase decreases and the peak, due to the soft mode, becomes clear at T_C. The pressure dependence of

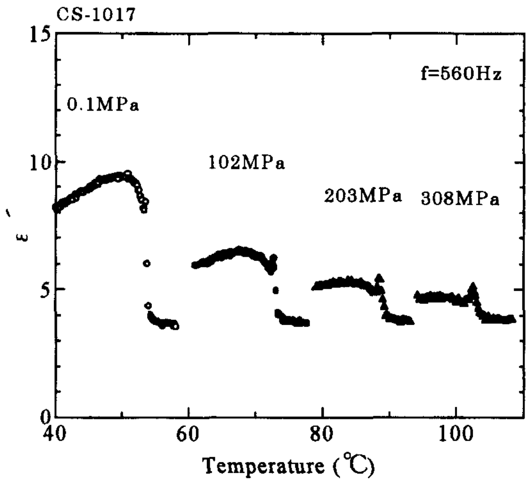

FIGURE 1 Temperature dependence of ε ' in the vicinity of the SmC*-SmA transition at various pressures

T_C is shown in Figure 2. Open circles show the SmA-N* and N*-Iso. transition temperatures observed using a polarized microscope at atmospheric pressure. In the dielectric measurements under pressure, these two transition temperatures were not confirmed. The SmC*-SmA transition temperature, T_C, linearly increases with an initial slope of dT_C/dp=0.19K/MPa, but the deviation from the linear relation between pressure and T_C becomes evident at high pressure.

To investigate why the dielectric constant in the SmC* phase changes with pressure, the dependencies of the dielectric strength, $\Delta\varepsilon_G$, and the relaxation frequency, f_G, of the Goldstone mode on the pressure were determined from the

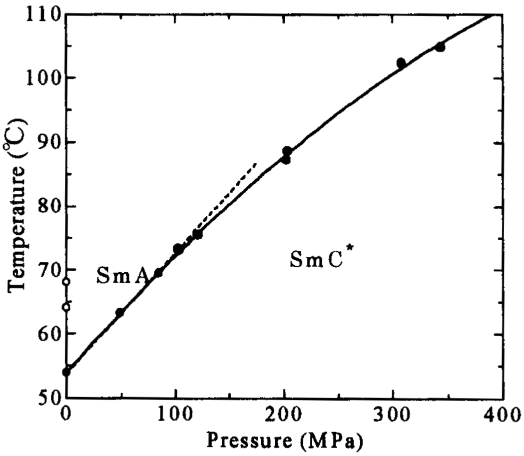

FIGURE 2 Pressure dependence of the SmC*-SmA transition temperature of CS-1017. Open circles show the SmA-N* and N*-Iso. transition temperatures at atmospheric pressure.

extended Debye type dispersion formula as below [6],

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta\varepsilon_G}{1+(if/f_G)^\beta} + \frac{1}{(if/f_C)^\gamma}, \tag{1}$$

where ε_∞ and β are the dielectric constant in the high-frequency limit and the distribution parameter of the relaxation time, respectively. The second and third terms of the right side are the contribution of the Goldstone mode and the conductivity terms, respectively. Figure 3 shows the frequency dependence of the real part, ε', and the imaginary part, ε'', at several pressures. The relaxation frequency of the Goldstone mode at atmospheric pressure is about 500Hz and a relatively large contribution of the conductivity exists in the low-frequency region.

The all experimental data were well-fitted to eq.(1). The fitting parameters at atmospheric pressure were estimated as ε_{∞}=3.4, $\Delta\varepsilon_G$=12.3, f_G=500Hz, β =0.92, f_c=130Hz and γ=0.96 from the data of ε' as a function of frequency, and similar values were also obtained by the fitting of ε''.

The pressure dependencies of $\Delta\varepsilon_G$ and f_G are shown in Figure 4. The value of $\Delta\varepsilon_G$ decreases for pressures up to about 100MPa, and then approaches a constant value above this pressure, while f_G decreases steadily. Therefore, the observed decrease in the dielectric constant with increasing pressure at a given frequency is mainly caused by a decrease in the relaxation frequency. In order to analyze the behavior of the Goldstone mode under pressure, we used the equations below that

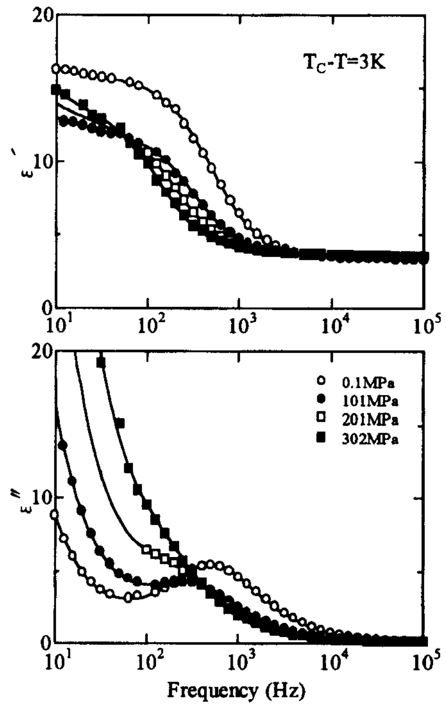

FIGURE 3 Comparison of the experimental and fitted results for ε' and ε'' at several pressures in the SmC* phase.

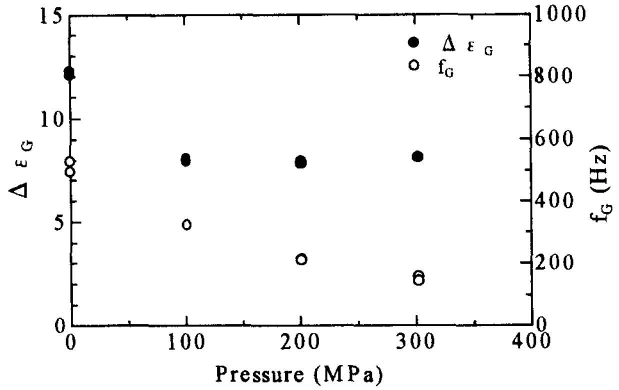

FIGURE 4 Dielectric strength, $\Delta\varepsilon_G$, and relaxation frequency, f_G, of the Goldstone mode obtained using eq. (1) as a function of pressure.

phenomenologically express $\Delta\varepsilon_G$ and f_G in terms of the spontaneous polarization, P_S, and the tilt angle, θ [7].

$$\Delta\varepsilon_G = \frac{P_S^2}{2Kq^2\theta^2}, \tag{2}$$

$$f_G = \frac{Kq^2}{2\pi\gamma}, \tag{3}$$

where q, γ and K are the wave vector of the helical pitch ($q=2\pi/p$, p: pitch), the rotational viscosity and the elastic constant, respectively.

The influence on the physical properties of increasing the pressure is similar to that for decreasing the temperature in liquid crystals. The P_S/θ and p are independent of temperature in a typical phenomenological theory [8]. Therefore, for simplicity, we regard the values of P_S/θ and p as being independent of pressure. In order to obtain the values of K and γ under pressure, the parameters used are P_S/θ =0.43nCcm^{-2}deg^{-1} (T_C-T=3 K) and p=1 μm (25℃) measured at atmospheric pressure. Kuczynski has reported that the elastic constant, K, has a tendency to saturate at low temperature, and that the rotational viscosity increases linearly [9]. Applying the analogy to the effects on temperature and pressure, it is expected that the elastic constant should saturate at high pressures. In Figure

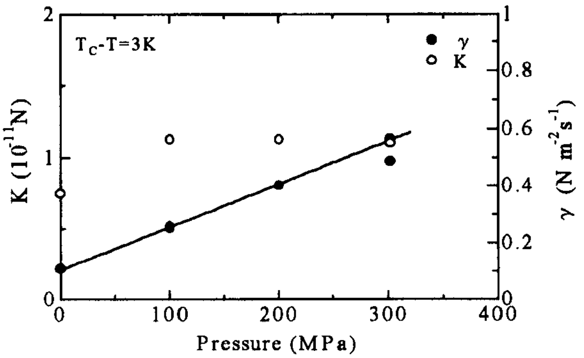

FIGURE 5 Pressure dependence of γ and K.

5, we have plotted the pressure dependencies of K and γ. The dielectric strength of the Goldstone mode decreases as the pressure is increased and approaches a constant value at a high pressure. The dependence of K on the pressure qualitatively agrees well with that of the elastic constant on the temperature. The rotational viscosity γ linearly increases with increasing pressure. The rotational viscosity in the SmC* phase of FLCs which was reported previously [2] has a linear relation to the applied pressure and is also qualitatively consistent with that obtained in the present study. Therefore, it is concluded that the reduction of the dielectric constant at a given frequency by increasing pressure in the SmC* phase is mainly caused by an increase in the rotational viscosity. From the above analysis, we can derive the dependencies of the elastic constant and the rotational viscosity on the pressure on the basis of the mode separation of the dielectric dispersion.

The relaxation frequency of the soft mode, f_S, just above T_C at atmospheric pressure (about 2.6kHz) is five times larger than that of the Goldstone mode. However, we cannot estimate the pressure dependence of f_S at T_C with high accuracy, because f_S is especially sensitive to T-T_C and the mode is observed only in the quite vicinity of T_C. However, the dielectric strength of the soft mode decreases with increasing pressure and approaches a constant value. The dielectric strengths of the soft mode and the Goldstone mode show similar dependencies on the pressure.

SUMMARY

We wish to summarize the following significant points to arise from this investigation.

1. The complex dielectric constant of the ferroelectric liquid crystal CS-1017 was measured under pressures up to 350MPa.
2. The SmC*-SmA transition temperature increases with increasing pressure with an initial slope of $dT_C/dP=0.19K/MPa$.
3. The reduction of dielectric constant at a given frequency in the SmC* phase with increasing pressure is mainly caused by a decrease in the relaxation frequency of the Goldstone mode which in turn is due to an increase in the rotational viscosity.
4. We can derive the dependencies of the elastic constant and the rotational viscosity on the pressure on the basis of the frequency dependence of the complex dielectric constant.

Acknowledgments
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