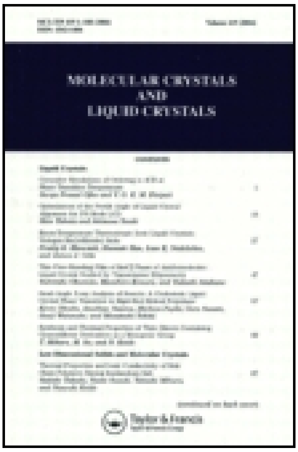

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Dielectric, Electrooptical and Magnetic Properties of Metallomesogens

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DIELECTRIC, ELECTROOPTICAL AND MAGNETIC PROPERTIES OF METALLOMESOGENS

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Abstract The dielectric behaviour of ferroelectric liquid crystals of copper (II) Schiff bases complexes were investigated by dielectric spectroscopy. The spontaneous polarization P_S and the switching time τ were determined by means of the polarization reversal method. Temperature dependent magnetic susceptibility measurements were carried out in the temperature range of 4.2 - 450 K to examine the magnetic properties of the copper (II) complexes.

INTRODUCTION

During the last years the synthesis and the investigation of nonchiral and especially chiral, ferroelectric liquid crystalline compounds incorporating transition metals is of considerable interest[1-7]. This is based on the new features of this kind of materials which combine the well known properties of usual liquid crystals as dielectric and electrooptical with the magnetic properties of transition metals.

It is known that ferroelectric liquid crystals[8,9] possess collective (Goldstone mode, Soft mode and Domain mode) and non collective relaxation processes (reorientation around long and short axis of the molecules) which could be detected by the dielectric spectroscopy with different characteristic frequencies and intensities. The Goldstone mode[10] describes the motion of the molecular director around the cone's surface with the angle 2θ. This process is usually observed at 10^2 - 10^3 Hz with high intensity. The Goldstone mode can be suppressed by an external d.c. electric field. The tilt angle fluctuation corresponds to a Soft mode[11]. It usually has a

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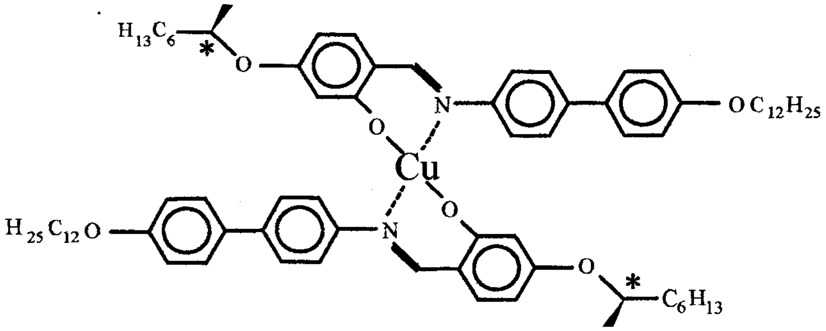
characteristic frequency of 10^4 to 10^6 Hz for low molar mass liquid crystals and is characterized by moderate intensity. This process can only be observed in the vicinity of the phase transition SmC*/SmA*. The Domain mode[9] can only be observed in FLC's with high spontaneous polarization ($P_s > 50$ nC/cm^2). This mode is observed at about 10^4 Hz with moderate intensity and can be suppressed by an external d. c. electric field. Two further non collective processes[12] could be detected, the rotation of the molecule around the long axis (frequency of 10^8 to 10^{10} Hz) and the rotation of the molecule around the short axis (frequency of 10^6 to 10^8 Hz). To our knowledge until now there is only one report on dielectic behaviour of metallomesogens in the literature[13].

In this contribution we present detailed dielectric investigations on ferroelectric copper (II) Schiff bases complexes. The electrooptical properties of these complexes as spontaneous polarization P_s and switching time τ have been determined as described elsewhere[14,15]. In addition we report on magnetic susceptibility measurements. An analysis of the magnetic susceptibility data offers the possibility to detect exchange interactions between the copper centers.

EXPERIMENTAL

Synthesis

The copper (II) Schiff bases complexes **1** (Bis[N-(4"-(n)-dodecyloxybiphenyl)-(R)-4-(1'-methylheptyloxy)salicylaldiminato]copper (II)) and **2** (Bis[N-(4"-(n)-dodecyloxy)-4-(n)-decyloxybenzoyloxy)salicylaldiminato]copper (II)) were synthesized according to a procedure as described elsewhere[16,17]. The chemical structure of the investigated copper (II) Schiff bases complexes is presented in Figure 1



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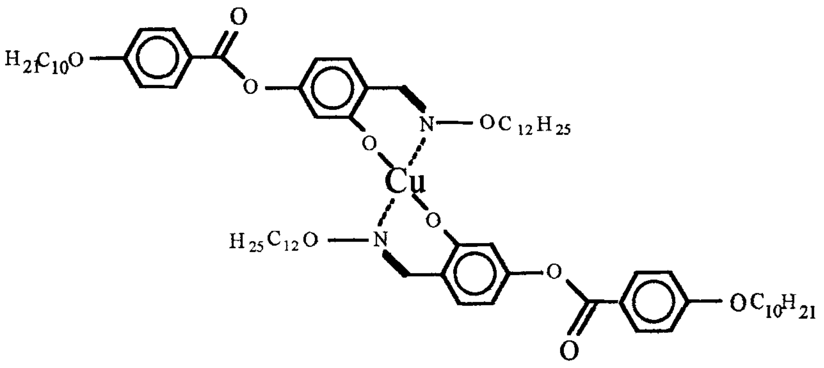

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FIGURE 1 Chemical structure of the investigated copper (II) Schiff bases complexes **1** and **2**

Electooptical measurements

The electrooptical and dielectric measurements were performed in ITO-coated cells (1.6 μm thickness, 0.133 cm^2 active area and 6.3 μm thickness, 0.142 cm^2 active area, respectively). The switching time and the spontaneous polarization P_S were measured by the polarization reversal method[18,19]. The cells were filled above the clearing point by capillary action. The thermodynamical properties of the investigated compounds were determined using a polarizing microscope (Leitz Orthoplan Pol) with an attached high resolution CCD-Camera (Panasonic WV-Cl-500HR) and a Video recording system.

Dielectric measurements

For the dielectric measurements in the frequency range of 10 Hz to 10 MHz a Hewlett-Packard impedance analyser (HP 4192 A), controlled by a modified Atari Mega St2 computer was used[20]. In order to separate the relaxation processes under consideration, the imaginary part ε'' of the complex dielectric permittivity was corrected, taking into account the influence of the cable inductivities, the connection resistivities and the dc-conductivity of the sample.

Magnetic susceptibility measurements

The magnetic susceptibilities of the compounds were recorded as a function of temperature using a Faraday type magnetometer[21] (computer controlled Cahn D-200 microbalance, Bruker B-MN 200 / 60 power supply). For magnetic susceptibility measurements in the temperature range of 300 - 500 K a heating mode of the system especially designed for this range was used. Diamagnetic corrections of the molar magnetic susceptibilities were applied using Pascal's constant[22]. The magnetic moments were obtained using $\mu_{eff} / \mu_B = 2.828 (\chi T)^{1/2}$

RESULTS AND DISCUSSION

Thermodynamical and electrooptical properties

The liquid crystalline phases of the copper (II) complexes were identified by optical microscopy. The chiral compound **1** shows a ferroelectric smectic C* phase, in addition a high ordered tilted smectic phase and a cholesteric phase. The nonchiral compound **2** exhibit a smectic C phase, a smectic A phase and a nematic phase. In order to induce a ferroelectric smectic C* phase a mixture consisting of 98.46 % of the nonchiral compound **2** and 1.54 % of a chiral dopant was prepared (compound **3**). The chemical stucture of the chiral dopant is presented in Figure 2.

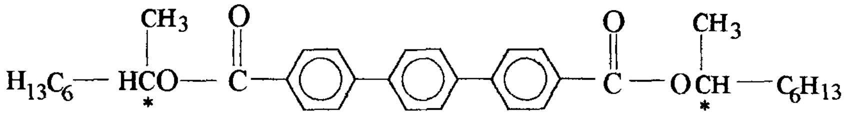

FIGURE 2 Chemical structure of the chiral dopant

The phase transition temperatures, the spontaneous polarization P_S and the switching times of the copper (II) complexes are summarized in Table I.

TABLE I Thermodynamical and electrooptical data of the copper (II) complexes

Compound	**Phase diagramm** [°C]	P_s [nC/cm^2]	τ [ms]
1	C 81.3 S_X* 144 S_C* 151.8 N* 162 I	25	10
2	C 104.7 S_C 108 S_A 115 N 132 I	-----	-----
3	C 91.2 S_Y* 98 S_C* 111 N* 129.5 I	2	10

C = crystal; S_X* = high ordered tilted smectic; S_C* = chiral smectic C; S_A = smectic A; N* = cholesteric; N = nematic; S_Y* = high ordered smectic; I = isotropic;

The compounds **1** and **3** show switching times in the millisecond range which are longer than those of most ferroelectric liquid crystals (switching times in the microsecond range). For compound **1** a spontaneous polarization of 25 nC/cm^2 was found which is comparable to the polarization value of a copper metallomesogen in the literature[23]. The doped mixture (compound **3**) possesses only a weak spontaneous polarization of 2 nC/cm^2. The high ordered tilted smectic X* phase of compound **1** is switchable by the application of an external a.c. electric field, whereas for the high ordered smectic Y* phase of compound **3** no switching could be observed.

Dielectric properties

In Figure 3 we present three exemplary spectra of the imaginary part ε'' of the complex dielectric constant $\varepsilon''(\omega)$ of compound **1** for some temperatures in the S_X* and S_C* phases. Two different relaxation processes denoted as **A** and **B** are clearly visible in the frequency range from 10 Hz to 10 MHz. The three dimensional spectrum ε'' versus frequency and temperature of compound **1** in the S_X* and S_C* phases is shown in Figure 4.

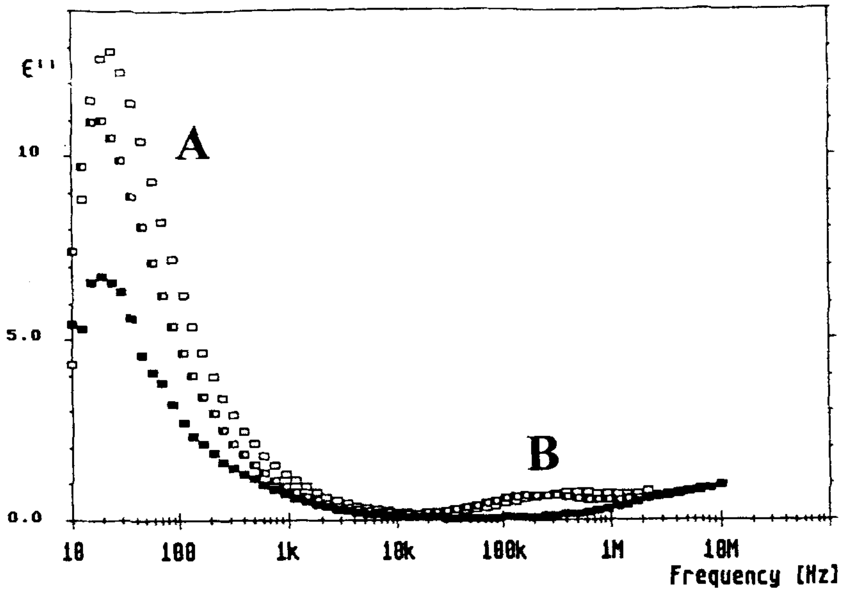

FIGURE 3 Dielectric spectra (imaginary part ε'' of the complex dielectric constant $\varepsilon''(\omega)$) of compound **1** at different temperatures (□ T = 150.4 °C; ▣ T = 145.2 °C; ■ T = 142.5 °C)

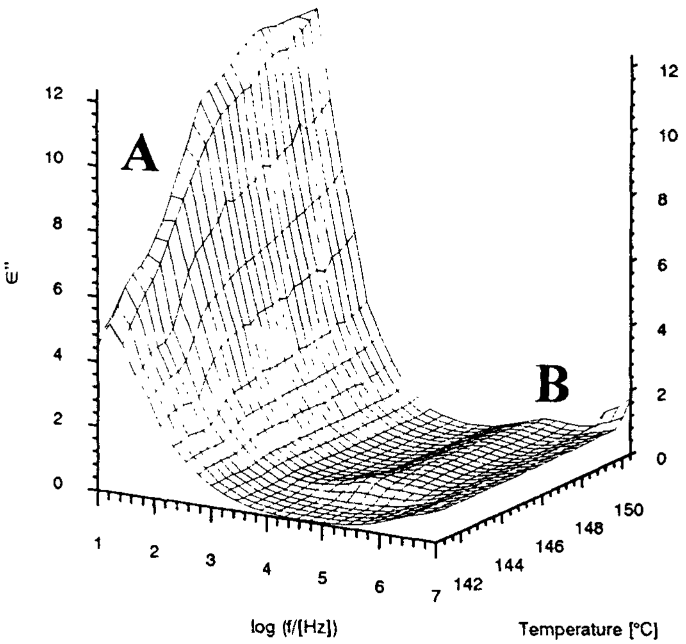

FIGURE 4 Three dimensional spectrum ε'' versus frequency and temperature of compound **1** in the S_X* and S_C* phases

The low frequency process **A** with characteristic frequencies at about 30 Hz was attributed to a Goldstone mode. The application of an external d.c. BIAS electric field leads to the suppression of this process. In the S_X* phase the relaxation strength is diminished, but still well pronounced. The high frequency process **B,** with critical frequencies at about 10^5 - 10^6 Hz shows a lower intensity and cannot be influenced by external d.c. electric fields. The intensity of this process is almost constant in the S_C* phase. In the S_X* phase this relaxation process **B** could not be observed, most probably due to a too low intensity in this phase. The relaxation process **B** was attributed to the rotation of the molecules around the long molecular axis. In order to obtain the characteristic parameters as relaxation frequency and relaxation strength for the relaxation processes under investigation a set of Cole-Cole functions[24] was fitted to the experimental data. From the Arrhenius plot (Figure 5) the activation energy of the relaxation process **B** was determined to be 62.8 kJ/mol.

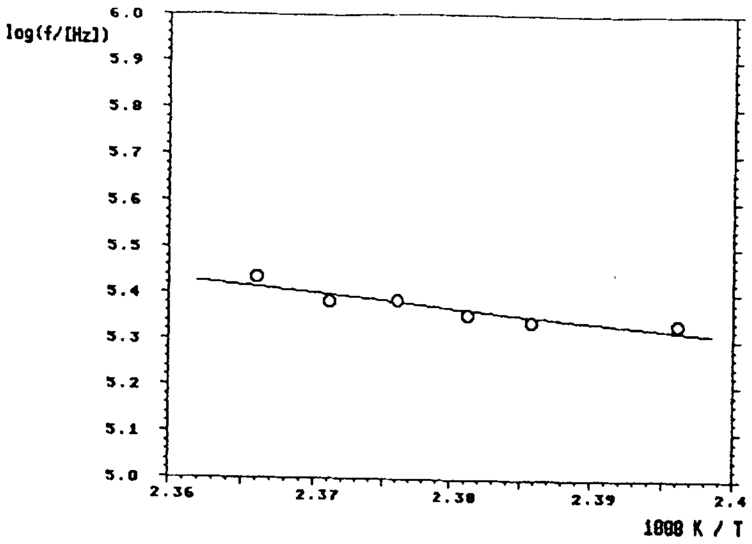

FIGURE 5 Arrhenius plot log(f / [Hz]) versus 1 / T [K^{-1}] of compound **1**

In Figure 6 the three dimensional spectra ε'' versus frequency and temperature of compound **3** in the S_Y* and S_C* phases is presented. Compared to the pure substance (compound **1**), in the ferroelectric S_C* phase of the mixture (compound **3**) only one relaxation process denoted as **A** (Goldstone mode) is visible. The temperature dependences of the critical frequency and relaxation strength of this process **A** in the S_C* phase are comparable to those, observed for the mode **A** in compound **1**. In contrary to the results obtained for compound **1**, the Goldstone mode can no longer be observed in the low temperature S_Y* phase. This is in addition to the texture observations and the switching behaviour of the S_X* and S_Y* phases a further argument that we have two different high ordered smectic phases.

Soft mode relaxation was not detected for compounds **1** and **3** in the ferroelectric S_C* phases. Also after the suppression of the Goldstone mode by means of a d.c. electric field no Soft mode could be observed.

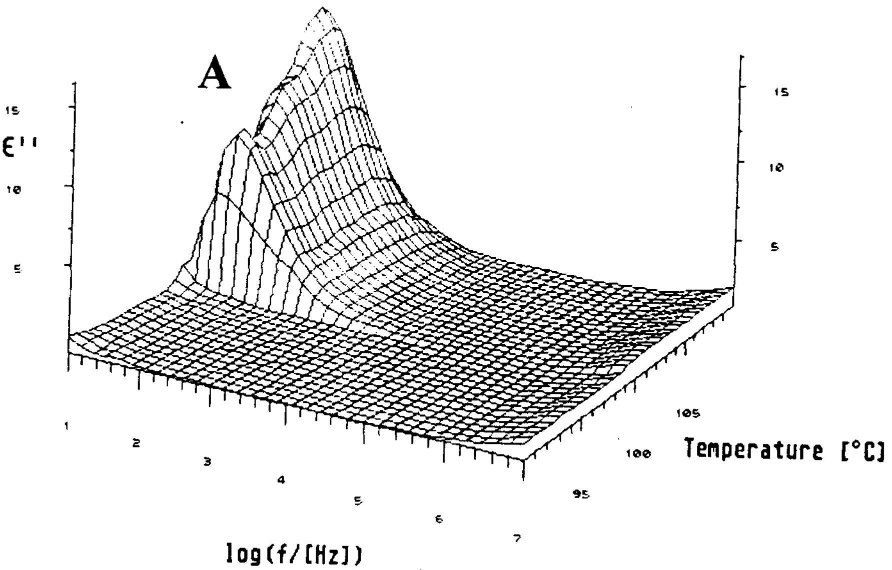

FIGURE 6 Three dimensional spectrum ε'' versus frequency and temperature of compound **3** in the S_Y* and S_C* phases

Magnetic properties

The temperature dependent magnetic susceptibilities and the effective magnetic moments of the copper (II) Schiff bases complexes **1** and **2** are displayed in Figures 7 and 8. The obtained effective magnetic moments for compounds **1** as well as for **2** are nearly temperature independent. Further on, no changes in the magnetic behaviour of the copper (II) complexes **1** and **2** were observed at the phase transitions. In order to prove, if deviations from Curie-law occur, the experimental data were fitted to a Curie-Weiss expression with S = 1/2 (Eq. (1)), including a term describing the temperature independent paramagnetism of copper (II) ($N_\alpha = 60 \cdot 10^{-6}$ cm^3/mol).

$$\chi = \frac{N_L g^2 \mu_B^2}{3k(T - \Theta)} S(S+1) + N_\alpha \qquad (1)$$

The best fit parameters are g = 2.23, Θ = 0 K for compound **1** and g = 2.24, Θ = 0 K for compound **2**. The values of Θ = 0 K indicate that no exchange interactions between the copper centers exist.

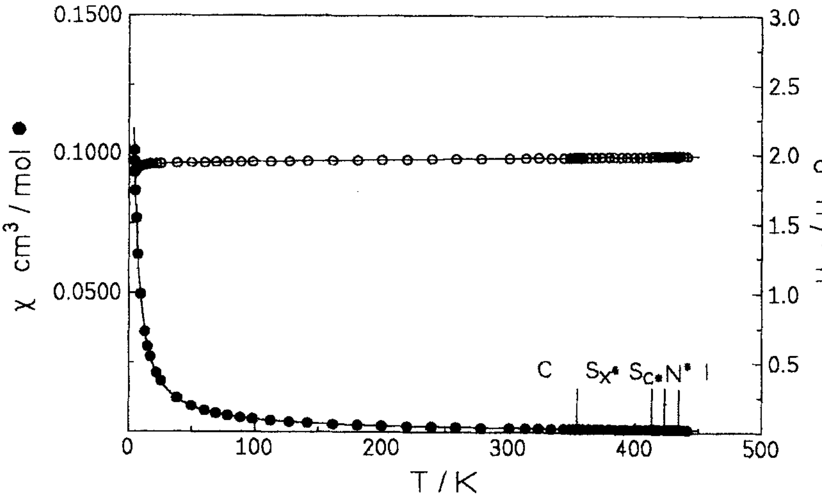

FIGURE 7 Experimental and calculated magnetic susceptibilities χ and effective magnetic moments μ_{eff} of compound 1

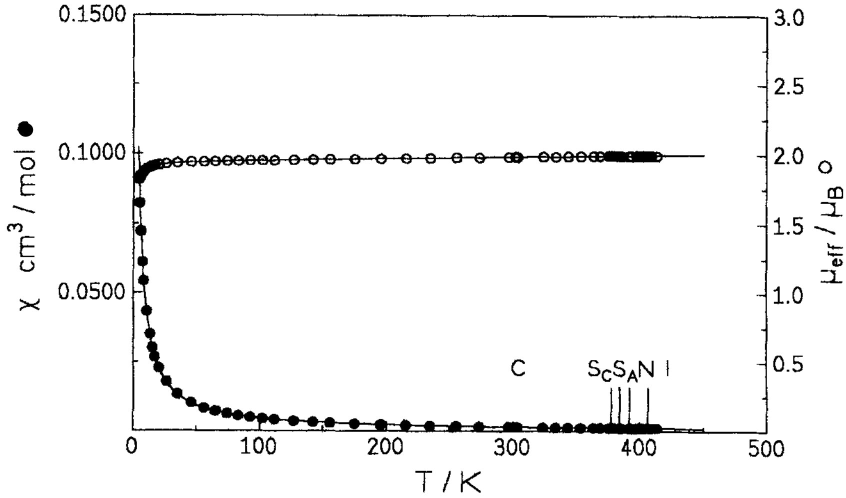

FIGURE 8 Experimental and calculated magnetic susceptibilities χ and effective magnetic moments μ_{eff} of compound 2

CONCLUSIONS

In the ferroelectric S_C* phase of the pure compound **1** two different relaxation processes denoted as **A** (Goldstone mode) and **B** (molecular process) were observed. The low frequency process **A** can be suppressed by an external d.c. electric field, whereas the high frequency process **B** cannot be influenced. In the high ordered tilted smectic X^* phase which is switchable by application of an a.c electric field, the Goldstone mode **A** can be observed with lower intensity. The molecular process **B** was not detected in the S_X* phase. A possible explanation for this observation could be the too low intensity of the process in this phase.

In the ferroelectric S_C* phase of the mixture (compound **3**) only one relaxation process **A** (Goldstone mode) is visible. The Goldstone mode can no longer be observed in the high ordered smectic Y^* phase. This phase shows no switching behaviour, applying an external a.c electic field.

The pure compound **1** possesses a spontaneous polarization of 25 nC/cm^2, whereas for the doped mixture (compound **3**) only a weak spontaneous polarization of 2 nC/cm^2 was found.

Further on, for the copper Schiff bases complexes **1** and **2** no changes in the magnetic behaviour at the phase transitions were observed and no exchange interactions between the copper centers were found.

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