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Polarized luminescence in a cubic liquid crystal

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In a liquid-crystalline cubic phase the kinetics of the luminescence induced by pulsed excitation of a luminescing dopant has been studied. The influence of the molecular reorientation on the decay kinetics of the polarized components of the light has been investigated. The correlation times of the molecular reorientation and the magnitude of the local order parameter have been determined.

Among the polymorphic thermotropic liquid-crystalline structures the cubic mesophases with a three dimensional lattice are of special interest. Up to now, two types of such structures are known: the blue phases of chiral substances [1, 2] and the cubic mesophases occurring in smectogenic compounds [3, 4]. The optical methods conventionally applied to study the orientational order of the molecules in liquid crystals (e.g. absorption, double refraction, Raman scattering) cannot be used for the investigation of the cubic structures. However, the use of different non-standard methods of investigation (e.g. transmittance spectra, diffraction in the long wavelength optical region and rotation of the plane of polarized light) led to a remarkable advance in knowledge about the structures of quasi-crystalline blue phases [1, 2, 5, 6]. For these phases the symmetry and the local order parameters of the molecules have been determined and theory which describes the experiments adequately has been developed. All this has allowed us to understand how the broad distribution of locally anisotropic regions leads to a macroscopic cubic symmetry, O^2 and O^8.

The experience of the investigation of the cubic blue phases suggest the importance of applying a range of methods for the investigation of complicated liquid-crystalline structures which contain a large number of molecules in the unit cell. The cubic phases in smectogenic compounds differ substantially from the blue phases: the lattice constant of the blue phases is 1000–4000 Å, whereas that of the cubic phases is about 50 Å, and the molecules of the latter are non-chiral. There are X-ray investigations of the cubic phases [3, 4, 8]. The lattice constants, the type of symmetry and the number of molecules in the unit cell have been determined. However, nearly nothing is known about the local arrangement of the nearest neighbour molecules and the molecular dynamics within these structures. In this paper we present experimental data of the polarized luminescence of a dopant, and from this we derive the correlation times of the molecular orientational movement of the molecules in the cubic mesophase and the values of the local order parameter.

The investigation has been performed for 1,2-bis-(4-*n*-decyloxybenzoyloxy)-hydrazine, which is a liquid-crystalline compound with a cubic mesophase in the temperature interval 143–152°C [3]. As a luminescing dopant we used 4-diethylamino-4-nitrostilbene (DEANS) at a concentration of about 0·03 wt %. The molecular structure of DEANS is very similar to that of a liquid crystal and therefore the orientation in the liquid-crystalline environment is likely to be high. The first electronic transition of DEANS is in the non-absorbing region of the liquid crystal; the dipole moment of the electronic transition in absorption and luminescence lie parallel to the long molecular axis [7, 9]. The luminescence was excited with a dye laser having a pulse half width of about 0·3 ns ($\lambda_{\text{excit}} \approx 480$ nm). The luminescence was measured with an opto-electronic camera also having a resolution of 0·3 ns [10] ($\lambda_{\text{luminesc}} \approx 630$ nm). The investigations were made for unaligned samples with a thickness of 200 μm.

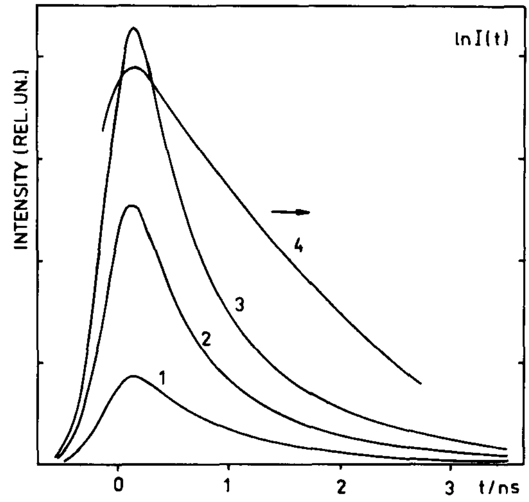

Figure 1. Kinetics of the polarized luminescence perpendicular $I_{\perp}(t)$ (curve 1) and parallel $I_{\parallel}(t)$ (curve 2) to the polarization of the exciting radiation. Curve 3, $I(t) = I_{\parallel}(t) + 2I_{\perp}(t)$; curve 4, $\ln I(t)$. The maximum of the exciting pulse corresponds to $t = 0$. Temperature 148°C.

In figure 1 we present the results of the investigation of the components of the luminescence which are polarized perpendicular $I_{\perp}(t)$ (curve 1) and parallel $I_{\parallel}(t)$ (curve 2) to the exciting radiation. The lifetime τ of the excited state was evaluated from the kinetics of the total intensity $I(t) = I_{\parallel}(t) + 2I_{\perp}(t)$ (figure 1, curves 3 and 4) and found to be approximately 1 ns. The kinetics of the decay of the single components $I_{\parallel}(t)$ and $I_{\perp}(t)$ have been evaluated by consideration of excited molecules and the orientation of the long axes of the excited molecules with respect to the polarization direction of the measured radiation. Both of these values can be obtained by the observation of the luminescence [9, 10]. In order to separate the orientation processes (see figure 2, curves 1 and 2) we use the ratio

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)}, \tag{1}$$

which is independent of the kinetics of the irradiative and non-irradiative decay of the excited electronic state. $r(t)$ is the correlation function which characterizes the orientational dynamics of the molecular long axes. In the first interval of 3 ns there is a substantial change in $r(t)$, which indicates the large amplitude of the rotational movement of the molecules in the cubic phase. $r(t)$ clearly has a distinct non-exponential character (see figure 2). $r(t)$ in the cubic phase (see figure 2) can be described by a sum of two exponents

$$\left(\tfrac{2}{5} - B\right)\exp(-t/\tau_i) + B\exp(-t/\tau_j)$$

with $\tau_j > 5\tau_i$; the main contribution to the change of $r(t)$ for the time interval studied comes from the fast component $(\exp(-t/\tau_i))$. The non-exponential time dependence of the luminescence anisotropy may indicate that there are several mechanisms of molecular reorientation with essentially different characteristic times. The molecular dynamics of the liquid crystal depends on the local organization of the molecules and on the macrostructure. Nearly all liquid crystals consisting of elongated molecules which have been investigated so far, either have macroscopic order of the molecular long axes (nematics, smectics A and C) characterized by the order parameter $\langle P_2 \rangle$, or local order of the molecular axes (N*, blue phases, smectic C*) characterized by a local order parameter $\langle P_2 \rangle_l$. The results of X-ray investigations suggest that in the cubic phase the orientation of the long axes of neighbouring molecules are also correlated so that there is local order which may be expressed by the order parameter $\langle P_2 \rangle_l$. Excitation of molecules by polarized light yields an orientationally anisotropic distribution of excited molecules in the macroscopically isotropic cubic phase. The reorientation processes lead to a loss of the anisotropy of the orientational distribution of the excited molecules. In the short times characteristic of molecular orientational movements τ_R (with $\tau_R \leqslant \tau$) the reorientational dynamics may lead to the formation of an orientational equilibrium in a local frame, enclosing the nearest molecules in a unit cell. However, the complete disappearance of the anisotropy created by the radiation would demand reorientational movements of large groups of molecules (time τ'_R) or translational movements of single molecules to large distances accompanied by their reorientation (time τ'_T). Both processes correspond to relaxation times τ'_R and τ'_T which exceed τ_R. The orientational movements of groups of molecules are hindered also by the fact that the molecular dynamics must preserve the cubic structure, so that the rotation of a sufficiently large number of the molecules in the cubic cell cannot be independent of the reorientation of the rest of the molecules. The situation in our case is quite similar to the earlier theoretical consideration of polydomain liquid crystal structures [11, 12]. The time behaviour $r(t)$ which leads to a local

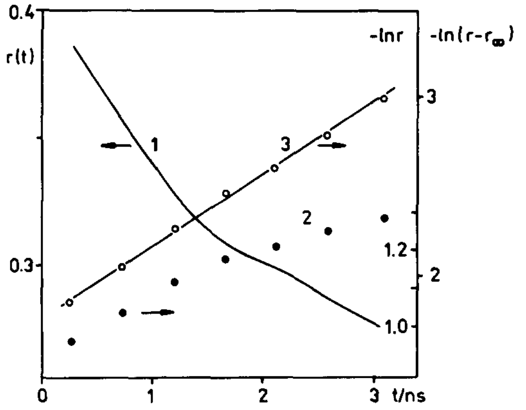

Figure 2. Time dependence of the anisotropy of the luminescence. Curve 1, $r(t)$ calculated according to equation (1); curve 2, $\ln r(t)$; curve 3, $\ln(r(t) - \frac{2}{5}\langle P_2 \rangle_l^2)$; $r(t) = \frac{2}{5}\langle P_2 \rangle_l^2$.

orientational distribution may be characterized by several relaxation times τ_i and order parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$ [11, 12]. The use of the value $r(t, \tau_i, \langle P_j \rangle)$ in general [11, 12] for the analysis of the experimental data is not realistic because of the great number of arbitrary parameters (τ_0, τ_1, τ_2, $\langle P_2 \rangle$, $\langle P_4 \rangle$). However, as computer simulations of the molecular movements [13] have shown and in addition estimates with diffusional models [11, 12, 14, 15], even with an order parameter $\langle P_2 \rangle$ of 0·8 the times τ_i do not differ by more than 20 per cent. By neglecting these different correlation times, $r(t)$ may be expressed by

$$r(t) = \tfrac{2}{5}[(1 - \langle P_2 \rangle_l^2)\exp(-t/\tau_R) + \langle P_2 \rangle_l^2]. \qquad (2)$$

Using the experimental data (figure 2, curve 1) for the evaluation of $r(t)$, equation (2) yields $\langle P_2 \rangle_l \approx 0{\cdot}75$ and $\langle \tau_R \rangle \approx 2{\cdot}4$ ns (figure 2, curve 3). For values of the order parameter $\langle P_2 \rangle$ greater than 0·7 the time dependence of correlation functions $\phi_{m0}(t)$ may be distinguished from an exponential one [11, 14]. The value of the local orientational order parameter can be estimated to be in the range 0·6–0·8 by taking account of [11, 16].

Our data on the polarized luminescence show that in the cubic phase the molecules have a high local orientational order. The optical isotropy of the structure in the cubic unit cell, which contains about 115 molecules, is obviously possible by changes of the direction of the local director. Irrespective of the large local (orientational) and macroscopic (cubic) order the molecules possess high mobility. The change of $r(t)$ (see figure 2) corresponds to an effective rotation of the long molecular axes by an angle of about 20°.

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