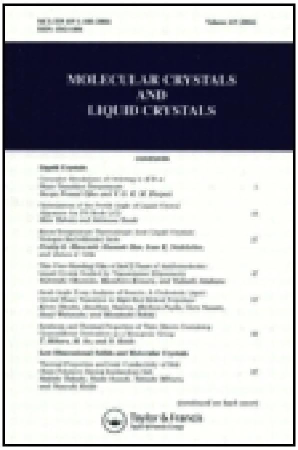

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A Study of a Ferroelectric Liquid Crystal Using Second Optical Harmonic Generation†

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The phase-matched generation of the optical second harmonic was investigated in the chiral smectic C^* phase of a classical ferroelectric liquid crystal (DOBAMBC). The phase-matching was achieved either by incidence angle or by temperature tuning. The temperature behaviour of the second order nonlinear susceptibility was studied.

INTRODUCTION

There are several papers[1–7] where the effect of the second harmonic generation (SHG) was investigated for the nematic, cholesteric and smectic A phases of liquid crystals. Both the nematic and smectic A phases were proved to be centrosymmetric with the nonlinear susceptibility $\chi^{(2)}$ equal to zero. The latter is approximately true even for the cholesteric phase. Thus, such nonlinear optical phenomena as SHG, parametric generation and Pockels' effect should not occur in these phases in the framework of the dipolar interaction mechanism with an electric (optical) field. Only the electric quadrupolar (or the supposedly magnetic dipolar) interaction[7] could be responsible for a weak SHG effect observed in the phases mentioned.

So, the investigation of the SHG effect in the polar ferroelectric phases, such as the chiral smectic S^* or smectic H^* (G^*) is of special interest. The only previous paper[8] has, as expected, confirmed the idea that the center of symmetry is absent in the smectic C^* phase of p-decyloxy-benzylidene-p′-amino-2-methylbutyl cinnamate (DOBAMBC). The aim of the present paper is to measure the magnitude

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of the quadratic nonlinear susceptibility $\chi^{(2)}$ and to find a correlation between $\chi^{(2)}$ and the magnitude of the spontaneous polarization P_S if such a correlation takes place. The investigation was carried out in the regime of the phase-matched (synchronous) optical harmonic generation.

EXPERIMENTAL TECHNIQUE

When an external field is absent the director in chiral ferroelectric phases of DOBAMBC forms a helical structure with an axis perpendicular to the smectic layer plane. The vector of the spontaneous polarization also rotates in space being perpendicular to the director and lying in the layer plane. The *d.c.* electric field applied perpendicularly to the helical axis untwists the helix resulting in a uniform ferroelectric structure with the spontaneous polarization vector directed along the external field. At the same time, the field induces some additional electric polarization according to the usual (Debye's) mechanism. Both the terms provide a contribution to the SHG intensity. The problem to be solved in this work is the separation of these terms from each other.

The usual way to obtain a phase-matched SHG in nematic or smectic *A* phases is to change the angle between the wave vector of the fundamental beam and the optical axis of a liquid crystal by rotating a cell around the direction of the *d.c.* field inducing SHG.[6,7] Such a procedure has also been used to study the temperature behaviour of SHG in the smectic C^* phase of DOBAMBC. In addition, we show the possibility of using the temperature dependence of the molecular tilt angle Θ in this phase to achieve the phase-matching condition. The calculated values Θ_S for the direction of the phase synchronism obtained from refraction indices N_e and N_o of DOBAMBC correspond to angles ~23.5° and 33.8° for the *ee-o* and *oe-o* interaction, respectively (here *ee-o*, e.g., means that two waves of the extraordinary type result in the ordinary wave of the second harmonic). Thus, for DOBAMBC where the molecular tilt angle $\Theta(T)$ increases from 0 to 29°, ref 12, with decreasing temperature, there is an opportunity to obtain the temperature induced phase-matched condition in the case of the ee-o interaction.

An experimental set-up for the SHG investigation has been described earlier.[6] We use cells of the sandwich type, Figure 1a, with thicknesses of liquid crystal layers from 20 to 90 μm. The cell surfaces were treated by chromium stearyl chloride to have the helical axis

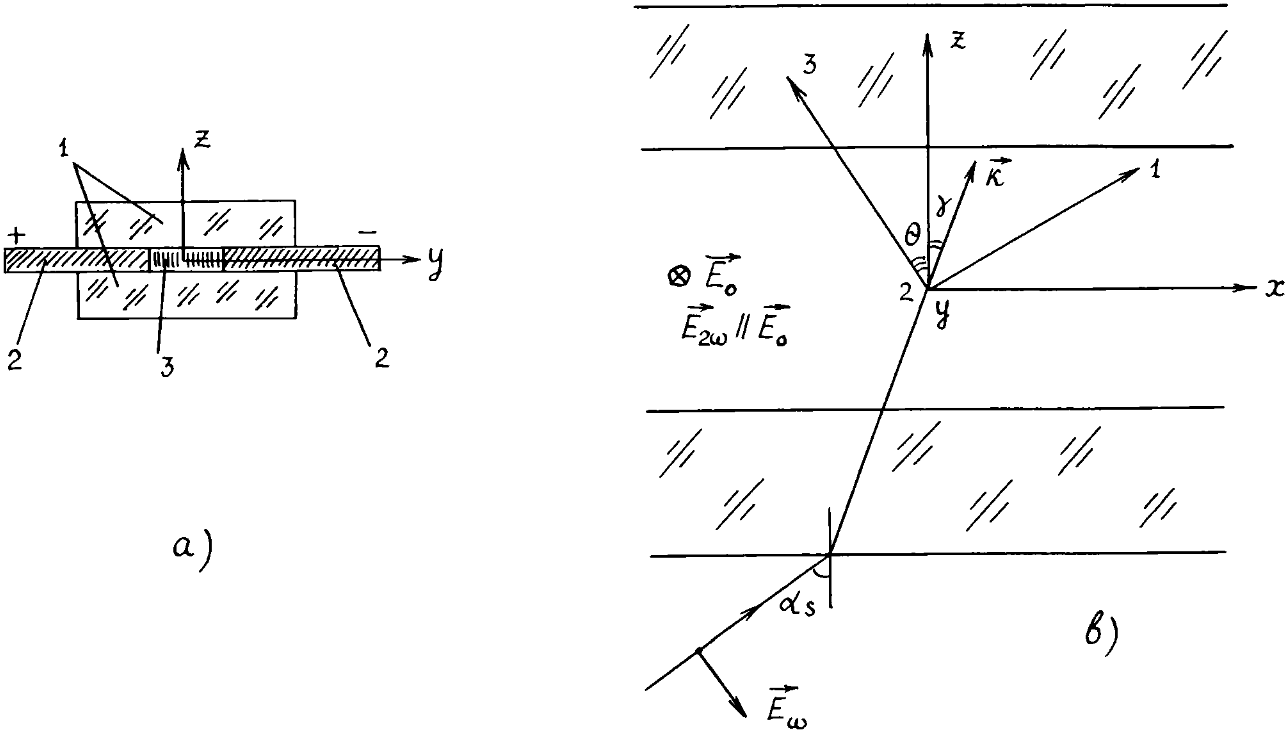

FIGURE 1 Geometry of a cell; a) total view (1 - glass, 2 - electrodes, 3 - liquid crystal); b) optical scheme.

(z-axis) perpendicular to them. A *d.c.* electric field untwisting the helix was perpendicular to the helical axis (ie the y-axis), Figure 1b. In the untwisted structure smectic planes remained parallel to the cell surfaces.

RESULTS

Figure 2 shows the temperature behaviour of second harmonic intensity $I_{2\omega}$ for a light beam incident normally on a cell. The phase-matching is observed at a temperature $T_{C^*A} - T = 8°\text{C}$ which corresponds to the molecular deviation angle (from the normal to smectic layers) of 23°, ref 12. The latter agrees well with the calculated angle $\Theta_S \approx 23.5°$. A small half-width of the phase-matching curve and a high degree of the polarization ratio for second harmonic light, $\rho = 0.95$, are indicative of a uniform orientation of a liquid crystal layer.

The dependence of $(I_{2\omega})^{1/2}$, taken at the maximum of the synchronism for various temperatures, upon an external electric field E is shown in Figure 3. The experimental curves have three different parts: a) the region of a weak field where the helix is almost not distorted and the SHG signal is very small; b) the region of a sharp increase of $I_{2\omega}$ corresponding to the untwisting of the helix and appearance of the phase-matching conditions; and c) the region of the rather slow linear increase in $I_{2\omega}$ which is due, supposedly, to the polarization induced by the field. The extrapolation of the latter part of the curves to the zero value of E, gives nonzero intensity of SHG only in the smectic C^* phase $(I_{2\omega})_S^{1/2}$ (and not in the smectic A phase) which confirms the existence of the spontaneous dipolar ordering in this phase. The extrapolated values for the effective quadratic susceptibilities d_s were calculated from experimental data on $(I_{2\omega})_S^{1/2}$ and shown in Figure 4 as functions of temperature. The total effective susceptibility d in the smectic C^* and smectic A phases is shown in Figure 5.

The molecular tilt angle Θ may be calculated from our data. Let us assume that refractive indices N_e and N_o in the smectic C^* phase do not differ strongly from the same indices in the smectic A phase near the A-C^* transition point. Then the phase-matching angle should be the same in both phases $\Theta_S^A = \Theta_S^{C^*}$ and the molecular tilt angle cound be found from equation

$$\Theta_S^A = \Theta - \gamma = \Theta - \arcsin\frac{\sin\alpha_S}{N_g}$$

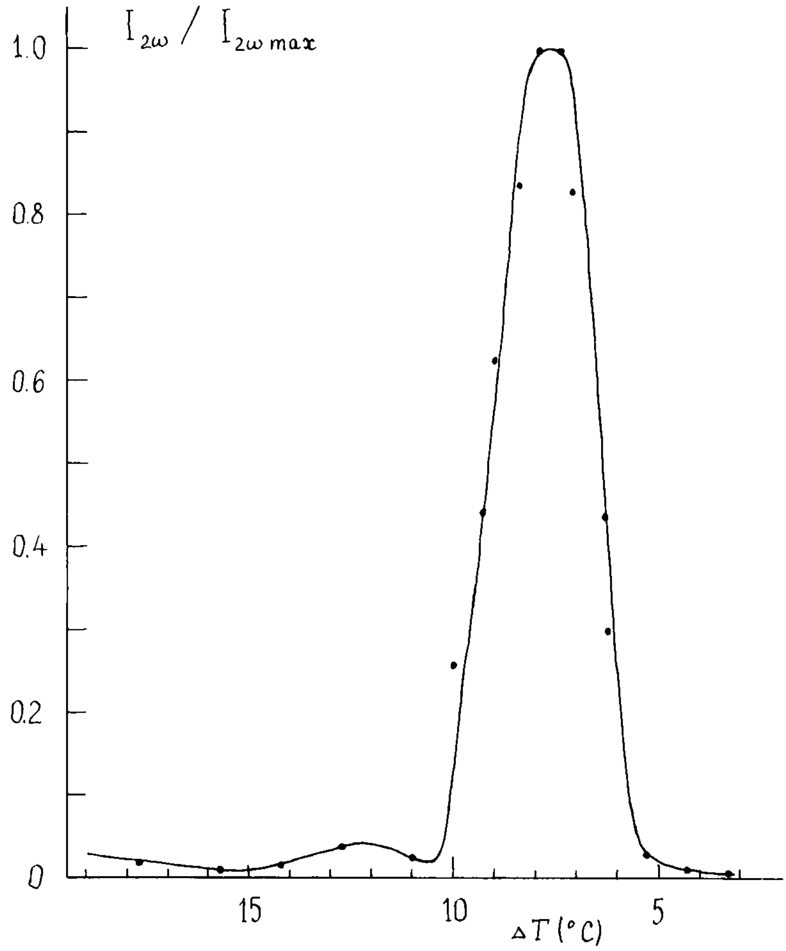

FIGURE 2 Temperature behaviour of the second harmonic intensity (layer thickness = 90 μm, d.c. field = 3 kV · cm^{-1}).

where Θ_S^A is the phase-matching angle in the smectic A, α_S is the angle of light incident at the phase-matching (Figure 1b), and N_g is the refractive index of glass. In this equation the refraction at the glass-liquid crystal interface is not taken into account. The result of such a calculation is shown in Figure 6 where a solid line corresponds to data taken from reference.[12] It is seen that our method gives rather accurate results.

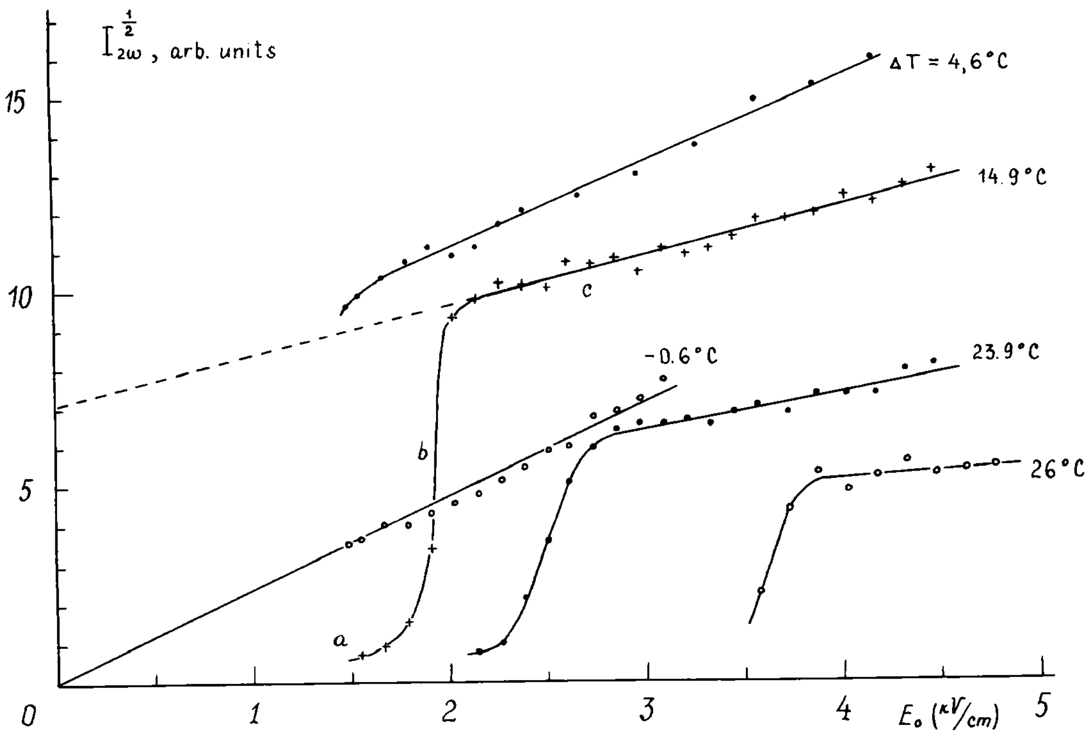

FIGURE 3 Second harmonic intensity in the maximum of synchronism as a function of an electric field for various temperatures.

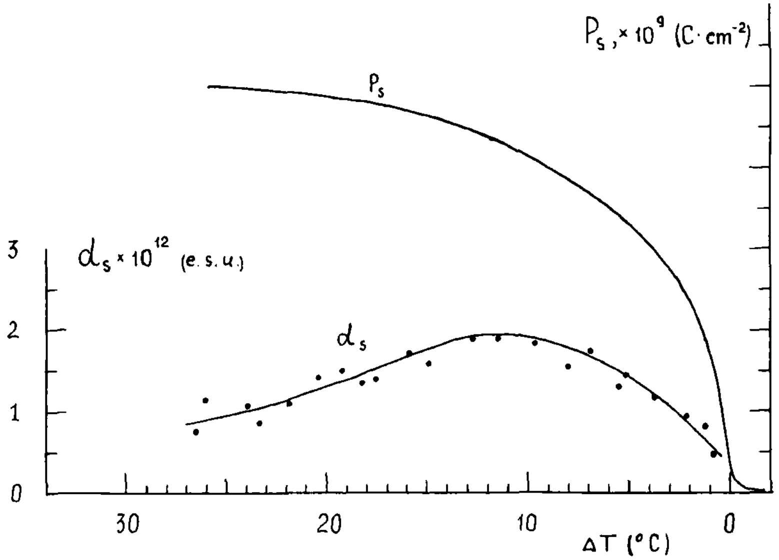

FIGURE 4 Temperature dependence of the spontaneous effective nonlinear susceptibility and the spontaneous polarization for DOBAMBC.

DISCUSSION

There is no strict theoretical consideration for the $\chi_S^{(2)}$ value. Thus, we will try to analyse qualitatively the dependence $\chi_S^{(2)}$ on microscopic parameters of a liquid crystal following the method described in refs. 9 and 10. For a liquid crystalline ferroelectric with its helical structure untwisted by an external field we have

$$\chi_{ijk}(E) = NL\left\{\langle\beta_{ijk}\rangle + \left[\langle\gamma_{ijkl}\rangle + \frac{\langle\mu_e\beta_{ijk}\rangle}{k_BT} - \frac{\langle P_e\beta_{ijk}\rangle}{Nk_BT}\right]E_l\right\}. \quad (1)$$

Here, L is a local field factor, β_{ijk} is a second order polarizability, γ_{ijkl} is a hyperpolarizability of third order, μ_l is a molecular dipole moment, P_l is the spontaneous polarization, E_l is a *d.c.* electric field, N and k_B are number of molecules in unit volume and Boltzman's constant respectively. Angular brackets mean a statistical average over the zero-field distribution for the molecular axes of a ferroelectric liquid crystal.

It is easily seen from equation (1) that the total nonlinear suscep-

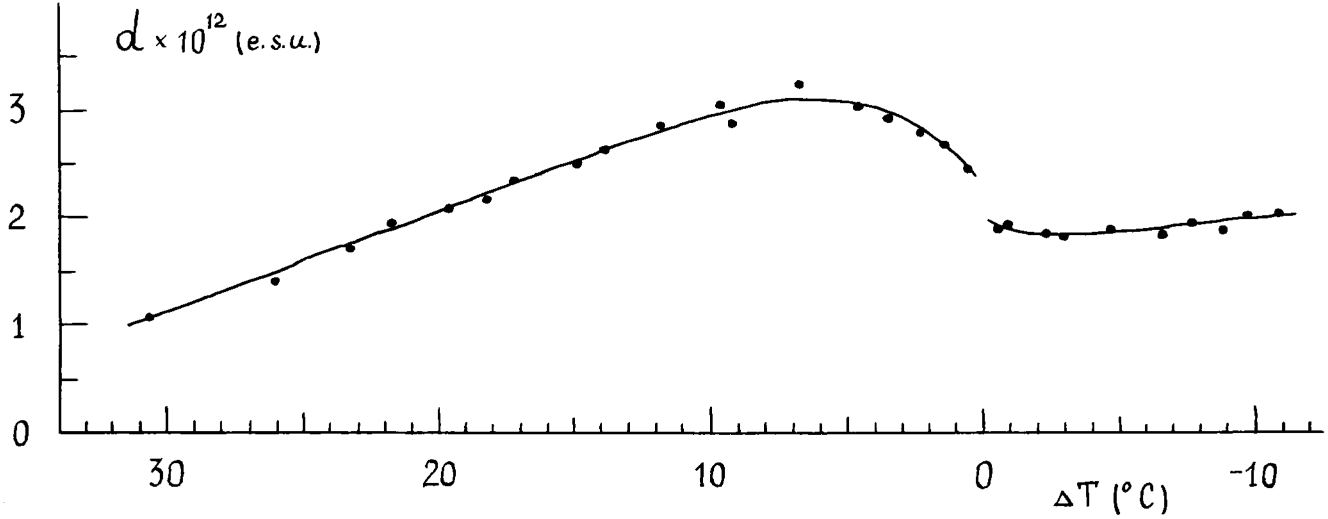

FIGURE 5 Temperature behaviour of the total effective susceptibility ($\Delta T = T_{C\cdot A} - T$, field $= 3$ kV · cm^{-1}).

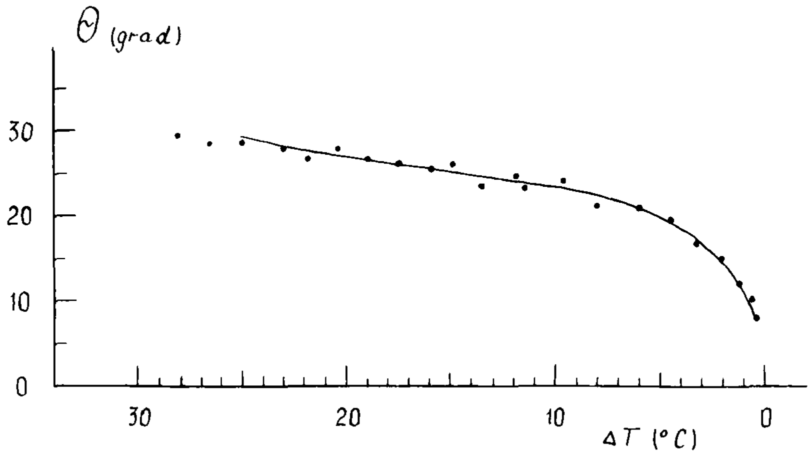

FIGURE 6 Temperature dependence of the averaged molecular tilt angle.

tibility consists of two parts, (a) a part independent of the external field which is due to the polar structure of a ferroelectric and (b) the field-induced part which is analogous to the field-induced nonlinear susceptibility in nonpolar phases.[9,10] The only difference is in the averaging procedure. In the case of a ferroelectric phase averaging γ_{ijkl} and $\mu_l\beta_{ijk}$ is carried out over the polar orientational distribution function and the results, in principle, differ for the two cases. These is also an additional term in equation (1) which depends on the magnitude of the spontaneous polarization. The equation may be rewritten in the simplified way:

$$\chi^{(2)}(E) = \chi_S^{(2)} + \Gamma(P_S) \cdot E \tag{2}$$

According to ref. 11 a ferroelectric liquid crystal layer has a C_2 symmetry. For this point group (ie helix untwisted by a field E) the tensor of the quadratic nonlinear susceptibility in the Cartesian (1, 2, 3) system has the form

$$\chi_{ijk}(E) = \begin{pmatrix} O & O & O & \chi_{123} & O & \chi_{112} \\ \chi_{211} & \chi_{222} & \chi_{233} & O & \chi_{213} & O \\ O & O & O & \chi_{323} & O & \chi_{312} \end{pmatrix}. \tag{3}$$

The effective susceptibility d measured in our experimental geometry, Figure 1, is defined by equation

$$d = \chi_{211}\mathrm{Cos}^2(\theta - \gamma) + \chi_{233}\mathrm{Sin}^2(\theta - \gamma) - \chi_{213}\mathrm{Sin}\,2(\theta - \gamma), \quad (4)$$

where Θ is the molecular tilt angle and γ is the angle between smectic layer normal and the wave vector $\vec{k}$ for a fundamental beam. Angle γ is positive to the left from the z-axis and negative to the right from it. The polar 2-axis and the electric field E are directed along the y-axis. Taking into account the structure of tensor $\chi_{ijk}(E)$, eqs.(1) and (2) the effective quadratic susceptibility may be written as follows

$$d = d_S + A \cdot E, \quad (5)$$

where the part d_S is due to the polar dipolar ordering. Equation (4) is also true for d_S if one takes only that part of χ_{ijk} (E) which is independent of E. The A-value includes hyperpolarizabilities and determines the slope of linear high field parts of curves $(I_{2\omega})^{1/2}$ in Figure 3. It is seen that the slope decreases monotonically with decreasing temperature. It follows from eq.(1) that this decrease results from the third term $\langle P_l\beta_{ijk}\rangle/Nk_BT$ which increases with increasing spontaneous polarization $P_S = \{P_l\}$. The decrease in A also follows from consideration of the difference $d - d_S = A\cdot E$ which is largest near the phase transition from the smectic A to the smectic C^* phase.

Unfortunately, using only the *ee-o* interaction it is impossible to separate three different terms in d_S resulting from different components of χ^S_{ijk}. Thus, it is difficult to discuss the temperature behaviour of d_s, which is probably due to the different dependencies of components of χ^S_{ijk} on the value of the spontaneous polarization.[8] It should be noted that near the $C^* - A$ phase transition the temperature dependences of d_S and P_S are correlated.

Such a correlation between the spontaneous polarization and the corresponding (spontaneous) term of the nonlinear quadratic susceptibility d_s was observed over the whole temperature range of the chiral smectic C^* phase for another liquid crystalline ferroelectric. It consisted of an achiral ester compound doped with a chiral dipolar impurity. The temperature behaviour of P_S and d_s for this mixture is shown in Figure 7. It should be noted that for almost equal P_S values for DOBAMBC (Figure 4) and for the mixture the value of d_s for the ester mixture is 2–3 times less than that for DOBAMBC. The reason is a lower value of molecular polarizability for ester compounds confirmed by smaller values of the refractive indices.

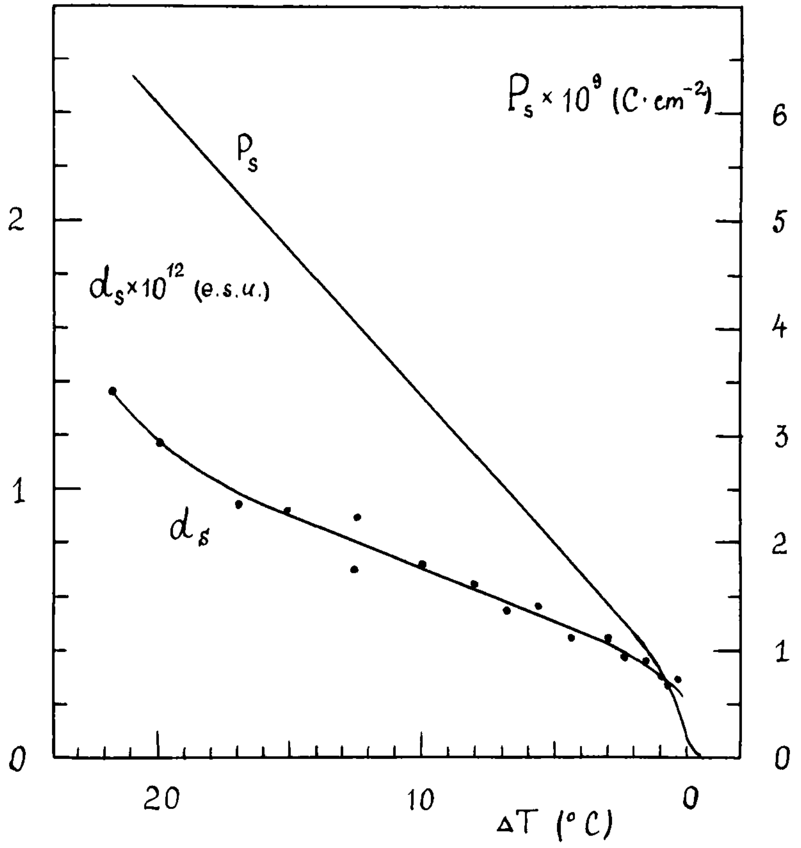

FIGURE 7 Temperature dependences of the spontaneous polarization P_S and spontaneous term in nonlinear susceptibility d_s for a mixture of an ester matrix with a chiral additive.

In conclusion, the temperature dependence of the second order nonlinear susceptibility of the ferroelectric phase of DOBAMBC has been measured using a phase-matched second harmonic generation.

Acknowledgments

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