applies to the result for Tb.[3] The discussed effects are also important for other strongly anisotropic systems. A comprehensive analysis of the spin waves in the heavy-rare-earth metals on the basis of the systematic Bose operator expansion will be published elsewhere.

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Observation of Pyroelectricity in Chiral Smectic-*C* and -*H* Liquid Crystals*

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Pyroelectricity has been observed in the smectic-*C* and smectic-*H* phases of *l*-*p*-decyloxybenzylidene-*p*′-amino-2-methylbutylcinnamate after the material is poled in a dc field. The observed pyroelectric coefficient is consistent with an estimate of its theoretical value.

Recently Meyer *et al.*[1] have presented both theoretical arguments and some experimental evidence that *p*-decyloxybenzylidene-*p*′-amino-2-methylbutylcinnamate (DBC), when prepared as a pure enantiomer (using *l*-amyl alcohol), is ferroelectric in the smectic-*C* and smectic-*H* phases. It occurred to us that an indication of spontaneous polarization in these phases would be the presence of a *pyroelectric* effect. We have succeeded in measuring a pyroelectric current in the smectic-*C* and smectic-*H* phases of the *l*-enantiomer of DBC after aligning the phases in a dc electric field, and verified that no pyroelectric effect is observed in the racemic form of DBC.

l- and *dl*-DBC were synthesized in the following manner[2]: *p*-nitrocinnamic acid was converted to the acid chloride via treatment with thionyl chloride; *l*-amyl alcohol or *dl*-amyl alcohol was then added to form the *p*-nitrocinnamate ester, which was reduced to the p-aminocinnamate ester with stannous chloride and hydrochloric acid. Finally, the Schiff base DBC was made by condensing the p-aminocinnamate ester with n-decyloxybenzaldehyde. The phase transition temperatures were in good agreement with those previously reported.[1]

The pyroelectric measurements were performed on samples of l-DBC and dl-DBC aligned between two glass plates which had been coated with indium oxide and then with silicon monoxide to promote homogeneous alignment.[3] A 6.3-μm or 12.7-μm Mylar film with a 1.2×1.2-cm^2 hole was used as a spacer. The samples were heated to 125°C, 8° higher than the isotropic transition temperature, kept under a dc electric field of 5×10^4 V cm^{-1} for 1 h, and quenched to the smectic-C phase with the field still applied. This treatment serves two functions: Undesirable ionic species are removed by electrolysis, and the sample is "poled"; i.e., the dipoles are aligned in the field. Alternatively, the sample can be poled starting from the smectic-A phase (115–95°C). In the smectic-C and -H phases, the "spontaneous" currents are measured after the "background" current stabilizes, which takes ~2 h. A small residual background current is always observed; in l-DBC a pyroelectric current is also observed when the sample is heated (or cooled) at a rapid heating (or cooling) rate. The pyroelectric currents were measured in the smectic-C and -H (< 63°C) phases. In the smectic-A phase, in accord with theory, no pyroelectric current could be observed. However, the background current in this phase was always quite high, and it would therefore be difficult to distinguish a pyroelectric current in this phase in any event.

In the experiments reported in this work, the molecular axis is parallel to the glass; i.e., the smectic planes are perpendicular to the glass and an electric field is applied perpendicular to the glass plates. A macroscopic dipole moment will only occur when the helicoidal smectic array is "untwisted," i.e., when the pitch approaches infinity. We found that after poling, the infinite-pitch smectic-C and -H phases were partially retained for several hours even after the field was removed; i.e., a memory state was achieved. Microscopic observations indicated that a large portion of the sample did not relax back to the so-called fingerprint texture; the helical array may be partially restored but with a large pitch.[4] For this reason, the structures of both the smectic-C and the smectic-H phases, being untwisted, should have a macroscopic dipole moment and should therefore show a pyroelectric effect. As a control experiment dl-DBC was treated in an identical manner; because of the apolar character of this material, no pyroelectric effect should be observable.

Pyroelectric currents were measured in a manner previously described.[5] The samples are first held at a fixed temperature until a stable background current is observed and recorded; heating rates of 75 and 10°/min for the smectic-C and smectic-H phases, respectively, were applied and the phases heated to a 5° higher temperature. As can be seen in Fig. 1, this heating produces a current pulse as well as a rise in the background current. The background current stabilizes again as soon as the temperature stabilizes. When no pyroelectric current is produced, as in the experiments with dl-DBC, one observes the rise in the background current, but no pyroelectric current pulse.

The pyroelectric coefficient dP/dT can be calculated from the data of Fig. 1 from the following expression for the pyroelectric current I:

$$I = A(dP/dT)dT/dt , \qquad (1)$$

where A is the electrode area and dT/dt is the heating rate. The highest value of the pyroelectric coefficient in the smectic-C phase is ~2×10^{-11} C deg^{-1} cm^{-2}, and ~3×10^{-11} C deg^{-1} cm^{-2} in the smectic-H phase. The magnitude of the ob-

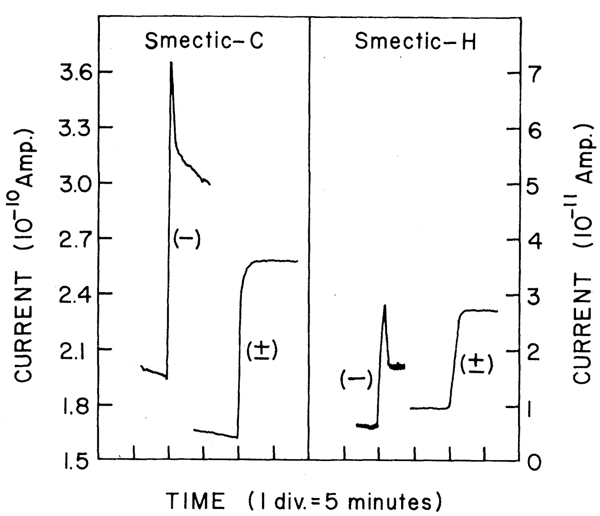

FIG. 1. Recorder tracings of observed currents in chiral (–) and racemic (±) DBC. The compounds are heated from 65 to 70°C at a rate of 75°/min in the smectic-C phase, and from 50 to 55°C at a rate of 10°/min in the smectic-H phase.

served pyroelectric coefficient was often as much as a factor of 2 less than this, the irreproducibility presumably related to the degree of alignment and memory state which exists in the individual sample.

An estimate of the theoretical value of dP/dT can be made in the following manner. Polarization P is defined as the macroscopic dipole moment per unit volume V:

$$P = N\bar{u}/V = \rho\bar{u}, \tag{2}$$

where N is the number of dipoles in the volume V, $\bar{u}$ is the dipole moment, and $\rho = N/V$. By differentiating Eq. (2) with respect to temperature T, one obtains

$$\frac{dP}{dT} = P\left(\frac{1}{\rho}\frac{d\rho}{dT} + \frac{1}{\bar{u}}\frac{d\bar{u}}{dT}\right). \tag{3}$$

The relative change in density $(1/\rho)d\rho/dT$ is approximately the volume expansion coefficient (negative sign) and should have the value of $\sim -1 \times 10^{-3}$ deg^{-1}.[6,7] The magnitude of the second term in Eq. (3) is -10^{-5} deg^{-1},[8] and can therefore be neglected.[9] P can be assumed[1] to have a value of ~ 125 esu cm^{-2} ($= 4.2\times 10^{-8}$ C cm^{-2}). Therefore an estimate of dP/dT is $\sim -4\times 10^{-11}$ C deg^{-1} cm^{-2}.

Thus the observed value of the pyroelectric coefficient [(2 to 3)$\times 10^{-11}$ C deg^{-1} cm^{-2}] is quite close to the theoretical value. Since neither perfect alignment of smectic-C and -H phases nor perfect untwisting of the chiral phases can be assured, the agreement is rather good. Further work on describing the properties of these interesting phases is underway.

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COMMENTS

Anomalous Angular Distribution in the Transition to the $2s_{1/2}$ State in ^{17}O

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The reaction $^{16}O(^{14}N, ^{13}N)^{17}O$ has been studied at a bombarding energy of 79 MeV. The angular distribution for the transition to the $2s_{1/2}$ state in ^{17}O showed an anomaly similar to that already reported in studies of $^{12}C(^{14}N, ^{13}N)^{13}C$ and $^{12}C(^{10}B, ^{9}Be)^{13}N$.

Recently, an anomaly has been reported in the angular distributions for population of $2s_{1/2}$ states of ^{13}C ($E_x = 3.09$ MeV) and ^{13}N ($E_x = 2.37$ MeV) in studies of the reactions $^{12}C(^{14}N, ^{13}N)^{13}C$ [1] and $^{12}C(^{10}B, ^{9}Be)^{13}N$,[2] respectively. In these studies it was found that exact finite-range distorted-wave Born-approximation (DWBA) calculations assuming a direct one-step transfer reaction mechanism gave theoretical angular distributions which oscillated completely out of phase with the