Chapter I

INTRODUCTION

I.1 Liquid Crystals

The liquid crystalline phase is distinguished from both the solid and the liquid phases. It mixes the properties of both liquid and solid forms and is intermediate between the two. It has the mobility of liquids and the optical properties of solids[1]. The dominant feature of the solid crystalline state is the strong interaction that exists between its constituent molecules and which gives rise to the orderly arrangement in the solid. When the temperature of the solid is high enough such that the average thermal energy of a molecule exceeds its bonding energy, the molecules escape from the influence of one another and the solid melts to a liquid. But there are compounds which are called " liquid crystals " that have a special property. When they are heated, before going to the proper liquid state, they exhibit the mesomorphic state which is called the liquid crystalline state.

I.1.1 Classification and properties of liquid crystals

There are two categories of liquid crystals[2].

(a) Thermotropic liquid crystals : they are prepared by heating

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[1] Glenn H. Brown, " Liquid Crystals ", Chemistry, 40(1967),10.

[2] Glenn H. Brown, " Liquid Crystals and Their Roles in Inanimate and Animate Systems," American Scientist, 60(1972),64.

a certain organic compound or organometallic compound.

(b) Lyotropic liquid crystals : they are prepared by mixing two or more components , one of which generally has rather polar molecules. The other component may be organic or inorganic compound.

(a) Thermotropic liquid crystals are divided into three classes, namely,

(1) Smectic liquid crystals,
(2) Nematic liquid crystals,
(3) Cholesteric liquid crystals.

(1. Smectic liquid crystals : There are at least seven types of smectic phases which are denoted by A,B,C,D,E,F, and G[2,3] Molecules in these phases are parallel. The centers of mass of the molecules are arranged in parallel equidistant planes. Motions of the centers of mass in each plane are allowed. The molecule can rotate about one axis.

Smectic A : The distribution of the centers of gravity of the molecules within the plane is irregular.[2] The symmetry property that distinguishes a smectic A phase of liquid crystals from the isotropic phase is that although it is translationally invariant to arbitrary displacements in two orthogonal spatial directions, it

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[3] Glenn H. Brown and J.W. Doane, Vernon D. Neff, *A Review of Other Structure and Physical Properties of Liquid Crystals* (Butterworths, London, 1971).

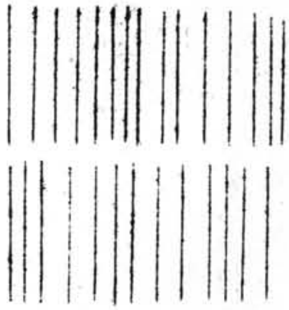

Fig. 1.1 The structure of a smectic phase

is not translationally invariant to the displacements in the third direction[4]. In smectic A there is no restoring force to either a uniform shear produced by sliding layers over each other or to a uniform rotation about an axis in the plane of the layers.

Smectic B : The arrangement of the centers of gravity of the molecules in the plane is hexagonal close-packed. This type has been observed only in substances in which at least smectic A also occurs and smectic B always occurs at the lower temperature range. The most solid of the liquid crystals is a smectic B liquid crystal. A model for smectic B has been proposed.[5]

Smectic C : It always exists at lower temperature, if it occurs together with smectic A. Smectic C has more highly ordered structure than smectic A. Smectic C differs from smectic A liquid crystals in only one respect, i.e., whereas the smectic A is invariant under all rotations about 3-axis, which is the direction in which

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[4] P.C. Martin, O.Parodi and P.S. Pershan, " Unified Hydrodynamic Theory for Crystals , Liquid Crystals, and Normal Fluids, " Physical Review A , 6(1972),2401.

[5] P.G. De Gennes and G.Sarma," Tentative Model for the Smectic B Phase,"Physics Letters, 38A (1972),219.

smectic A is not translationally invariant, a smectic C phase is not, because it is tilted from the 3-axis. Smectic C has been found to be biaxial[5a].

2. Nematic liquid crystals: In the nematic phase, there exist the spontaneous orientations of the molecules with their long axes approximately parallel[6]. In the absence of the special measures, the preferred direction of the long axis is not constant over large areas,[7] but varies with position. The nematic phase is ordered to a lesser extent than the smectic phase since there is no separation into layers. The molecules are mobile in three directions and there is rotational invariance about the direction of alignment.

3. Cholesteric liquid crystals : The cholesteric phase resembles the nematic phase. The direction of the longest molecular axis in each layer is slightly displaced with respect to the neighboring layers. The overall displacement follows a helical path[8] (Fig. 1.2). A layer structure of these cholesteric liquid crystals will lead

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[5a] T.R.Taylor, J.L. Fergason and S.L. Arora," Biaxial Liquid Crystals," Physical Review Letters, 24(1970),359.

[6] P.Pincus, " Magnetic Properties of Liquid Crystals," Journal of Applied Physics, 41(1970),974.

[7] A. Saupe, " Recent Results in the Field of Liquid Crystals," Angew Chemistry international Edition , 7(1968),97 .

[8] P. Diehl and C.L. Khetrapal, NMR Basic Principles and Progress Vol.1 (Springer-Verlag,Berlin. Heideberg, New York, 1969),pp. 5 .

in many respects to behaviors similar to those of smectic liquid crystals.

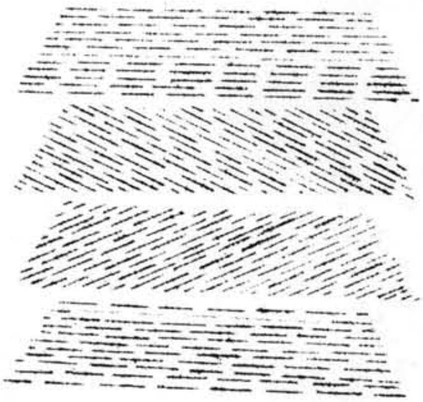

Fig. 1.2 The structure of a cholesteric phase

I.2 Nuclear Relaxation[9,10]

Generally nuclei are not isolated; they are found in atoms or molecules in solid, liquid or gaseous state. When the appropriate form of matter is placed in a static magnetic field, the spin population will arrange themselves, approximately, according to Maxwell-Boltzmann statistics. Consider, for example, N spin ½ nuclei in a magnetic field H_0 , applied in z-direction. The populations of the $m = \frac{1}{2}$, $-\frac{1}{2}$ states are, respectively, N_+ and N_- . This total system consists of two constituent systems, the spin system and the lattice. Let the lattice be characterized by a single constant temperature T. Assume that the heat capacity

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[9] Robert T. Schumacher, Introduction to Magnetic Resonance, (W.A. Benjamin, Inc. New York, 1970).

[10] N. Bloembergen, Nuclear Magnetic Relaxation, (W.A. Benjamin, Inc., New York , 1961).

of the lattice is large compared with the interaction energy between the nuclear moments and the magnetic field.

The Zeeman energy of each spin is

$$E = -\gamma \hbar H_0 m \tag{1.1}$$

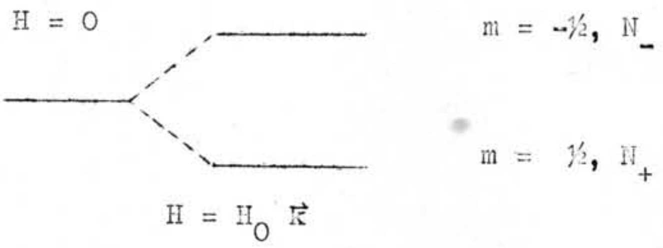

Fig. 1.3 The Zeeman energy levels of a spin ½ in a magnetic field H_0 .

If the spin system is disturbed, i.e., it absorbs the energy $\hbar\omega = \gamma\hbar H_0$ from the rf field, which phenomenon is usually referred to as resonance absorption, the transition is induced. The rate of change of spin population can be written as

$$\frac{dN_+}{dt} = N_- W_\downarrow - N_+ W_\uparrow \quad , \tag{1.2}$$

where $W_\downarrow$ = probability per second that such a coupling will induce a spin transition downward,

$W_\uparrow$ = probability per second of the reverse process.

Let $n = N_+ - N_-$.

Eq. (1.2) becomes

$$\frac{dn}{dt} = N\left[W_\downarrow - W_\uparrow\right] - n\left[W_\downarrow + W_\uparrow\right] , \tag{1.3}$$

$$\frac{dn}{dt} = \frac{n_0 - n}{T_1} \quad , \tag{1.4}$$

where

$$n_0 = N\left[\frac{W_\downarrow - W_\uparrow}{W_\downarrow + W_\uparrow}\right] ,$$

$$\frac{1}{T_1} = W_\downarrow + W_\uparrow .$$

In Eq.(1.4) T_1 , the spin-lattice relaxation time, is defined. It is the time constant of the approach of the spin system to the thermal equilibrium with the lattice.

According to Eq.(1.4) and the equation[9] for the driving of the magnetization, M , by the torque, the equation of M can be written as

$$\frac{dM_z}{dt} = \frac{M_o - M_z}{T_1} + (\vec{M} \times \vec{H})_z \quad . \tag{1.5}$$

Similarly, the equation that describes the magnetization in the x,y plane are

$$\frac{dM_x}{dt} = - \frac{M_x}{T_2} + (\vec{M} \times \vec{H})_x \quad , \tag{1.6}$$

$$\frac{dM_y}{dt} = - \frac{M_y}{T_2} + (\vec{M} \times \vec{H})_y \quad , \tag{1.7}$$

T_2 is described in Eq.(1.6) and Eq.(1.7) as the transverse or spin-spin relaxation time. T_2 can be accounted as the time for which the precession maintains phase memory.

I.3 The Scope of This Thesis

The behaviors of the spin-lattice relaxation time (T_1) of the smectic liquid crystals,

(1) 4-((p- Pentyloxycarbonyloxybenzylidene)amino)valerophenone (PCBAV)

(2) Diethyl 4,4-Azoxybenzoate (DADB) ,

have been in vestigated in the temperature ranges 80-110°C and 114-123°C at the three different frequencies 7.85 , 10.25 and

11.65 MHz. the spin-spin relaxation time (T_2) has also been investigated in the smectic range at 10.25 MHz. . The pulse method was used to obtain the relaxation times T_1 and T_2 . The principle and detail of methods of measurement are described in chapter II .

The theory[11] for the calculation of T_1 predicts its resonance frequency dependence such that T_1 is proportional to the square root of the resonance frequency. The theory also predicts that T_1 is proportional to the inverse of the temperature. The mechanisms contributing to T_1 is based on the orientational fluctuations and the diffusive motion of the molecules. The detail of the calculation and a comparison between the experimental and the theoretical results are given in chapter IV.

The mechanisms contributing to T_1 are particularly very interesting. Since the smectic liquid crystal possesses both solid and liquid properties, the mechanisms causing T_1 cannot be the same as in a solid or a liquid. NMR investigations have previously, been carried out principally in the nematic phase[12,13,14]

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[11] P.Pincus, " Nuclear Relaxation in a Nematic Liquid Crystals ," Solid State Communications , 7(1969),45.

[12] N.Bravo, J.W. Doane, S.L. Arora and J.L. Fergason," NMR Study of Molecular Configuration and Order in a Fluorinated-Liquid-Crystalline Schiff Base," The Journal of Chemical Physics, 50(1969),1398.

[13] Ronald Y.Dong, W.F.Forbes,and M.M.Pintar, " Proton Spin Relaxation in the Liquid Crystal PAA," Ibid. , 55(1971)145.

[14] Assin F. Martins," Interpretation of the Nuclear Spin-Lattice Relaxation Time Behavior in the Nematic Mesophases," Physical Review Letters, 28(1972),289.

It has also been found that at the smectic-nematic transition, the value of T_1 has no discontinuity[15]. The distinctive difference between a smectic and a nematic liquid crystal is that a smectic liquid crystal has a layer structure. There is an interesting question here, whether the mechanisms contributing to T_1 in a smectic liquid crystal could be the same as those in a nematic liquid crystal.

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[15] J.W. Doane and J.J. Visintainer, "Proton Spin-Lattice Relaxation in Liquid Crystals," Physical Review Letters, 23(1969), 1421.