

nal  $P_T$ .<sup>12,14</sup> Our investigations strongly indicate that the onset of SRS and/or SBS depends on the steady-state gain factors, the lifetimes of the material excitations, the duration and the rise time of the laser pulse.

A detailed account of this work will be given elsewhere.

<sup>1</sup>R. Y. Chiao, E. Garmire, and C. H. Townes, *Phys. Rev. Letters* **13**, 479 (1964).

<sup>2</sup>For a summary of recent literature see S. A. Akhmanov, A. P. Sukhorukov, and R. V. Khokhlov, *Usp. Fiz. Nauk* **93**, 609 (1968) [*Soviet Phys. Usp.* **10**, 609 (1968)].

<sup>3</sup>R. G. Brewer, J. R. Lifshitz, E. Garmire, R. Y. Chiao, and C. H. Townes, *Phys. Rev.* **166**, 326 (1968); see also Ref. 2.

<sup>4</sup>M. M. Denariez-Roberge and J. P. Taran, *Appl. Phys. Letters* **14**, 205 (1969).

<sup>5</sup>G. L. McAllister, J. H. Marburger, and L. G. DeShazer, *Phys. Rev. Letters* **21**, 1648 (1968).

<sup>6</sup>M. M. T. Loy and Y. R. Shen, *Phys. Rev. Letters* **22**, 994 (1969), and *Appl. Phys. Letters* **14**, 380 (1969).

<sup>7</sup> $\epsilon_2$  values were calculated from the Kerr constants, Landolt-Börnstein, *Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik* (Springer-Verlag, Berlin, 1962) Vol. II, Pt 8. The number for CS<sub>2</sub> is in good agreement with measurements of M. Paillette, *Comp. Rend.* **262**, 264 (1966).

<sup>8</sup>P. L. Kelley, *Phys. Rev. Letters* **15**, 1005 (1965).

<sup>9</sup>E. L. Dawes and J. H. Marburger, *Phys. Rev.* **179**, 862 (1969); V. N. Goldberg, V. I. Talanov, and R. W. Erm, *Izv. Vysshikh Uchebn. Zavedenii Radiofiz.* **10**, 674 (1967).

<sup>10</sup>For small incident light powers and plane-wave initial conditions the beam diameter increases by only 5% due to diffraction of the Gaussian beam within the short cell.

<sup>11</sup>Quasistationary behavior is expected in CS<sub>2</sub> where the change of  $\epsilon$  is due to the optical Kerr effect with a relaxation time of 2 psec.

<sup>12</sup>M. Maier, W. Kaiser, and J. A. Giordmaine, *Phys. Rev. Letters* **17**, 1275 (1966); *Phys. Rev.* **177**, 580 (1969).

<sup>13</sup>V. N. Lugovoi and A. M. Prokhorov, *Zh. Eksperim. i Teor. Fiz. Pis'ma Redakt.* **7**, 153 (1968) [*JETP Letters* **7**, 117 (1968)].

<sup>14</sup>M. Maier, *Phys. Rev.* **166**, 113 (1968).

<sup>15</sup>The onset of the self-focusing action may be defined as the time when the beam at the exit window shows a measurable reduction in diameter. This effect starts at low power level and continues during the rise of the laser pulse leading to a monotonic decrease of beam diameter. The signal  $P_S$  obtained from mirror  $M$  indicates the enhanced light power in the center of the beam;  $P_S$  is the power integrated over a diameter of 190  $\mu$  and does not show rapid changes at very small beam diameters.

<sup>16</sup>D. Pohl, M. Maier, and W. Kaiser, *Phys. Rev. Letters* **20**, 366 (1968); N. M. Kroll, *J. Appl. Phys.* **36**, 34 (1965).

## MÖSSBAUER INVESTIGATION OF THE SMECTIC LIQUID CRYSTALLINE STATE\*

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(Received 5 November 1969)

We have observed the Mössbauer effect in the smectic liquid crystalline state. To our knowledge this is the first report of a Mössbauer-effect observation in this particular state of matter. Orientation effects of solute molecules are exhibited and methods of obtaining structure information for both the solute molecules and the liquid-crystalline solvent are indicated.

Ordinary liquids are, of their nature, not amenable to Mössbauer-effect investigation because of the extremely low probability for a recoil-free event. In contrast, the strong bonding between atoms in solids is conducive to the recoilless emission and absorption of low-energy gamma rays because of the quantized collective vibrational modes which are present. This report is concerned with a state of matter, namely, the smectic liquid crystalline phase, which possesses both solidlike and liquidlike properties.<sup>1,2</sup> The liquid crystal is characterized by long, rod-like molecules which possess particular degrees of translational and rotational freedom (in the

sense of a liquid) but still maintain a kind of crystalline order (in the sense of a solid). In particular, the smectic state is a layered structure wherein the molecules are allowed free translation in the layers but are not allowed free translation perpendicular to them. This means that the intermolecular forces which provide the layered structure result in a viscosity anisotropy. The viscosity is high only in a direction that is normal to the layers. This is in contrast to the uniformly viscous solvents such as glycerin in which solute molecules have exhibited the Mössbauer effect.<sup>3</sup> The high viscosity of glycerin-like liquids results from the presence of strong

hydrogen bonding which is not present in liquid-crystalline systems. The existence of the Mössbauer effect in the smectic liquid-crystalline phase, therefore, is due to phenomena not previously used to provide recoil-free gamma absorption.

The thickness of the layers is typically less than (smectic *C*) or equal to (smectic *A*) the length of one molecule. In the smectic *C* the long axes of the molecules are tipped at an angle with respect to the normal to the planes of the layers. In contrast, the molecules of the less ordered and therefore higher temperature nematic phase possess three degrees of translational mobility. The molecules of the nematic, however, are on the average parallel as in the smectic phase. The nematic liquid crystal is easily aligned so that the molecules form a monocrystal. The alignment may be accomplished by means of the container walls or by electric or magnetic fields. The molecules of the smectic are not easily aligned in this way but they can be aligned by slowly cooling from the ordered nematic through the nematic-smectic phase transition.<sup>2</sup> In this way a smectic monocrystal can be constructed.

A convenient way to incorporate the required Mössbauer isotope (<sup>57</sup>Fe) in the liquid-crystal system, which in this case was zone refined 4, 4'-bis(heptyloxy)azoxybenzene,<sup>4</sup> was to dissolve 1, 1'-diacetylferrocene<sup>5</sup> (7% by weight) into the liquid crystal. The presence of the solute altered the temperature ranges of the liquid-crystalline phases only slightly and did not noticeably alter the smectic and nematic textures as seen via microscopic observation. The nematic liquid crystal-isotropic liquid phase transition as measured by differential thermal analysis, however, was broadened from ~1° to ~15°C.

1, 1'-diacetylferrocene (DAF) was chosen for this study for the following reasons: (1) In the solid state it is a molecular crystal and as a result the most important hyperfine interactions involving the iron are intramolecular. Therefore, the Mössbauer spectrum should not be appreciably changed when the molecule is in solution. (2) It has an extended molecular axis as opposed to ferrocene itself which is nearly spherical. One can reasonably assume, therefore, that the diacetylferrocene molecules (the solute) will be aligned by their liquid crystal environment. (3) The molecules are unlikely to interact chemically with the liquid crystal solvent which is in direct contrast to solutions of iron(III) salts

in liquid-crystalline materials. (4) DAF exhibits a relatively large quadrupole splitting of the nuclear excited state<sup>6</sup> and provides the iron nucleus with a site of less than axial symmetry. Assuming, therefore, that the DAF molecules will be aligned by their environment, then an orientation dependence of the relative intensities of the quadrupole-split lines will allow a determination of the asymmetry parameter of the electric field gradient.<sup>7,8</sup>

4, 4'-bis(heptyloxy)azoxybenzene was chosen because it possesses the following properties: (1) The molecule is symmetric on either side of the azoxy linkage, and it is relatively inert chemically. (2) It possesses a low solid-smectic *C* transition temperature (71°C) and a higher smectic-nematic transition temperature (94°C). The low transition temperature and the 23°C range allows for experimental ease and the presence of the nematic phase facilitates ordering the smectic liquid.

The first part of this investigation consisted of the observation of the recoil-free fraction (percent effect) as a function of temperature (heating and cooling) from room temperature through the smectic-nematic phase transition. The second part included the measurement of the relative intensities (areas) of the quadrupole-split lines as a function of the angle between the gamma-ray beam and the molecular direction as determined by a 4000-G magnetic field which was used to align the molecules in the nematic phase. These experiments were performed at 75°C and therefore in the layered smectic phase. Experimentally, the sample was aligned with the magnetic field while in the nematic phase and then allowed to cool slowly (0.5°C/min) in the field to 75°C. This temperature was maintained and the sample was then taken out of the magnetic field and placed in the Mössbauer spectrometer. The reason for this technique is that a smectic cannot be ordered with ordinary field strengths but it will retain the nematic order, which is easily achieved, even if the sample is removed from the magnetic field.<sup>9</sup>

The Mössbauer spectrometer was of the constant-acceleration variety and employed a Kankeleit shaker which was driven by the address-advance stair-step triangle from a Hewlett-Packard 5400-A multichannel analyzer which was operated in the up-down multiscale mode. As a result the shaker was synchronous with the analyzer and to a first approximation there was no evidence of the geometric effect characteristic-

ly present when up-up multiscaling is employed.<sup>10</sup>

All the Mössbauer parameters discussed in what follows were obtained from computer fits of Lorentzian lines to the experimental peaks. Examples of the experimental spectra are given in Fig. 1.

The liquid-crystalline absorbers were melted into a Teflon washer and then sandwiched between two beryllium discs which were covered with Teflon tape. The sandwich was placed into a cylindrical brass oven and maintained to  $\pm 0.4^\circ\text{C}$  for the duration of each Mössbauer measurement. The Mössbauer source which was 20 mCi of  $^{57}\text{Co}$  on a palladium matrix was obtained from the International Chemical and Nuclear Corporation. Figure 2 demonstrates the rather abrupt change of the sum of the two peak heights (as percentages of the background) at the solid-smectic transition temperature and then the complete loss of the Mössbauer effect at the smectic-nematic transition temperature. The latter is to be expected because in the nematic liquid-crystalline phase the molecules possess three degrees of translational mobility and the viscosity is more nearly that of water. The former indicates that the rigidity of the solid is lost but that the probability for a recoil-free event is saved by the layered structure of the smectic phase. The peak height (percent effect) is used in the above rather than the area because the linewidths remained constant independent of the tempera-

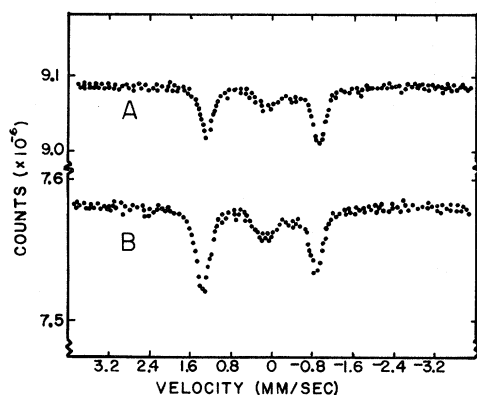


FIG. 1. Experimental Mössbauer spectrum of  $^{57}\text{Fe}$  in a 7-wt% solution of 1, 1'-diacetylferrocene in 4, 4'-bis(heptyloxy)azoxybenzene at  $75^\circ\text{C}$  in the smectic liquid-crystalline state. The source was  $^{57}\text{Co}$  in Pd. The liquid-crystalline absorber was aligned in a magnetic field which made an angle  $\theta$  with respect to the gamma-ray beam. (a)  $\theta = 0^\circ$ , (b)  $\theta = 75^\circ$ . The outer pair of lines are the 1, 1'-diacetylferrocene absorption lines. The smaller center line is due to the Fe in the Be discs.

ture.

It is interesting to note that the isomer shift and the quadrupole splitting remained constant ( $2.19 \text{ mm/sec}$ )<sup>6</sup> as the temperature increased and showed no evidence of the phase transition. This is to be expected because the origin of both is intramolecular and therefore not a function of the molecular environment. In contrast, the relative intensities (areas) of the quadrupole-split lines were equal during the heating cycle but once the sample was taken into the nematic phase ( $90^\circ\text{C}$ ) the container walls aligned (partially) the molecules and an asymmetry resulted. This asymmetry persisted throughout the smectic phase as well as the solid state to room temperature. Upon reheating to  $75^\circ\text{C}$  the asymmetry remained. At this point the sample (while still in the oven) was shaken vigorously and then cooled to room temperature. The subsequent Mössbauer spectrum lacked the asymmetry it possessed before shaking. This showed that indeed the solute molecules were aligned by the solvent liquid crystal which itself had been partially aligned by the sample container while in the nematic phase ( $90^\circ\text{C}$ ).

Because the asymmetry remained even when the sample was cycled from  $75^\circ\text{C}$  to room temperature and back to  $75^\circ\text{C}$ , it may be possible to perform alignment studies at room temperature. This would be extremely convenient and provide a means for faster accumulation of data.

The alignment of the solute molecules with a magnetic field (4000 G) is evidenced by the plot of relative intensities (i.e., the ratio of the peak areas) of the quadrupole-split lines as a function of the angle ( $\theta$ ) between the molecular long axes (as determined by the field) and the direction of

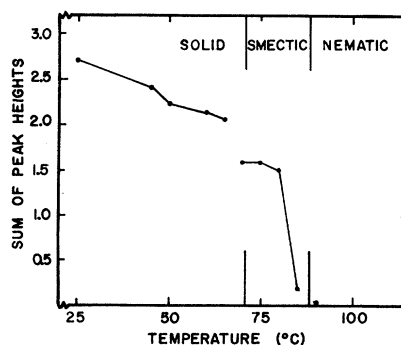


FIG. 2. Temperature dependence of the sum of the peak heights (as percentages of the background) for the two quadrupole-split lines of the unoriented 7-wt% solutions of 1, 1'-diacetylferrocene in 4, 4'-bis(heptyloxy)azoxybenzene. This plot is for the heating cycle.

the gamma-ray beam (Fig. 3). In effect, the smectic liquid-crystal matrix was used to construct a "monocrystal" of 1,1'-diacetylferrocene. From the angular variation of the relative intensities of the quadrupole-split lines, therefore, the goal is to evaluate the asymmetry parameter of the electric field gradient for non-axial molecules such as DAF. In this case, however, it must be noted that the molecular axis of DAF is not a principal axis of the electric field gradient tensor. In addition, all the molecules are not exactly parallel to the orienting magnetic field and the result is an orientational distribution which can be measured via electron-spin resonance.<sup>11</sup> These facts will be included in our calculations which will be published at a later time.

This method is particularly simple experimentally since all orientations can be achieved with a single sample and a magnetic field. This contrasts with the need for several single-crystal platelets cut at different angles with respect to the crystallographic axes in normal single-crystal studies. The most stringent limitations are the solubility of the metal-organic in a liquid crystal system and the stability of the resulting solution. This method is the Mössbauer analog of the nuclear magnetic resonance technique which Saupe and Englert used to study solute molecules in a liquid-crystal system.<sup>12</sup>

Finally, by perfectly aligning a smectic such that all the planes are parallel, an observation of the absolute intensity of the Mössbauer spectrum as a function of the angle between the normal to the planes and the gamma-ray beam will provide a measure of the anisotropy of the planar smectic state. For example, since the structure of the layer resembles a two-dimensional liquid of relatively low viscosity, then the Mössbauer intensity ought to approach zero when the gamma-ray direction is contained in the layers and become a maximum when the gamma-ray direction is normal to the layers. The recoil-free fraction would then be a measure of the anisotropy of molecular diffusion in the smectic state. In addition, by accomplishing perfect planar alignment along with a determination of the molecular direction in a smectic C, the tilt angle between the molecular direction and the normal to the planes can be obtained. Unfortunately, in our experiment the magnetic field determined only the molecular direction, and a cone of planes was formed such that a constant tilt angle was maintained. Therefore, a measure of the

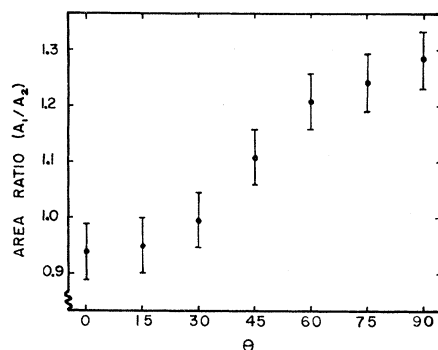


FIG. 3. Plot of the area ratio for the two quadrupole-split lines of 1,1'-diacetylferrocene (7% by wt) in 4,4'-bis(heptyloxy)azoxybenzene at 75°C in the smectic phase as a function of the angle ( $\theta$ ) between the aligning magnetic field and the gamma-ray beam.

anisotropy of molecular diffusion could not be obtained. However, in a smectic A when the molecular axis is defined, all of the planes are perfectly aligned inasmuch as the tilt angle is 0°. The alignment of a smectic A can be accomplished as described previously if the system possesses a higher temperature nematic phase or with the aid of a strong magnetic field (~20 000 G).<sup>13</sup> As a result, such an absolute intensity study is possible for an ordered smectic A and will allow a Mössbauer observation of the anisotropy of molecular diffusion in the smectic state. These experiments are in progress.

In conclusion, the potential utility of the Mössbauer effect for studying both the smectic liquid-crystalline state and solute "monocrystals" has been demonstrated.

One of the authors (D.L.U.) would like to acknowledge several helpful discussions with Professor G. H. Brown, Professor J. W. Doane, and Professor A. Saupe. We are also in debt to Dr. D. Fishel and Dr. J. T. S. Andrews who respectively made and purified the liquid-crystalline material. The help of Mr. R. Detjen with the computer programming is also gratefully appreciated.

\*Research was sponsored in part by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research, under Contract No. F44620-69-C-0021.

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<sup>3</sup>P. P. Craig and N. Sutin, *Phys. Rev. Letters* **11**,

460 (1963).

<sup>4</sup>The zone-refined 4,4'-bis(heptyloxy)azoxybenzene was generously provided by Dr. J. T. S. Andrews, Liquid Crystal Institute, Kent State University.

<sup>5</sup>The 1,1'-diacetylferrocene was purchased from Alfa Inorganics, Inc.

<sup>6</sup>A. V. Lesikar, J. Chem. Phys. **40**, 2746 (1964).

<sup>7</sup>P. Zory, Phys. Rev. **140**, A1401 (1965).

<sup>8</sup>J. Danon and L. Iannarella, J. Chem. Phys. **47**, 382 (1967).

<sup>9</sup>Dr. J. W. Doane of Kent State University found via

nuclear magnetic resonance on 4,4'-bis(heptyloxy)-azoxybenzene that the nematic order was retained in the smectic phase in the absence of a magnetic field for periods of greater than 24 h.

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<sup>11</sup>P. Diehl and C. F. Schwerdtfeger, Mol. Phys. **17**, 423 (1969).

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### BIAXIAL LIQUID CRYSTALS\*

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Convergent light observations have been made on three liquid crystalline substances with nematic and smectic phases. The nematic phase was observed to be uniaxial as expected, but smectic *C* was found to be biaxial. The optic axial angle  $2V$  for smectic *C* was found to be on the order of  $20^\circ$  for all three compounds. Also, the tilt angle for smectic *C* is nearly  $45^\circ$  for all three liquid-crystal systems. Anisotropy of the degrees of order is suggested as a partial explanation for the biaxial character of smectic *C*.

We have studied three compounds which exhibit a nematic phase and a single smectic phase of the type classified by Sackmann and Demus<sup>1</sup> as type *C*. The smectic phases classified by Sackmann and Demus correspond to different molecular arrangements and are separated from each other by first-order phase transitions.

The nematic phase has a long-range order such that the long axes of the molecules are nearly parallel and the parallelism of the long axis generally varies continuously throughout the bulk of the liquid. Assuming a random arrangement of the center of mass and free rotation about the long molecular axis, nematic liquids would be uniaxial. All observations do show the nematic phase to be uniaxial. Smectic *A* is a system in which the molecules are arranged in layers with the long molecular axis perpendicular to the layer.<sup>2</sup> If the centers of mass within the layers are random and free rotation is assumed, then smectic *A* would be uniaxial. Experimentally, all smectic-*A* phases have been shown, in general, to be uniaxial. Smectic *C* is generally considered to have a structure such that the molecules are arranged in layers but with the long molecular axis tilted with respect to the layer normal.<sup>2</sup> In general, it has been assumed that all smectic phases including smectic *C* would show uniaxial character and, in fact, Friedel<sup>3</sup> argued that all smectic phases would be uniaxial. Recently, Saupe<sup>2</sup> pointed out that due to symme-

try considerations, smectic *C* should be biaxial. The observations we report in this Letter show that smectic *C* phases are biaxial.

An alternate molecular arrangement, from x-ray data, for smectic-*C* phases has been proposed by Chistyakov *et al.*<sup>4</sup> Chistyakov proposes that instead of the direction of alignment being parallel throughout the sample, the direction of tilt is constant but alternates from layer to layer. This results in a herringbone type of molecular structure.

It has been reported by Arora, Fergason, and Saupe<sup>5</sup> that smectic-*C* phases can be oriented by surface action so that the layers are parallel to the surface. It was also reported that apparently the smectic-*C* phase of the compound bis-(4'-*n*-decyloxybenzal)-2-chloro-1,4-phenylenediamine (DOBCP) has a tilt angle of nearly  $45^\circ$ . Since the smectic *C* can be oriented, it was assumed that an area large enough for convergent-light observation could be uniformly oriented.

Optical observations upon compounds which have a smectic-*C* phase were made using a Leitz Panphot-pol polarizing microscope, equipped with a heated stage. Since the orientation of the layers of smectic *C* are parallel to the containing surfaces and the molecules are tilted with respect to the layers, the interference figure is off center if flat glass slides perpendicular to the microscope axis are used. In fact, the interference figure is so badly off center that little in-