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A New Classification System for Thermotropic Smectic Phases†

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Abstract—In the presently used classification (S_A, S_B, etc.) there is no logical relationship between the symbol identifying a phase and the molecular packing characteristic for that phase. For this reason a new classification system is introduced in which the phases are classified on the basis of their structure, and in which a similarity in phase symbol indicates a similarity in structure. In this classification system, the phases are grouped into three main classes (α, β, γ) according to the degree of order in the molecular packing. Within each main class the different phase types are designated as α_1, α_2, etc. After a description of this classification, a number of comments are made concerning some questions prompted by the classification and concerning the structure of the various phase types.

1. Introduction

One of the first proofs of the existence of different types of smectic phases is found in a 1932 paper by Herrmann and Krummacher.(1) In the course of their X-ray studies, these authors found that most smectic phases had a diffraction pattern with one or more sharp inner rings and a *diffuse* outer ring. Some other smectic phases, however, were found to have a diffraction pattern with one or more sharp inner rings and a *sharp* outer ring. Because of this difference in diffraction pattern, there must also be a difference in molecular arrangement, and thus Herrmann and Krummacher concluded that they were dealing with two different types of smectic phases.

The most detailed and systematic study of the classification of smectic phases into various phase types is the work of Sackmann, Demus and coworkers (see Ref. 2 and the papers cited therein). On

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the basis of miscibility relations, microscopic textures, and X-ray diffraction patterns, these investigators have assigned a large number of smectic phases to seven different phase types,$^{(2-5)}$ *A*, *B*, *C*, *D*, *E*, *F*, *G*. On the basis of X-ray and microscopic studies we have recently added to these an eighth type,$^{(6)}$† *H*. This classification system is an extremely valuable one, but it also has some drawbacks. Relevant to this paper is the fact that in the sequence *A* through *H* we sometimes find rather dissimilar types standing side by side, while quite similar types are sometimes widely separated. For instance, the recently found *F* phase$^{(5)}$ appears to be very similar to the *C* phase, whereas the *F* phase seems rather different from the *E* phase$^{(8)}$ and the *C* phase seems rather different from the *D* phase.$^{(8)}$ This lack of correspondence between the structure of a phase and its identification symbol is, of course, a consequence of the fact that the assignment of letters to the different phase types is simply done in the order in which these phase types are discovered. Because of this situation, it would be helpful to have a different classification scheme which would arrange the phases according to their structure. Much more will have to be known about the structures of the various phase types before such a classification can be carried out rigorously, but a preliminary classification seems already possible and will be attempted below.

2. Classification

For our classification we shall divide the smectic phases into main classes, according to the degree of order in the molecular packing. This degree of order will be judged by the appearance of the outer ring(s) in the diffraction patterns (by "outer rings" we mean diffraction rings with Bragg angles of about 10° or more).

The first class is the one with the least amount of order. The diffuse outer ring which characterizes this class indicates a disordered arrangement of the parallel molecules within the smectic layer. In

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† With respect to smectic *H* there appears to be a conflict between the different ways of classification: According to the miscibility criterion, *H* phases are the same as *B* phases,$^{(7)}$ but according to the X-ray diffraction patterns, *H* and *B* phases are quite different;$^{(6)}$ the microscopic textures of the two phase types are similar but possibly not identical.$^{(6)}$

this class fall the phases S_A, S_C, and S_F, and maybe S_D† (Table 1). For this class we propose the symbol S(α), and from this symbol we derive the new symbols for the phase types belonging in this class: α_1 for S_A, α_2 for S_C, α_3 for S_F, and α_D for S_D.‡ This particular assignment of the symbols α_1, α_2, and α_3 has been so chosen because this is the order in which the phases appear with decreasing temperature:(2,5) α_1 comes always before α_2, and α_3 comes at a still lower temperature. Assuming that a lower temperature smectic phase has a higher degree of order than a higher temperature phase, it then follows that within the S(α) class the α_1 phase has the lowest degree of order and the α_3 phase the highest.

TABLE 1 Classification of Smectic Phases

Outer ring	Phase type	Class symbol	New phase type symbol[a]
diffuse	S_A, S_C, S_F, (S_D)	S(α)	α_1, α_2, α_3, (α_D)
sharp, one	S_B	S(β)	β_1
sharp, several	S_E, S_G, S_H	S(γ)	γ_1, γ_2, γ_3

[a] α_1 is the new symbol for S_A, α_2 for S_C, etc. If one wants to emphasize that these phases are smectic, one could write "smectic α_1" or "$S(\alpha)_1$", etc.

The second class of phase types is characterized by a single sharp outer diffraction ring. This sharp ring indicates the presence of a well defined repeat distance in the molecular packing within the smectic layer, and thus signifies a higher degree of order than present in the smectic phases of the first class. For this second class we propose the symbol S(β), and from this we derive the symbol β_1 for the S_B phase which is the only phase type falling in this class (Table 1).

The third class of phase types is the one with the highest degree of order, and it is characterized by a number of sharp outer rings in the

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† The symbols for S_D in Table 1 are placed in brackets because there is some doubt as to whether (and where) S_D should be included in this classification. Its diffraction pattern does have a diffuse outer ring, but for the inner ring one sometimes obtains a hexagonal arrangement of spots, and the structure proposed on the basis of this hexagonal arrangement is quite different from the structure of all other smectic phases.(8)

‡ If the S_D phase is to be included in the S(α) class, its place would be between α_1 and α_2. For the time being we have used the symbol α_D which does not assign this phase any particular position in the sequence.

diffraction pattern. The presence of a number of sharp rings indicates the existence of a number of well defined repeat distances in the molecular packing, and thus a higher degree of order than in the preceding class which had only one well defined repeat distance. The phase types in this class, S_E, S_G, and S_H, always appear as the lowest temperature smectic phase (if more than one smectic phase is present). They never occur together in one compound and thus it is not possible to assign to them a specific sequence which can be identified as one of increasing order, as could be done for the phase types in the $S(\alpha)$ class. For this reason the assignment of γ_1 to S_E, γ_2 to S_G, and γ_3 to S_H (Table 1) has been rather arbitrary.

3. Comments

We want to stress here again that the above classification is a preliminary one. A good deal more will have to be known about the structure of the various phase types before a classification based on structure can be carried out rigorously. It may be, for instance, that some types which at present seem different will turn out to be merely slight variations of the same building principle. On the other hand, there may exist important structural differences between phases which now appear very similar.

Still, we consider the proposed classification to be a useful one. For one thing, the use of the same main symbol "α" in the new classification symbols α_1, α_2, and α_3, stresses the great similarity in structure which appears to exist between these phase types. An indication of this similarity is completely absent in the conventional symbols S_A, S_C, and S_F. Also, putting the phase types S_A, S_C, and S_F together in one class may stimulate thought and investigations concerning what then, given the similarity between these phases, are the differences between them that cause the first order phase transitions between these phases (in another paper we hope to discuss this question in some detail with regard to α_1 (S_A) and α_2 (S_C) phases).

Another question prompted by the proposed classification scheme is whether the differences which apparently exist between α_1, α_2, and α_3 phases are similar to the differences between γ_1, γ_2, and γ_3 phases, and why in class β we do not find correspondingly different phases. Related to this is the following question: If we assume, as is generally done, that in the α_1 (S_A) phase the molecules stand more or less perpendicular to the smectic planes (α_1 may be called a "normal" smectic phase) and that in the α_2 (S_C) phase there is a considerable angle between the normal to the plane and the molecular axis (α_2 may be called a "tilted" smectic phase), why don't we find similar differences between "normal" and "tilted" (or "skewed") phases among the phase types in the other classes? E.g., one would expect that β phases that give (on heating) the α_1 phase could be "normal" S_B phases, and that β phases that give the α_2 phase would be "tilted" S_B phases (see also Ref. 9), but according to the present criteria (miscibility relations, microscopic textures) there does not seem to be any distinction between these S_B phases. Shifting our attention to class γ, we find a similar situation for S_E phases. The S_E phase discussed by Diele, Brand and Sackmann(8) appears, according to the X-ray diffraction pattern, to be a "normal" S_E phase.† The "smectic 3" phase (which is probably an S_E phase) described by Coates, Harrison and Gray(11) appears, from optical data, to be a "tilted" smectic phase, but nevertheless it is miscible in all ratios with the "normal" S_E phase.(11) As far as S_H phases are concerned—which are also γ phases—the phase most definitely classified as an S_H phase(6) is a "tilted" phase. We do not know yet whether there are also "normal" S_H phases and if they will be distinguishable from the tilted ones on the basis of miscibility relations and microscopic textures. But, since the tilted S_H phase appears to be completely miscible with an S_B phase(7) and since among S_B phases the miscibility criterion does not appear to distinguish between normal and tilted phases, one would expect normal and tilted S_H phases also to be indistinguishable. All available evidence, therefore, points to the conclusion that for the more ordered smectic phases (S_B, S_E, S_H) the miscibility criterion does not distinguish between normal and tilted phases. If this is true, one would expect the same to be true for the less ordered smectic phases (S_A, S_C). The fact that S_A and S_C phases are nevertheless distinguishable suggests then that the difference between S_A and S_C is something more than a mere difference between

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† This is confirmed by a comparison between smectic layer thickness and molecular length. For DPTC (dipropyl-*p*-terphenyl-4,4′-carboxylate) we have found a layer thickness of 25.56 Å and a calculated molecular length of 26.2 Å. This difference of 0.6 Å is comparable to similar differences found for S_A phases,(10) and thus appears quite compatible with a "normal" arrangement.

normal and tilted phases.(15) At present, however, we have no idea yet as to what this difference might be.

The next point we want to raise concerns the S_B and S_H phases. According to the miscibility criterion these phases are identical(7) and thus it is relevant to ask whether S_B and S_H phases really should be classified as structurally different (as we have done here), or that S_B phases should be merely regarded as "underdeveloped" S_H phases. From our description of the structure of the S_H phase(6) it is clear that this is a structure with a three-dimensional lattice which results from a combination of three kinds of order. (1) There is "packing order", i.e., there is order in the packing of the molecules within the smectic layer. (2) There is "rotational order" in the arrangement of the smectic layers: The *a* and *b* axes of each layer† are usually parallel to the *a* and *b* axes (respectively) of the adjacent layers. Another way to say this is that the smectic layers cannot rotate freely with respect to their neighboring layers but rather are locked into a specific position. (3) There is "translational order" in the stacking of the smectic layers: The smectic layers are not free to slide‡ at random over each other; each layer is shifted over a fixed distance in a given direction with respect to its neighboring layers in such a manner that the total effect of "packing", "rotational", and "translational" order is for the combined lattice points from the *ab* lattices of a packet of smectic layers to form a regular three-dimensional lattice.(6) It is the combination of these three kinds of order which we think should be regarded as the characteristic feature of class γ smectic phases, and phases lacking one or more of these kinds of order should be assigned to other classes. The question of whether S_B and S_H phases should be put in the same class thus boils down to the question of whether S_B phases have all three kinds of order. The presence of "packing order" in S_B phases follows directly from the fact that the outer diffraction ring (Fig. 1a) is a well defined sharp ring rather than a diffuse ring. The presence of "rotational order" may be deduced from Fig. 1b: if there was no rotational coupling between neighboring layers, the outer ring would be continuous and

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† The *a* and *b* axes are axes in the plane of the smectic layer.(6)

‡ With "slide" we mean a translation without rotation [the rotational positions of the layers are already fixed by the "rotational order" mentioned under (2)].

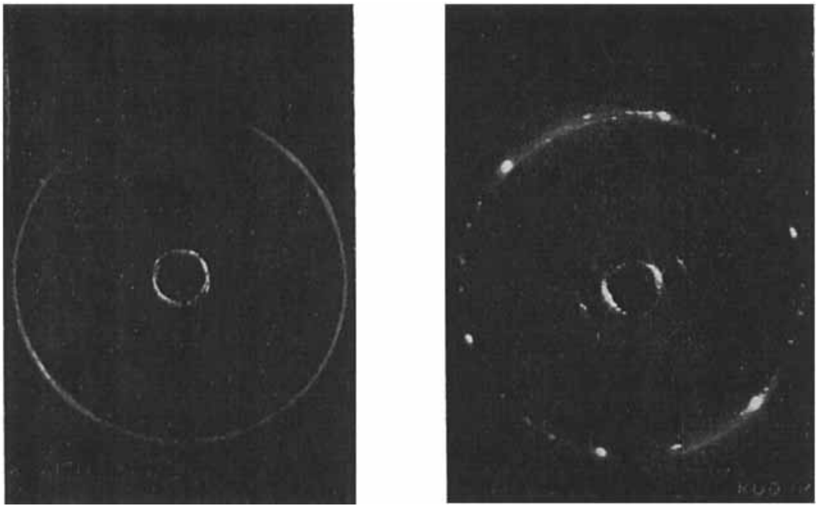

Figure 1. Diffraction patterns from the smectic *B* phase of *p*-*n*-hexyloxybenzylidene-5-amino-2-butoxypyridine.

could not show the discrete spots seen in Fig. 1b.† The crucial point in the distinction between S_B and S_H phases therefore appears to be the question of whether or not S_B phases have "translational order" in the stacking of the smectic layers. As far as we know, there is, for the large majority of S_B phases, no evidence that they have a three-dimensional lattice.‡ Since "translational order", given the presence of "packing order" and "rotational order", would automatically lead to three-dimensional order, the apparent absence of a three-dimensional lattice indicates the absence of translational order

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† The discrete spots indicate the presence of individual "crystallites". They also show that within these "crystallites" the rotational position of all layers is the same, i.e., they indicate "rotational order". Without this order the spots would be smeared out.

The absence of discrete spots, as in Fig. 1a, does not necessarily indicate the absence of rotational order. It only means that from such photographs it is not possible to decide whether "rotational order" exists or not. The continuous ring is caused by the presence of all directions of alignment within the sample; in this case the ring is always continuous, whether there is "rotational order" or not.

‡ The fact that a few phases classified as S_B phases have been found to possess a three-dimensional lattice(9) merely means (in our opinion) that these phases should have been classified as S_H phases.

and thus suggests that S_B phases and S_H phases do indeed belong in different classes.†

The next comment we want to make concerns the difference or similarity between S_G and S_H phases (both assigned to class γ). The only data available on the diffraction pattern of the S_G phase is that it shows "several outer rings".(5) Thus S_G and S_H might be identical, for a powder pattern of an S_H phase would also show several outer rings.(12) On the other hand, miscibility tests point towards differences between S_G and S_H: S_H is miscible with S_B(7) but S_G is not.(5)‡

Our last comment concerns the S_E phase. The fact that a photograph of an aligned S_E phase(8) shows reflections in addition to those on the meridian and the equator proves the existence of a three-dimensional lattice (with one axis perpendicular to the plane of the smectic layer). For this reason the S_E phase has been classified as a γ phase (Table 1). The packing of the molecules within the smectic layer appears, however, to be quite different from the one in the S_H (γ_3) phase. In the S_H phase the molecules pack in a pseudohexagonal lattice,(6) but the positions of the three strong outer diffraction rings from the S_E phase(8) indicate a totally different packing mode.§

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† If the absence or presence of "translational order" is indeed the main difference between S_B and S_H phases, it is not surprising that these phases cannot be distinguished on the basis of the miscibility criterion, for it seems quite plausible that translational order would not have much influence on the miscibility of the phases.

‡ It is not clear, however, how this lack of miscibility has to be interpreted. The absence of an uninterrupted series of liquid crystals may be caused by a difference in chemical constitution (the compound with the S_G phase has a *p,p'*-diphenylpyrimidine center!) rather than by a difference in the structure of the smectic phase. Examples of this are a number of cases in which S_C phases have been found not to be completely miscible with each other.(13,14)

§ Our measurements on DPTC yielded the following *d* values: 4.60, 4.09, and 3.29 Å.

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