

# A Rapid Reversible Solid-State Transition in the A' Form of Pentadecanoic Acid

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The A' form of pentadecanoic acid can be divided into two phases: A'<sub>h</sub> and A'<sub>l</sub>. Under certain conditions, a single crystal of the A'<sub>l</sub> phase performs a rapid reversible solid-state transition to the A'<sub>h</sub> phase on heating, accompanying its morphological change in the whole region. During this transition single-crystal state is held completely. The transition from A'<sub>h</sub> to A'<sub>l</sub> and that of the opposite direction can be induced also by a mechanical stress. These transitions can be recognized as martensitic transitions. By a mechanical stress, the B' phase transforms to A'<sub>l</sub> with two stages: B'→A'<sub>h</sub> and A'<sub>h</sub>→A'<sub>l</sub> transitions.

## Introduction

Despite their simple chemical structures, fatty acids exhibit various solid-state phase transitions.<sup>1,2</sup> Most of the transitions are caused by a temperature change, but recently we found that some transitions could be induced also by a mechanical stress, which can be recognized as a martensitic transition that is characterized by cooperative displacements of numerous molecules accompanied by a shear deformation of unit cell. As for fatty acids, a transition of this type was first confirmed in petroselinic acid,<sup>3</sup> followed by pentadecanoic acid.

Two martensitic transitions of pentadecanoic acid were reported in the previous paper: a transition from the A' form to the B' form and a transition of the opposite direction.<sup>4</sup> By imposing a small mechanical stimulation, a domain of a single-crystal transforms in an instant, accompanying a shear deformation. In these transitions, a quick subcell rearrangement takes place between O<sub>L</sub> and T//.

During the study on the A'→B' and B'→A' transitions, it has been clarified that the A' form of pentadecanoic acid performs a reversible solid-state phase transition by a temperature change as well as the A' form of tridecanoic acid.<sup>1</sup> We have found that this reversible transition of the A' form also shows the characteristics of a martensitic transition (i.e., cooperative shear deformations of numerous unit cells). A single crystal specimen shows a rapid morphological change, completely keeping its single-crystal state on the transition. Its overall transformation is accomplished within a period of order 0.1–0.01 s if it satisfies certain conditions. Furthermore, a stress-induced transition also takes place between the two modifications of the A' form. This paper deals with the unique characteristics of these transitions.

## Experimental Section

**Sample.** We prepared the sample of pentadecanoic acid (>99.9% purity) by a combination of urea adducts, acid soap,

and fractional distillation methods. Acetonitrile and *n*-hexane (>99% purity) were used as the solvents for growing single crystals.

**Microscopic, DSC, and Infrared Measurements.** Single-crystal specimens were observed with a stereomicroscope (Olympus SZ-60). Pictures were recorded with a CCD camera (SONY DXC-108) and a video recorder (SONY EV-FH10) or with an automatic exposing camera system (Olympus C-35AD-2). A DSC measurement was performed with a Seiko Denshi SSC5200 system. Polarized infrared spectra were taken with a Jasco Janssen micro-FTIR spectrometer equipped with an MCT detector and a wire-grid polarizer. The resolution was set at 2 cm<sup>-1</sup>.

## Results and Discussion

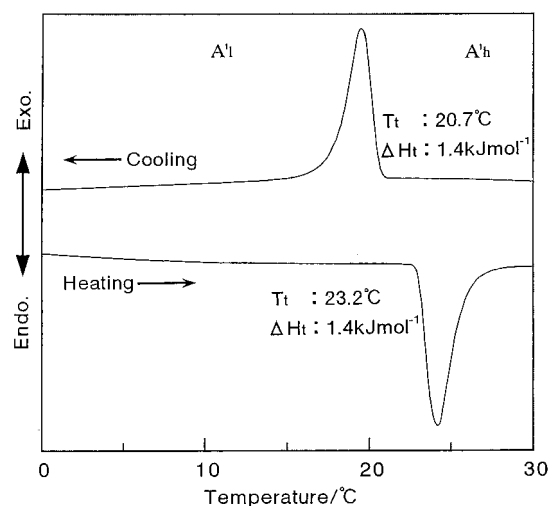
### 1. A reversible Solid-State Transition in the A' Form.

The A' form of odd-numbered saturated fatty acids is characterized by the T// subcell.<sup>5,6</sup> Single crystals of the A' form can be obtained from a solution below 30 °C for pentadecanoic acid, usually as a parallelogram crystal and seldom as a hexagon crystal.<sup>4</sup> We found that the A' form of pentadecanoic acid exhibited a reversible solid-state phase transition as depicted in Figure 1. The transition enthalpy of 1.4 kJ/mol is quite small compared with that in the other solid-state transitions of *n*-fatty acids (Table 1). A singlet IR band due to CH<sub>2</sub> rocking  $\nu(\text{CH}_2)$  mode appeared at 716 cm<sup>-1</sup> in both phases (Figure 2), which is a characteristic of the parallel-packing type subcell. Therefore, the higher and lower temperature phases can be recognized to belong to the A' form, and we named them A'<sub>h</sub> and A'<sub>l</sub>, respectively.

An overall morphological change took place on this reversible transition as shown in Figure 3: the acute interedge angle changes from 70° to 62° on heating process. However, a single crystal specimen kept its single-crystal state. In polarized microscopic observations, the resultant crystal showed clear extinction under the condition of crossed Nicols (crossed polars), and it also exhibited clearly polarized IR spectra. The transition

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**Figure 1.** DSC data of the transition behavior of the A' form. Samples (10 mg) were sealed in aluminum pans, and heating and cooling rates were 2 °C/min.

**TABLE 1: Transition Points and Transition Enthalpies for Fatty Acids**

		temperature (°C)	ΔH(kJ/mol)
stearic acid (ir) <sup>a</sup>	B → C	around 50	5.8 <sup>7</sup>
	E → C	around 45	4.4 <sup>7</sup>
oleic acid	γ → α	-2.2	8.8 <sup>8</sup>
erucic acid	γ → α	-1.0	8.8 <sup>9</sup>
	γ1 → α1	9.0	8.9 <sup>9</sup>
pentadecanoic acid	A' <sub>1</sub> → A' <sub>h</sub>	23.2	1.4
	B' → C'	45.6	5.7 <sup>10</sup>

<sup>a</sup> ir: irreversible transition.

behavior depended significantly on the condition of single-crystal specimens.

A fairly good single crystal, which has a morphology of elongated parallelogram, exhibited a rapid morphological change. We followed it with a video recorder that took 30 frames per second. Figure 3a shows an example. The transient state was recorded in only two frames both on heating and on cooling, which means that the crystal has completed its transition within 0.1 s. In this crystal, the transition started at a long edge and propagated toward the opposite side. A bend of the short edges was observed at the interface between the mother and product phases. In the case of the most rapid transition we could not record the transient state by the video recorder (i.e., the transition was completed within 0.03 s). Single-crystal specimens of this type show a larger hysteresis than that of 2.5 °C observed in the DSC measurement. The maximum value is 8.9 °C (A'<sub>1</sub> → A'<sub>h</sub> occurred at 28.2 °C and A'<sub>h</sub> → A'<sub>1</sub> at 19.3 °C). In other words, a single-crystal specimen performs a quick transition when it shows a large hysteresis.

In an individual crystal with defects, the transition took place more slowly. In this case the momentary morphological change in the overall region was not observed. Figure 3b shows an example on a heating process. A band of the A'<sub>h</sub> form appeared at first, and the width of the transformed region gradually spread. The band makes an angle of 3° with the long edge (on cooling: 4°). A bend at the interface between the mother and product phases clearly appeared. Sometimes the transition started at several points. The hysteresis was comparable to that observed with DSC. The period for this type transition was widely distributed. In several cases, it required a few minutes.

The A'<sub>1</sub> ↔ A'<sub>h</sub> reversible transition shows a quick shear deformation of a single crystal, holding its single crystal state,

which must come from cooperative molecular displacements in a large area. Therefore, this transition also can be recognized as a martensitic transition. It seems that the cooperativity is especially strong in the direction along the long edge. Both in the high and low quality crystals, the region of the product phase appears first as a band along this direction. The product phase grew so fast in this direction that the growth process could not be captured with a video recorder, contrary to the growth in the lateral direction of the band. In the rapid morphological change of Figure 3a, the transition proceeds in the lateral direction at a speed of about 5 mm/s. In the fastest case observed, it traveled at least at 8 mm/s.

Figures 2a and b reproduce the polarized IR spectra of the A'<sub>h</sub> and A'<sub>1</sub> states of a single crystal. We measured IR spectra changing the polarization direction of the incident radiation at intervals of 5°, and found that the polarizations of the ν(CH<sub>2</sub>) and δ(CH<sub>2</sub>) bands remained almost unchanged: the ν(CH<sub>2</sub>) and δ(CH<sub>2</sub>) bands are observed with parallel and perpendicular polarizations as to the long edge, respectively. Therefore, the a<sub>s</sub> axis of the T// subcell is set parallel to the long edge in both phases. Conspicuous changes were observed in the bands due to carboxyl groups. The bands due to O—H out of plane mode σ(O—H) appeared at 888 cm<sup>-1</sup> in A'<sub>h</sub> and at 900 and 919 cm<sup>-1</sup> in A'<sub>1</sub> with parallel polarization to the long edge. The bands due to α-methylene scissoring δ(α-CH<sub>2</sub>) and C=O stretch ν(C=O) also showed clear differences.

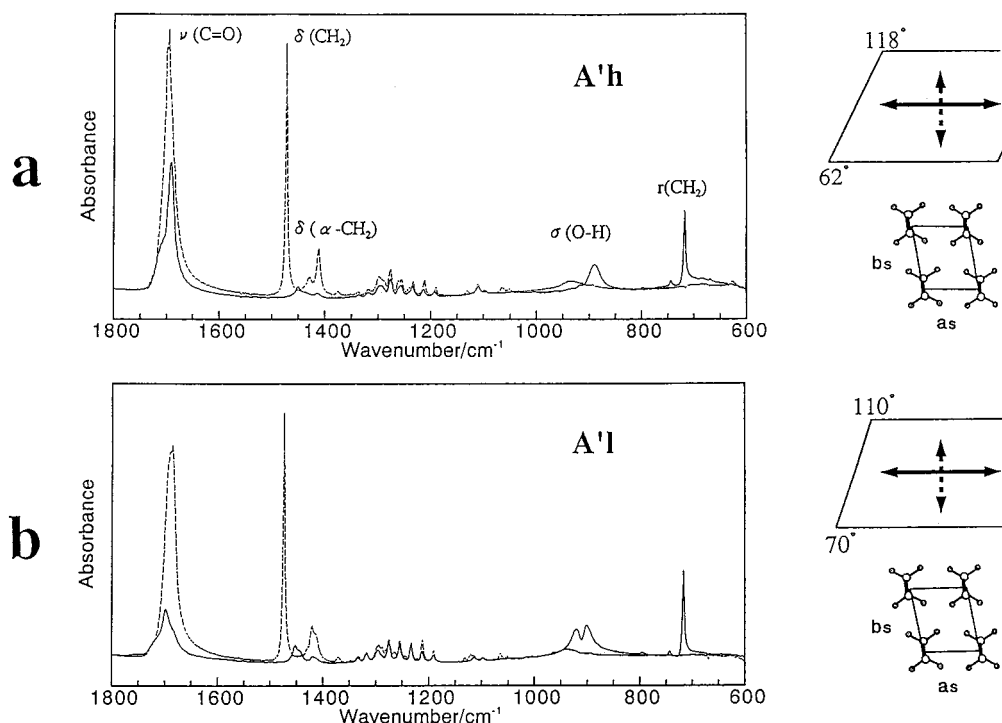
From the spectral and morphological changes, we infer that a structure change around carboxyl groups and a slight deformation or a slight orientation change of the T// subcell take place on this reversible transition.

**2. A'<sub>h</sub> ↔ A'<sub>1</sub> Transitions Induced by a Local Mechanical Stress.** Both the A'<sub>h</sub> → A'<sub>1</sub> and A'<sub>1</sub> → A'<sub>h</sub> martensitic transitions occurred also by a mechanical stimulation. We found that both transitions could occur even in the temperature region where the product phase was metastable.

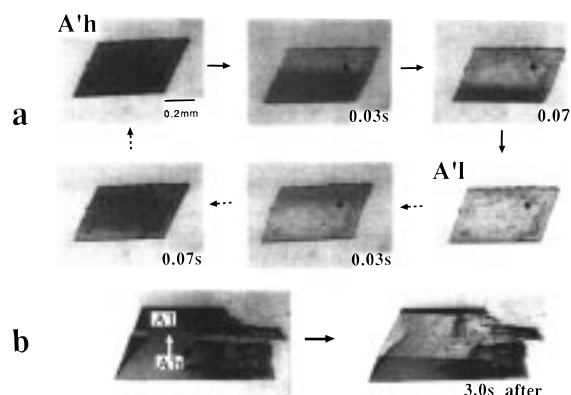
According to the DSC measurement, the free energies of the A'<sub>h</sub> and A'<sub>1</sub> forms cross at anywhere between 20.7 and 23.2 °C, and the A'<sub>1</sub> and A'<sub>h</sub> forms are stable in the lower and higher temperature regions, respectively. We imposed a mechanical stimulation, a press with the end of a needle, on a single crystal at various temperatures. The A'<sub>1</sub> → A'<sub>h</sub> and A'<sub>h</sub> → A'<sub>1</sub> transitions take place in a wide temperature region. These transitions are able to occur even in a temperature region where the product phase is metastable. At present we have confirmed the A'<sub>1</sub> → A'<sub>h</sub> transition until 17 °C and the A'<sub>h</sub> → A'<sub>1</sub> transition until 27.0 °C.

In both of the A'<sub>1</sub> → A'<sub>h</sub> and A'<sub>h</sub> → A'<sub>1</sub> transitions, the product phase appeared as bands in an instant. There are at least three different orientations for the bands, as shown in Figures 4a and 4b. In polarized microscopic observations, the three types of bands showed clear extinction under the condition of crossed Nicols at individual arrangements of specimens, which suggests three different orientations of the product phase. The band running along the long axis has been observed most frequently.

The band of the metastable product phase is sandwiched with the stable mother phase, when the A'<sub>1</sub> → A'<sub>h</sub> transition occurs below the energy crossing point or when the A'<sub>h</sub> → A'<sub>1</sub> transition occurs above it. The transformed region usually remained unchanged even though the product phase was in a metastable condition such as a relatively high supercooling or superheating state. However, we have observed the recovery to the mother phase several times when the mechanical stress is removed. When we kept the specimens having a metastable domain of A'<sub>h</sub> at 18.7 °C for 2 weeks, the A'<sub>h</sub> domain did not transform to the stable state. Similarly, an A'<sub>1</sub> domain did not transform at



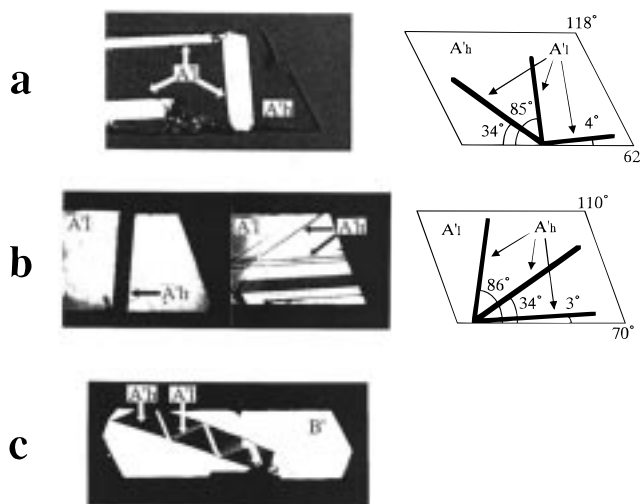
**Figure 2.** Polarized infrared spectra of single-crystal specimens of the  $A'_h$  form (a) and the  $A'_l$  form (b) and the relationship between crystal morphology and subcell arrangement. Solid and broken lines represent the spectra taken with polarized radiations parallel and perpendicular to the long edge of the lozenge crystals.



**Figure 3.** Optical micrographs showing the  $A'_l \leftrightarrow A'_h$  transition induced by a temperature change: (a) rapid morphological changes (—, cooling process and ---, heating process) and (b) a band structure of the transformed region upon heating.

25.2 °C for 2 weeks. This means that the stable phase on both sides hinders the transformation of the metastable domain. The recovery of this domain is accompanied with its deformation, and the deformation requires the overall displacements of the unchanged regions on both sides, which is an obvious disadvantage energetically.

These phenomena suggest that a mechanical stress changes the relative stability between the  $A'_l$  and  $A'_h$  forms and induces a nucleation of the product phase. Such a stress-induced transition to a metastable phase has been found in polymers, polyethylene, polyoxymethylene and so on.<sup>11,12</sup> We felt the necessity to reinvestigate the transition behaviors in the  $B' \rightarrow A'$  and  $A' \rightarrow B'$  transitions and performed similar experiments in these transitions (as described in the next section, this  $A'$  modification corresponds to the  $A'_h$  form). Both of the two transitions could be induced by a mechanical stimulation even in the temperature region where the product phase was metastable:  $T > 30$  °C for  $A'$  and  $T < 30$  °C for  $B'$ .



**Figure 4.** A product-phase region generated by a mechanical stress: (a)  $A'_h \rightarrow A'_l$  transition, (b)  $A'_l \rightarrow A'_h$  transition, and (c)  $B' \rightarrow A'_l$  transition.

Particularly, the transformation from  $B'$  to  $A'$  was confirmed at a relatively high ratio in a wide temperature region ranging to 40 °C. It is suggested that a similar transition behavior would occur between the other polymorphs of fatty acids.

**3. Transition from  $B'$  to  $A'_l$  in Two Steps.** As for the  $B' \rightarrow A'$  transition by a mechanical stimulation, we were interested in the possibility that the product phase changes from  $A'_h$  to  $A'_l$  around the energy crossing point between  $A'_h$  and  $A'_l$ . We studied the temperature dependence of the transition behavior. Above the  $A'_l \rightarrow A'_h$  transition point, the  $B'$  form transformed directly to the  $A'_h$  form, while at a lower temperature the transition was performed in the following two steps: the transition from  $B'$  to  $A'_h$  and the successive transition from  $A'_h$  to  $A'_l$ . Figure 4c shows an example observed at 18.5 °C. At first a band of the  $A'_h$  form appeared and then a zigzag pattern due to the  $A'_l$  form was generated soon. The occurrence

of the zigzag pattern was also confirmed when a specimen having an A'<sub>h</sub> region sandwiched with the B' regions was cooled. Judging from the experimental conditions, the B'→A' transition reported in the previous paper is the transformation to A'<sub>h</sub>.

We have not observed the direct transition to the A'<sub>l</sub> form. We conjecture that the energy barriers among polymorphs are the cause for the B'→A'<sub>l</sub> transition in two steps. It is likely that the energy barrier between B' and A'<sub>h</sub> is lower than that between B' and A'<sub>l</sub>. This relationship in relative barrier heights would result in the preferential transition to the A'<sub>h</sub> form, even in the condition that A'<sub>l</sub> is more stable than A'<sub>h</sub>.

For understanding these transition behaviors of the A'<sub>l</sub> and A'<sub>h</sub> forms profoundly, we are studying their crystal structures and detailed crystallographic relationship between the mother and product phases.

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## References and Notes

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