

## Neutron Incoherent Inelastic Scattering of Oriented Oleic Acid

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In order to investigate a hierarchical structure of vibrational modes we have observed neutron incoherent inelastic scattering of oriented oleic acid ( $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ ) in crystal and liquid states at several temperatures by using time-of-flight neutron spectrometer AGNES in JRR-3M. In the liquid and crystal phases the lattice vibration, the molecular vibration and the intermediate transition modes were assigned.

KEYWORDS: neutron incoherent inelastic scattering, vibration modes

### §1. Introduction

Lattice vibrational modes of infinite polymethylene chain  $-\text{C}(\text{CH}_2)_n\text{C}-$  of phonon and internal molecular modes of  $\text{CH}_2$  bending mode have been observed by means of neutron incoherent inelastic scattering method and infrared absorption and Raman scattering methods.<sup>1,2)</sup>

On the other hand a finite zigzag chain compound hierarchical spectra of local vibrational accordion modes are expected owing to its hierarchical bonding structure.

Oleic acid molecule consists of a couple of finite polymethylene chains connected by ethylene double bond carbon and makes a dimer along the chain axis connected by hydrogen bonds between carboxyl groups in liquid and crystal phases; molecular formula is  $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$ . Oleic acid crystal consists of two dimers in the unit cell. In other word there are four  $\text{C}(\text{CH}_2)_7\text{CH}=\text{}$  groups or two oleic acid molecules units in the unit cell. These units are connected by three kinds of bonds, hydrogen bonds, double bond and non-bond (van der Waals force). So a hierarchical bonding structure of polymethylene chains exists in the crystal. It is expected that it should exist a hierarchical vibrational accordion modes which consist of the accordion modes of dimer, molecular and  $\text{C}(\text{CH}_2)_7\text{CH}=\text{}$  group. We have planned to observe these hierarchical excitations of local modes by using neutron incoherent inelastic scattering of oriented oleic acid in oriented crystal and in liquid phases.

It is interesting to show that these internal molecular, coupled molecular and lattice vibrational modes exist in low frequency region. In liquid phase if any periodic structure does not exist then lattice vibrational modes should disappear. So we are also interested in how these three kinds of mode behave in liquid phase. In our previous study the spectra of oriented oleic acid in low energy region were observed by mean of TOF neutron spectrometer.<sup>3,4)</sup> But their bands are broad because of overlapped transitions of many excited levels. Then in order to reduce these overlapped transitions from higher energy levels, the incoherent inelastic scattering spectra have been

observed at lower temperature.

### §2. Experiments

In order to get an oriented crystal, a field cooling technique was adopted for ferrofluid solution of oleic acid. The ferrofluid was prepared by solvating 1 weight percent of oleic acid covered-magnetite ( $\text{Fe}_3\text{O}_4$ ) particle to ultra pure oleic acid liquid (99.9%, supplied by M.Suzuki on Nippon Oil and Fat Co.ltd.). A strong magnetic field tends to align the magnetic particles like beads along the magnetic field in liquid crystal phase. Then the sample was cooled down below the melting point, 286K of oleic acid, under applied magnetic field 0.6T. The solvent oleic acid was crystallized as  $\beta$  phase with the direction of the hydrocarbon chain perpendicular to the applied field but in the horizontal plane. In this experiment the magnetic field was applied in the horizontal scattering plane of neutron.

The inelastic incoherent neutron spectra of the oriented oleic acid were measured with time-of-flight neutron spectrometer AGNES with an incident neutron energy 4.59meV, installed at the cold neutron guide, C3-1-1, in JRR-3M.<sup>5)</sup> 118 detectors of the spectrometer cover the angle region from  $9^\circ$  to  $130^\circ$  per  $1^\circ$ . After the magnetic field cooling in the horizontal scattering plane, the solid oriented sample can be freely rotated in the scattering plane. The spectra were measured at each one temperature along two different directions angled 45 degrees, step by step. In the time-of-flight experiment the direction of scattering vector varied according to the time channel of each counter. So the directional dependence of phonon scattering function is obtained by summing up the data in the range of 10 degrees of each  $Q$  direction which are distributed over 118 detectors.

### §3. Results and Discussions

Figure 1 and 2 show the anisotropic phonon scattering function, which is normalized as follows for the neutron energy gain case,

$$G(Q, \omega) = \frac{4\pi m_n}{Q^2 \hbar^2} \frac{\omega}{e^{2W(Q)} n(\omega)} S(Q, \omega) \quad (3.1)$$

In order to get anisotropic contribution of  $G(Q, E)$ , it is necessary to select the same  $\mathbf{Q}$  direction component of  $G(Q, E)$  among the all detector data. Since the  $\mathbf{Q}$  vector is a function of the  $\xi$  angle which is the angle between the  $\mathbf{Q}$  vector and the  $c$ -axis,  $G(Q, E)$  for each  $2\theta$  direction has some dispersion for the  $\xi$ . Now we define a direction components of  $G(Q, E)$  for a  $\xi_0$  direction,  $D(Q_{\xi_0}, E)$ , as follows;

$$D(Q_{\xi_0}, E) = \sum_{\mathbf{Q}} \sigma(\xi - \xi_0) G(Q_{\xi}, E) \quad (3.2)$$

When the  $\mathbf{Q}$  direction is parallel to the  $\xi_0$ , the  $G(Q_{\xi_0}, E)$  is collected as a component of  $D(Q_{\xi_0}, E)$ .

Melting point of oleic acid is 289.6K. The crystal constants of  $\beta$  phase is  $a=9.3\text{\AA}$   $b=5.5\text{\AA}$   $c=35.3\text{\AA}$   $\alpha=87.9^\circ$   $\beta=82.8^\circ$   $\gamma=86.2^\circ$ . The asymmetric unit contains two crystallographically different dimers in the  $\beta$  crystal unit cell and lamellar interfaces consist of methyl and carboxyl groups. The  $c$ -axis is approximately parallel to the molecular chain.

One oleic acid molecule has two finite polymethylene carbon chains of  $\text{CH}(\text{CH}_2)_7\text{C}$  which has nine carbon atoms. It is expected that  $\text{CH}(\text{CH}_2)_7\text{C}$  of which number called  $m$  is a unit of molecular accordion mode. Then an oleic acid molecule is  $2m$  and a dimer is  $4m$ . Since displacement vectors of these modes are parallel to the  $c$ -axis, these modes show maximum intensities when the scattering vector is parallel to the  $c$ -axis ( $\mathbf{Q} // c$ ). Energy of the molecular accordion modes  $E_a$  is given by,<sup>6)</sup>

$$E_a = \frac{h\sqrt{E}\rho}{2nL_c} \quad (3.3)$$

where  $h$  is Planck constant,  $E$  Young's modulus,  $\rho$  density of the crystal ( $0.98\text{g/cm}^3$ ),  $n$  the number of carbon atoms and  $L_c$  length of inter methylene groups ( $-\text{CH}_2-$ ). The energy of the molecular accordion modes of  $m$ ,  $2m$  and  $4m$  are estimated by using this equation. Bands around  $33.1\text{meV}$  and  $31.5\text{meV}(\mathbf{Q} // c)$  were assigned to the molecular accordion modes of  $\text{CH}(\text{CH}_2)_7\text{CH}_3$  and  $\text{CH}(\text{CH}_2)_7\text{COOH}$ , respectively in the crystal. Bands around  $66.2\text{meV}$   $15.7\text{meV}$  and  $7.3\text{meV}(\mathbf{Q} // c)$  were assigned to the molecular accordion modes of  $\frac{1}{2}m$ ,  $2m$ (molecule) and  $4m$ (dimer), respectively in the crystal. Since the sample crystal was not a perfect crystal but an oriented crystal, the  $c$ -axis direction had some distribution and some modes was observed the direction perpendicular to the  $c$ -axis ( $\mathbf{Q} \perp c$ ).

Band around  $1.7\text{meV}(\mathbf{Q} // c)$  in the crystal phase is the lowest mode, then it was assigned to a longitudinal component of a zone boundary lattice mode of  $4m_c(\pi)$  ( $c$  indicates a crystal phonon) of a crystal accordion mode (longitudinal acoustic mode:LA( $\pi$ )), of which displacement vector is parallel to the  $c$ -axis. Band around  $3.6\text{meV}(\mathbf{Q} // c)$  was assigned to the zone boundary mode of  $2m_c$ . The energy of this mode is twice as larger as of  $4m_c$ . In the perfect  $\beta$  crystal the zone boundary mode of  $2m_c$  should not exist. But since the crystal stacking packing was disordered, new periodicity of unit cell is  $2m$  a half of the perfect  $\beta$  plane. Then the zone boundary

mode of  $2m_c$  appears.

Band around  $30\text{cm}^{-1}$  ( $3.7\text{meV}$ ) is a highest energy of the lattice modes, which was by low-frequency Raman scattering spectra of oleic acid in  $\alpha$  crystal.<sup>7)</sup> Then bands around  $2.7\text{meV}$  and  $4.4\text{meV}(\mathbf{Q} // c)$  in the crystal phase were assigned to longitudinal optical modes(LO) of  $4m_c$ , which corresponds to  $q=0$  and  $\pi$ , respectively.

In this experiment we observed neutron energy gain spectra, so there are two case of the energy cascade, one is from an excited state to a ground state and the other is an excited state to another excited state which is call intermediate transition. Bands around  $5.2\text{meV}$ ,  $6.1\text{meV}$ ,  $8.8\text{meV}$ ,  $12.5\text{meV}$  and  $55.7\text{meV}(\mathbf{Q} // c)$  in the crystal phase were assigned to the intermediate transition modes, energy level from  $7.3\text{meV}$  to  $1.7\text{meV}$  ( $7.3\text{meV}-1.7\text{meV}$ ),  $6.3\text{meV}-0.0\text{meV}$ (the ground state),  $10.0\text{meV}-1.7\text{meV}$ ,  $15.7\text{meV}-1.7\text{meV}$  and  $62.2\text{meV}-7.3\text{meV}$ , respectively.

It is expected that the energy of twisting mode is lower than that of a transverse component of the crystal accordion mode  $4m_c(\pi)$  (transverse acoustic mode:TA( $\pi$ )) and energy of these modes are lower than that of the other mode. Since the twisting and TA( $\pi$ ) modes are lowest modes whose direction is perpendicular to the  $c$ -axis, the lowest bands around  $1.9\text{meV}$  and  $2.2\text{meV}$ , which show maximum intensities when the scattering vector is perpendicular to the  $c$ -axis ( $\mathbf{Q} \perp c$ ), in the crystal phase were assigned to the twisting mode and the transverse component of the crystal accordion mode  $4m_c(\pi)$  ( $4m_c\text{TA}(\pi)$ ), respectively. Band around  $4.5\text{meV}(\mathbf{Q} \perp c)$  which is twice as long as the energy of  $4m_c\text{TA}(\pi)$  was assigned to the transverse component of the crystal accordion mode  $2m_c(\pi)$  ( $2m_c\text{TA}(\pi)$ ).

Since motion of a side chain are independent of unit cell length, it is expected that energy of a side chain in oleic acid crystal and polyethylene crystal would not be so much different. In the polyethylene crystal energy of  $\text{CH}_2$  rocking mode  $\nu_8(\pi)$  whose energy is  $731\text{cm}^{-1}$  ( $90.8\text{meV}$ ) was reported.<sup>2)</sup> Band around  $87.0\text{meV}$  in the crystal phase was assigned to  $\text{CH}_2$  rocking mode  $\nu_8(\pi)$ .

Since the molecular modes are independent of the crystal structure but depend on the molecular structure, their modes should exist both in the liquid and crystal phases. In the liquid phase the molecular accordion modes, the  $\nu_8(\pi)$  mode and the twisting mode were observed.

On the other hand the lattice modes are depend on the crystal structure. In the liquid phase they should disappear. But some modes, the  $4m_c(\pi)$ ,  $2m_c(\pi)$ , LO(0), LO( $\pi$ ) and  $4m_c\text{TA}(\pi)$  modes, were observed at 296K and 318K. Since just above melting point oleic acid molecules have some kind of short range order, the lattice modes were observed.

#### §4. Conclusions

We have observed neutron incoherent inelastic scattering of oriented oleic acid in the liquid and crystal phases. In the crystal phase the polarization displacement of the molecular vibration modes, the lattice vibration modes and the intermediate transition modes which are parallel

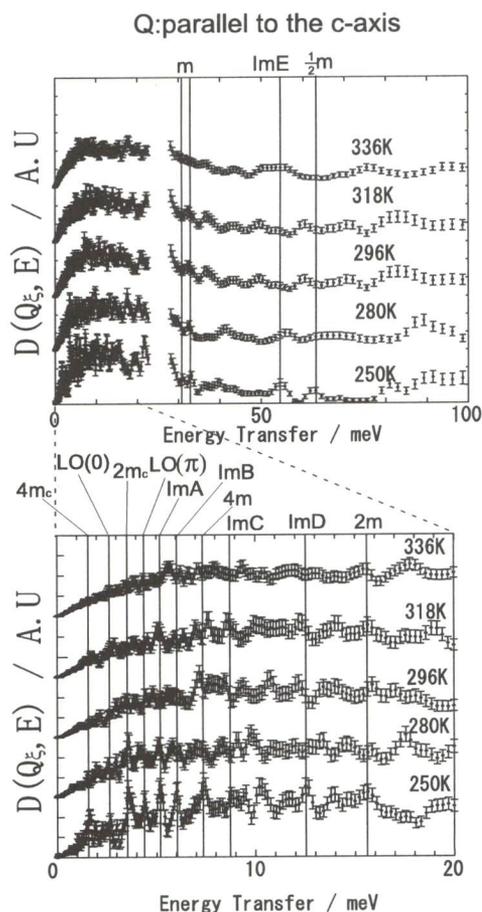


Fig.1. Normalized phonon scattering function at several temperatures for the scattering  $Q$  vector parallel to the chain axis  $c$  of oleic acid. The melting point of oleic acid is 289.6K. Here,  $\frac{1}{2}m$ ,  $m$ ,  $2m$  and  $4m$ : the molecular accordion modes of  $\frac{1}{2}m$ ,  $m$ ,  $2m$  and  $4m$ ,  $4m_c$ ,  $2m_c$ : zone boundary lattice modes of  $4m_c$ ,  $2m_c$ ,  $LO(0)$ ,  $LO(\pi)$ : longitudinal optical modes of  $4m_c$  which correspond to  $q=0$  and  $\pi$ ,  $ImA$ : the intermediate transition mode of energy level from 7.3meV to 1.7meV,  $ImB$ : the intermediate transition mode of energy level from 6.3meV to 0.0meV,  $ImC$ : the intermediate transition mode of energy level from 10.0meV to 1.7meV,  $ImD$ : the intermediate transition mode of energy level from 15.7meV to 1.7meV,  $ImE$ : the intermediate transition mode of energy level from 62.2meV to 7.3meV.

and perpendicular to the chain axis were well separated. Using the energy versus wavelength relation of accordion modes of various standing waves, the assignment of energies of molecular accordion modes as well as lattice zone boundary modes have been done.

Since the energy of the molecular accordion modes are inversely proportional to the molecular length, the molecular accordion modes of  $m$ ,  $2m$ ,  $4m$  were assigned in the liquid and crystal phases. Just above melting point oleic acid molecules have some kind of short range order, the lattice vibration modes,  $4m_c(\pi)$ ,  $2m_c(\pi)$ ,  $LO(0)$ ,  $LO(\pi)$ ,  $4m_cTA(\pi)$  and  $2m_cTA(\pi)$ , which are depend on the crystal structure were assigned in the crystal phase and the liquid phase of just above melting point. But in the liquid phase at 336K the short range order dis-

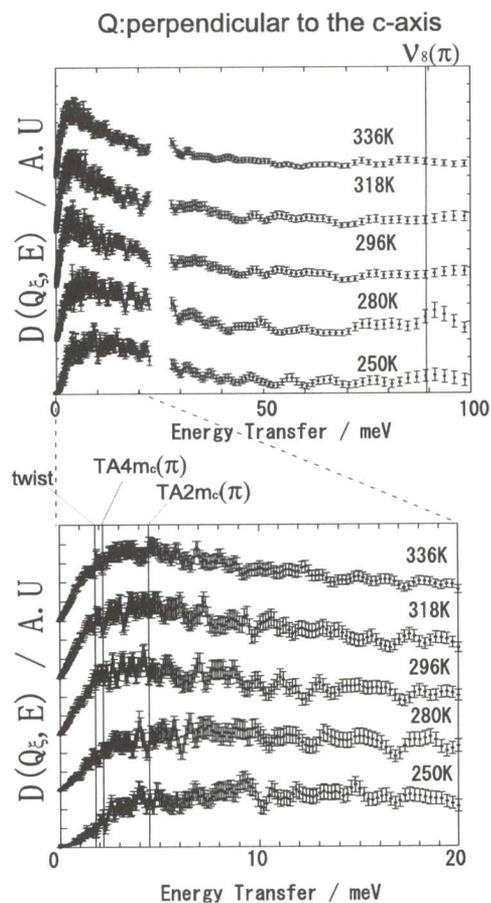


Fig.2. Normalized phonon scattering function at several temperatures for the scattering  $Q$  vector perpendicular to the chain axis  $c$  of oleic acid. The melting point of oleic acid is 289.6K. Here, twist: the twisting mode,  $TA4m_c(\pi)$ : the transverse component of the crystal accordion mode  $4m_c$ ,  $TA2m_c(\pi)$ : the transverse component of the crystal accordion mode  $2m_c$ .

appears, then the modes disappeared. The intermediate transition modes are the energy cascade from one excited lattice vibration mode to the other excited mode, temperature dependence of their modes are as same as that of the lattice vibration modes. So the intermediate transition modes were assigned in the crystal phase and just above the melting point but disappeared in the liquid phase at 336K.

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