原著論文

# A Consideration on the Orientation of L-Alanine Crystals under a Magnetic Field

鈴木映一, 小川 薫*, 小川 智, 八木文子, L. A. Guzman, 清水健司

岩手大学工学部応用化学科,

* 岩手県先端科学技術研究センター (いわて産業振興センター)

Eiichi Suzuki, Kaoru Ogawa*, Satoshi Ogawa, Fumiko Yagi,
Luis Americo Guzman and Kenji Shimizu

Department of Chemical Engineering, Iwate University
* Advanced Science and Technology Institute, Iwate Industrial Promotion Center

The effect of a magnetic field on the orientation of diamagnetic, non-aromatic L-alanine crystals was investigated. L-alanine was crystallized from a supersaturated aqueous solution in a magnetic field of 5 T. Short prismatic crystals were oriented so that their crystallographic c-axes were aligned parallel to the direction of the magnetic field. A newly designed microscope-interferometer was used for *in situ* observation of crystallization processes under the magnetic field. According to the observation, the c-axes of small nucleated crystals were forced to align parallel to the magnetic field direction even when the crystals were migrating in the solution due to thermal convection. Characteristic features of the orientation were explained by the small magnetic anisotropy of the L-alanine crystal, which should be derived from the $CO_2^-$ groups.

e-mail : esuzuki@iwate-u.ac.jp

岩手大学工学部応用化学科
〒 020-8551 岩手県盛岡市上田 4-3-5
Department of Chemical Engineering, Iwate University
4-3-5 Ueda, Morioka 020-8551, Japan

岩手県先端科学技術研究センター
〒 020-0852 岩手県盛岡市飯岡新田 3-35-2
Advanced Science and Technology Institute,
Iwate Industrial Promotion Center
3-35-2 Iioka-shinden, Morioka 020-0852, Japan

## §1　Introduction

In order to improve the properties of functional materials in the fields of medicines, food additives and optical materials, useful methods to control the structure, quality and morphology of crystals have been required. Recently, the application of a magnetic field has attracted attention as one of the methods that can control the sizes, shapes and orientations of crystalline materials.[1,2] It has been established that a static magnetic field affects the orientations of diamagnetic proteins or several organic molecular crystals.[1-8] The magnetic orientations of those crystals were explained in terms of their diamagnetic anisotropy. Among them, aromatic molecules have relatively large ($>10^{-5}$ $cm^3 \cdot mol^{-1}$) anisotropy,[6-8] which is advantageous for the magnetic orientation. On the other hand, only a few studies have been published on the magnetic orientation of non-aromatic crystals.[9]

In this paper, the crystallization of L-alanine, which is diamagnetic and non-aromatic, from a supersaturated aqueous solution in a magnetic field of 5 T was investigated. From the observed results, it was found that the particular direction of the nucleated crystals was forced to align parallel to the direction of a magnetic field. The origin of the orientation is discussed based on the estimated magnetic susceptibility.

## §2 Experiment

### 2-1 Sample preparation and crystallization for observation of magnetic orientation

L-Alanine, purchased from Ajinomoto (100.0%) and used without any purification, was added to hot water and stirred at 40°C for 2 h. After allowing the mixture to stand for 1 h, the saturated solution (saturated temperature $t_s = 40°C$) was filtered through a glass filter paper (pore size 1 $\mu$m). 5 ml of the solution was transferred to a crystallization cell (petri dish) and allowed to stand for crystallization on the inside or the outside of a static high magnetic field at room temperature.

The magnetic field was supplied by a superconducting magnet (Japan Magnet Technology, Inc., JMTD-5T 300M, bore size $\phi$300 mm). The direction of the magnetic field was horizontal. The crystallization cell was placed at the center of the magnet, where the intensity of the magnetic field was 5 T. After a lapse of 3 h, the shapes and orientations of crystals at the bottom of the cell were observed and recorded with a digital camera.

The crystallographic axes of the obtained L-alanine crystals were determined based on the observation of X-ray reflection (Rigaku Corp., ATX-G) from the {120} faces and the structural data.[10]

### 2-2 *In situ* observation of crystallization under a magnetic field

A newly designed microscope-interferometer was used for *in situ* observation of crystallization under a magnetic field. **Fig. 1** shows an illustration of the observation system. The apparatus consists of a laser diode ($\lambda = 680$ nm), a Mach-Zehnder interferometer, the crystallization cell holder with a temperature control unit, an objective lens and a CCD camera. The temperature of a sample solution in the cell was controlled with Peltier elements. The microscope-interferometer system was inserted in the superconducting magnet described above so that the position of the crystallization cell was at the center of the magnet. The direction of the magnetic field was vertical.

A solution of L-alanine ($t_s = 40°C$, prepared as described above) was injected into an ordinary quartz cell ($12 \times 4.5 \times 45$ mm, optical path length 3 mm) and placed in the cell holder of the apparatus, which was placed in the magnet. The temperature of the solution was lowered to 25°C, and the crystallization process was recorded with the CCD camera and a VTR system.

## §3 Results and Discussion

### 3-1 Orientation of L-alanine crystals

Short prismatic crystals were obtained from L-alanine solutions both on the inside and the outside of the magnetic field. Photographs of these crystals (top view of the crystallization cell) are shown in **Fig. 2**. The direction of the applied magnetic field was horizontal. As might be expected, crystals at the bottom of the cell were randomly oriented without a magnetic field (Fig. 2(a)). In a magnetic field of 5 T, however, the prismatic directions of the crystals were obviously oriented parallel to the direction of the magnetic field (Fig. 2(b)).

According to the X-ray diffraction results, the crystallographic structure of L-alanine was unchanged by
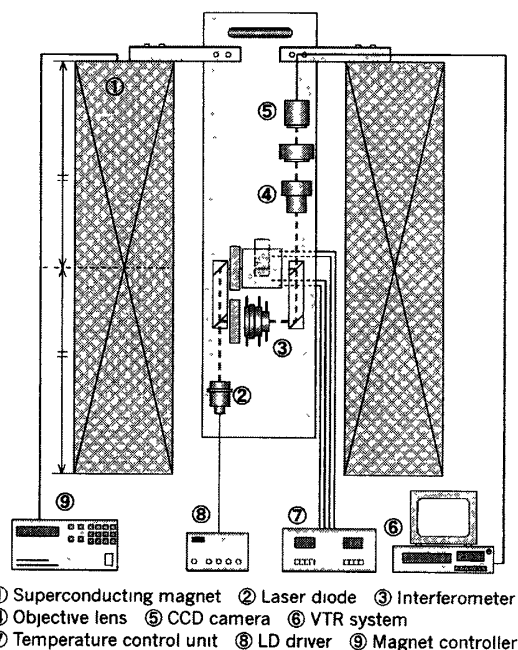


① Superconducting magnet ② Laser diode ③ Interferometer
④ Objective lens ⑤ CCD camera ⑥ VTR system
⑦ Temperature control unit ⑧ LD driver ⑨ Magnet controller

**Fig. 1** Schematic illustration of the experimental setup for *in situ* observation of crystallization under a magnetic field.

the application of a magnetic field. It was also found that the prismatic direction of the L-alanine crystal coincides with its crystallographic $c$-axis. Therefore, the crystals of L-alanine obtained in a magnetic field were oriented so that their crystallographic $c$-axes were parallel to the direction of the field.

### 3-2 *In situ* observation of crystallization under a magnetic field

As the temperature of the solution decreased, small crystals were observed to nucleate and migrate in the solution due to thermal convection. **Fig. 3** shows the VTR snapshots of nucleated crystals from supersatu-

rated aqueous solutions of L-alanine in magnetic fields of 0 and 5 T. Because of the thickness of crystallization cell, only the crystals in focus were clearly observed. No particular orientations were observed for nucleated crystals in the field of 0 T (Fig. 3(a)). At 5 T however, it was clearly observed that the $c$-axes of migrating crystals were oriented parallel to the applied magnetic field (Fig. 3(b)). The oriented crystals continue to grow during thermal convection and finally fall downward. The orientation of nucleated crystals seemed to be unaffected by the direction of migration. It was also observed that several oriented crystals were migrating with rotation around their $c$-axes, which were parallel to the applied magnetic field.

### 3-3 Origin of magnetic orientation of L-alanine crystals

From the above results, the L-alanine crystals were found to be oriented in the magnetic field so that their $c$-axes were parallel to the field. The crystallographic structure of L-alanine was not affected by the application of a magnetic field of 5 T. The orientation of L-alanine in a magnetic field must then be explained in terms of the magnetic anisotropy of the crystallographic structure.

The L-alanine crystal is orthorhombic, and its principal axes of diamagnetic susceptibility are considered to coincide with the crystallographic axes. Unfortunately, however, the principal values of susceptibility along each axis for L-alanine could not be
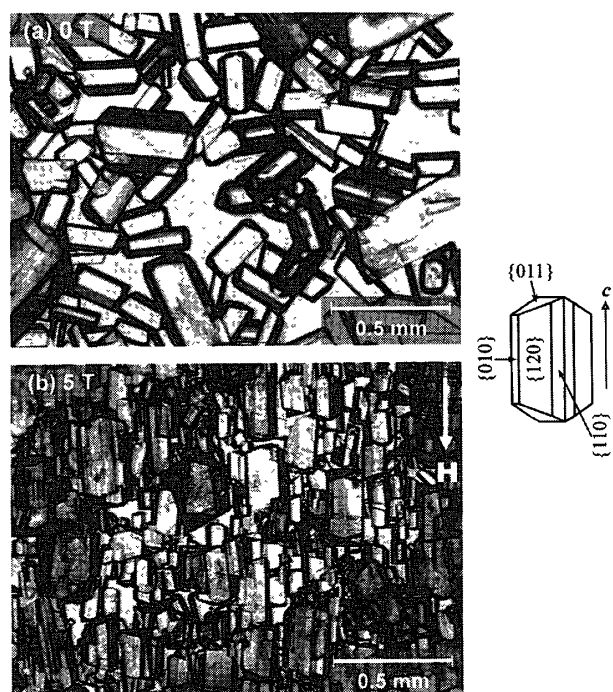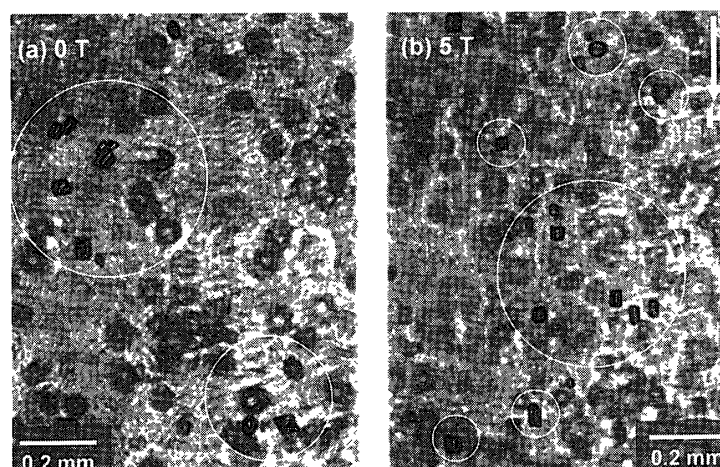


**Fig. 2** Photographs of the L-alanine crystals obtained from aqueous solutions. (a) Under 0 T. (b) Under 5 T. A typical morphology of the L-alanine crystal is also illustrated.



**Fig. 3** VTR snapshots of the small crystals nucleated from supersaturated aqueous solutions of L-alanine. (a) Under 0 T, (b) Under 5 T.
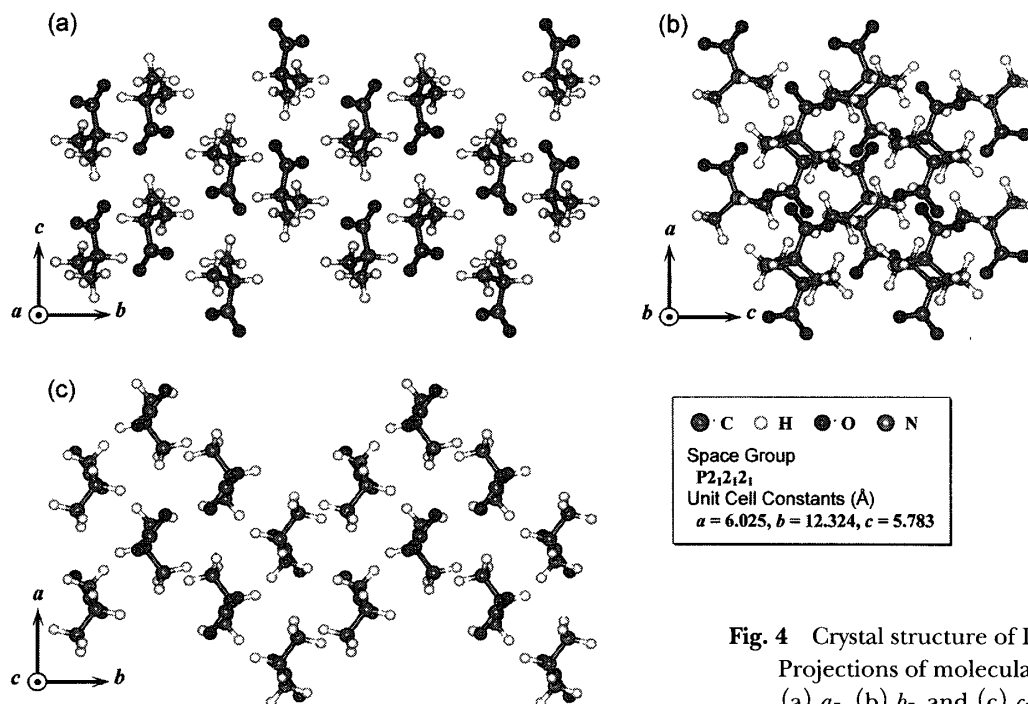
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Space Group
$P2_12_12_1$
Unit Cell Constants (Å)
$a = 6.025, b = 12.324, c = 5.783$

**Fig. 4** Crystal structure of L-alanine.
Projections of molecular arrangement along
(a) $a$-, (b) $b$-, and (c) $c$-axes.

obtained. Therefore, we tried to estimate the magnetic anisotropy based on the molecular arrangement in a unit cell.

The projections of molecular arrangement in the L-alanine crystal along three crystallographic axes are shown in Fig.4. When we look along the $c$-axis (Fig.4(c)), we find that the $CO_2^-$ planes of all molecules are almost parallel to the $c$-axis. On the other hand, we can see in the projections along the $a$- and $b$-axes that all $CO_2^-$ planes have substantial components perpendicular to each axis (Fig.4(a),(b)). The $CO_2^-$ group is considered to have the largest (i.e., numerically the smallest) principal value of susceptibility along the in-plane direction. If we assume that the $CO_2^-$ group plays a dominant role in the magnetic anisotropy of the L-alanine crystal, the susceptibility along the $c$-axis must be larger than the others. In general, the energy of materials in a static and uniform magnetic field is minimized when the axis of the largest magnetic susceptibility coincides with the direction of the field. Therefore, the characteristic feature of the magnetic orientation of the L-alanine crystals would be explained in terms of the energetic stabilization in a magnetic field.

To confirm the above consideration, we made a crude estimation of the anisotropic diamagnetic sus-

ceptibility of the L-alanine crystal. If we assume that the crystallographic axes $a$, $b$ and $c$ are orthogonal, which holds true for orthorhombic crystals, the principal axes of magnetic susceptibility coincide with the crystallographic axes. When the magnetically anisotropic structural units (such as the $CO_2^-$ group in the L-alanine crystal, hereafter, MAU) are placed in a crystallographic unit cell, the principal values of molar magnetic susceptibility for the crystal are given by

$$\chi_j = \frac{1}{n} \sum_{k=1}^{n} \sum_{i=X,Y,Z} K_i^k \cos^2 \theta_{ij}^k$$
$$(j = a, b, c) \qquad (1)$$

where $X$, $Y$, $Z$ represent the Cartesian coordinate axes fixed on each MAU, $K_i^k$ is the molar magnetic susceptibility along the $i$-axis of the $k$ th MAU, $\theta_{ij}^k$ is the angle between the $i$-axis of the $k$ th MAU and the crystallographic $j$-axis, and $n$ is the number of MAU's in a unit cell. We now assume, for simplicity, the axial symmetry of the MAU. The in-plane and the out-of-plane susceptibilities ($K_{//}$, $K_\perp$) and the magnetic anisotropy ($\Delta K$) of MAU are then defined as follows.

$$K_{//} \equiv K_X = K_Y, \quad K_\perp \equiv K_Z, \quad \Delta K_\perp \equiv K_{//} - K_\perp. \quad (2)$$

Using these quantities and the relationship between direction cosines, we can obtain

$$\chi_J = \frac{1}{n} \sum_{k=1}^{n} \{K_{\parallel}^k - \Delta K^k \cos^2 \theta_{ZJ}^k\}$$

$$(j = a, b, c). \qquad (3)$$

The average susceptibility of the crystal is given by averaging the above values over three directions.

$$\overline{\chi} = \frac{1}{3}(\chi_a + \chi_b + \chi_c) = \frac{1}{n} \sum_{k=1}^{n} \left\{ K_{\parallel}^k - \frac{\Delta K^k}{3} \right\}. \quad (4)$$

From Eqs. (3) and (4), the following final expression is obtained.

$$\chi_J = \overline{\chi} + \frac{1}{n} \sum_{k=1}^{n} \left\{ \frac{\Delta K^k}{3}(1 - 3\cos^2 \theta_{ZJ}^k) \right\}$$

$$(j = a, b, c). \qquad (5)$$

We must then estimate the magnetic anisotropy of the $CO_2^-$ group. Lonsdale[11] proposed the following values for the molar susceptibility of the oxalate group, which were estimated from the susceptibility tensor of the oxalic acid dihydrate crystal.

$$K_X = -53.13, \quad K_Y = -52.73, \quad K_Z = -62.40$$
$$[\times 10^{-6}\,cm^3 \cdot mol^{-1}]. \qquad (6)$$

Now, we approximate, for simplicity, the susceptibility tensor of the oxalate group to be axially symmetric. By averaging the in-plane susceptibilities ($K_X$ and $K_Y$), the following magnetic anisotropy for the oxalate group is obtained.

$$\Delta K_{Ox} = (-53.13 - 52.73)/2 - (-62.40) = 9.47$$
$$[\times 10^{-6}\,cm^3 \cdot mol^{-1}]. \qquad (7)$$

Because the oxalate group contains two co-planar $CO_2^-$ groups, we can reasonably estimate the magnetic anisotropy for one $CO_2^-$ group as follows.

$$\Delta K_{CO_2^-} \approx 4.7 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}]. \qquad (8)$$

The average molar susceptibility of L-alanine is given in the literature.[12]

$$\overline{\chi} = -50.5 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}]. \qquad (9)$$

Using these values and based on the crystallographic structure of L-alanine,[10] we can calculate Eq. (5) over the $CO_2^-$ groups of four molecular sites in a unit cell. The results are

$$\begin{cases} \chi_a = -50.5 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}] \\ \chi_b = -52.1 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}] \\ \chi_c = -49.0 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}]. \end{cases} \qquad (10)$$

The differences between the largest susceptibility (along the $c$-axis) and the other two are then

$$\begin{cases} \Delta\chi_{ca} = \chi_c - \chi_a = 1.5 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}] \\ \Delta\chi_{cb} = \chi_c - \chi_b = 3.1 \; [\times 10^{-6}\,cm^3 \cdot mol^{-1}]. \end{cases}$$
$$(11)$$

The stabilization energy for N mol of magnetically anisotropic material due to the orientation in a magnetic field is estimated by[13]

$$\Delta E = \frac{N}{2} \Delta\chi H^2, \qquad (12)$$

where $\Delta\chi$ is the difference between two principal susceptibilities, and $H$ is the intensity of the field. The magnetic orientation of a diamagnetic crystal is considered to occur when the stabilization energy increases with crystal growth and overcomes the thermal energy $k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the absolute temperature.[2-9] The orientational stabilization energy for 1 mol of L-alanine in a magnetic field of 5 T ($H \simeq 50\,kOe$) is estimated as follows.

$$\Delta E = \frac{1}{2} \times 1.5 \times 10^{-6} \times (50 \times 10^3)^2 \qquad (12)$$

$$= 1.9 \times 10^3 \; erg \cdot mol^{-1}$$
$$= 1.9 \times 10^{-4} \; J \cdot mol^{-1}. \qquad (13)$$

The thermal energy at 298 K ($\simeq 25°C$) is given by

$$E_T = 1.380658 \times 10^{-23} \times 298$$
$$= 4.11 \times 10^{-21} \; J. \qquad (14)$$

Therefore, considering that four molecules of L-alanine are included in a unit cell, the number of unit cells ($N_c$) needed for the magnetic orientation is given by

$$1.9 \times 10^{-4} \times \frac{4 \times N_c}{6.022 \times 10^{23}} > 4.11 \times 10^{-21}$$

$$\therefore N_c > \frac{4.11 \times 10^{-21} \times 6.022 \times 10^{23}}{1.9 \times 10^{-4} \times 4} = 3.3 \times 10^6,$$

$$(15)$$

which corresponds to ca. $2.0 \times 10^{-15}$ g or $1.4 \times 10^{-15}$ $cm^3$ ($\sim 0.1\,\mu m$ for each side) of the L-alanine crystal. Typical dimensions of the oriented crystal in Fig. 3 (b) are approximately $30 \times 30 \times 40\,\mu m$. The magnetic energy of the crystals of such size is large enough ($1.1 \times 10^{-13}$ J) to explain the observed orientation of the L-alanine crystals.

## §4 Conclusions

The effect of a magnetic field on the orientation of diamagnetic and non-aromatic L-alanine crystals was investigated and the following results were obtained.

(1) The L-alanine crystals obtained from a supersaturated aqueous solution in a magnetic field were ori-

ented so that the $c$-axes of the crystals were parallel to the field.

(2) According to the *in situ* observation, the $c$-axes of the small nucleated crystals in a magnetic field were forced to be parallel to the field direction even when the crystals were migrating in a solution due to thermal convection.

(3) The above results would be explained in terms of the anisotropy of diamagnetic susceptibility of the L-alanine crystal.

(4) Most of the magnetic anisotropy of the L-alanine crystal should be derived from the anisotropy of the $CO_2^-$ group.

These results suggest that control of the crystal orientation using a magnetic field would be possible even for diamagnetic materials with relatively small anisotropy.

## Acknowledgments

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