Crystal morphology change by magnetic susceptibility force

Akio Katsuki[1*], Shigeo Aibara[2], and Yoshifumi Tanimoto[3*]

[1]*Department of Chemistry, Faculty of Education, Shinshu University, 6-Ro, Nishi-Nagano, Nagano 380-8544, Japan*

[2]*Division of Applied Life Sciences, Graduate School of Agriculture Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

[3]*Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*

*Corresponding author,

Akio Katsuki

Fax: +81-26-238-4123;

E-mail: akatuki@shinshu-u.ac.jp

Yoshifumi Tanimoto

Fax: +81-82-424-7409

E-mail: tanimoto@sci.hiroshima-u.ac.jp

Abstract

We found a change in morphology when lysozyme crystals were grown in a magnetic field. The phenomenon was caused by the magnetic force derived from the magnetic susceptibility gradient. We propose that this force should be called the “magnetic susceptibility force”.

Keywords

Magnetic susceptibility gradient, Magnetic susceptibility force, Lysozyme

1. Introduction

Generally, a magetic gradient is required to generate a magnetic force. However, under certain conditions, magnetic forces are observed in a homogeneous magnetic field [1,2]. In particular, these forces appear to work at interfaces, such as those between solid and liquid phases. We propose another type of magnetic force, which works at interfaces, that is, a “magnetic susceptibility gradient force” [3].

In the crystal growth field, the chicken egg white lysozyme is often used as a model protein since the high-pure commercial sample is obtainable easily. Additionally, some magnetic orientation of the compound have been reported [4,5]. According to their reports tetragonal crystals, which grew in a weak acid solution, aligned their *c*-axis in the direction of a magnetic field.

In this paper, we observed the growth of lysozyme crystals, which was prepared in a weak alkaline solution, in a high magnetic field, and found a change in crystal morphology. Mechanisms of the phenomenon are discussed.

2. Experimental

Lysozyme crystals were obtained as follows. Commercial Lysozyme (Seikagaku corporation) was used without purification. This was dissolved in a weak alkaline buffer solution (pH 8.6) with sodium chloride. The solution was poured into a glass vessel (diameter: 15 mm). Lysozyme grew as an orthorhombic needle crystal at 298 K for 2 to 3 days. The temperature of the vessels was controlled by circulating water from a thermostat.

The experiments with high magnetic fields were carried out in the vertical bore tube (40 mm diameter) of a superconducting magnet (JMTD-LH15T40; Japan Superconductor Technology, Inc.). The distribution of the magnetic flux density $B(z)$ and the product of magnetic flux density and the flux gradient $(\mathrm{d}B(z)/\mathrm{d}z)B(z)$ are displayed in Fig. 1. The three vessels were placed in the magnet bore, of which $B(z)$ and $(\mathrm{d}B(z)/\mathrm{d}z)B(z)$ were 9.87 T and -1500 T^2/m for the top position, 15.0 T and + 50 T^2/m for the middle position, and 11.5 T and + 1230 T^2/m for the bottom position, as shown in Fig. 1. The other vessel was placed outside the bore for control. Images of the crystals were recorded by a digital camera after taking the vessels out of the bore.

3. Results and Discussion

Figure 2 shows photographs of lysozyme crystals in the absence and presence of the magnetic field. Although all crystals were composed of colorless needle-like ones, their morphology was remarkably affected by the magnetic field (see especially Fig. 2 (a’) and (b’)). The almost all crystals in the absence of the magnetic field (Fig. 2 (a) and (a’)) show butterfly-like form. In contrast, almost all ones in the presence of the magnetic field (Fig. 2 (b), (b’), (c), and (d)) show dense and spherical form. Though the magnetic field gradient conditions were very different, the forms resembled each other. That implies that the morphology change was not caused by the magnetic field gradient, but by the magnetic field intensity, and that usual magnetic force did not act on this system.

Lysozyme itself is non ionic compound, and the ionic concentration of the solution does not change during the growth of crystals. Therefore this change is not caused by the Lorentz force.

A possible mechanism is a force caused by magnetic susceptibility gradient. The usual magnetic energy E is given by the following equation,

$$E = -\frac{1}{2}\mu_0 \chi_v V H^2 \quad (1)$$

where μ_0 is a magnetic permeability of vacuum, χ_v is a volume magnetic susceptibility, V is a sample volume, H is a magnetic field. The general magnetic force F is given by a gradient of the magnetic energy as follows,

$$F = -\mathrm{grad}E \quad (2)$$

Substituting eq. (1) into eq. (2) gives the following equation.

$$F = -\mathrm{grad}E = \mu_0 \chi_v V H \frac{dH}{dz} + \frac{1}{2}\mu_0 \frac{d\chi_v}{dz} V H^2 \quad (3)$$

The first term shows the usual magnetic force. Because this term contains a magnetic field gradient at a position z, dH/dz, the degree of the magnetic field gradient determines the magnitude and direction of this force. This force will be negligible at the middle position because of no magnetic field gradient. The second term is governed by the magnetic susceptibility gradient. Although this force is known as “paramagnetic force” in electrochemistry [6,7], this will be effective not only for paramagnetic species but also for diamagnetic species under high magnetic fields, as in the present case. We shall call this additional force the "magnetic susceptibility force", F_{MS}. Namely,

$$F_{MS} = \frac{1}{2}\mu_0 \frac{d\chi_v}{dz} VH^2 \tag{4}$$

The character of this force is described as follows,

1. This force is effective in a homogeneous magnetic field.
2. The direction of this force is determined by the sign of the magnetic susceptibility gradient dχ_v /dz, not that of the magnetic susceptibility χ_v.
3. The magnitude of this force is very sensitive to the magnetic susceptibility gradient dχ_v /dz at interfaces, and depends on the square of a magnetic field H.
4. This force is insensitive to the direction of the magnetic field.

We estimate the magnetic susceptibility force in the present experiment. The magnetic susceptibility gradient will be generated by lysozyme concentration gradient at a diffusion layer between a lysozyme crystal interface and bulk solution. The magnetic susceptibility force works at the diffusion layer (Fig. 3 (a)). Generally the rate-determining step of the crystal growth is nucleation process. In a gravitational field, usually the process progresses in interface control. According to the growth of glycine crystals, a concentration gradient exists around a crystal, and its thickness of diffusion layer is reported to be 0.04 mm [8]. Since the concentration at the interface is very low, we put the concentration at nothing for simplification. The bulk concentration is assumed 25 mg/mL, according to the experimental condition. The thickness of the diffusion layer δ is estimated to be 1 mm. It is well known that this value varies significantly depending on reaction conditions. Probably the thickness value δ, 1 mm, will be very large, therefore nearly minimum value of the magnetic susceptibility force will be estimated. The volume susceptibility χ_v can be approximated by multiplying mass susceptibility χ by the concentration of the material,

$$\chi_v = \chi \cdot c\,. \tag{5}$$

Using eq. (5) the magnetic susceptibility gradient is described as follows,

$$\frac{d\chi_v}{dz} = \chi \frac{dc}{dz} \tag{6}$$

Since the concentration gradient at the diffusion layer is estimated to be 2.5 × 10^4 (kg/m^3)/m and the mass magnetic susceptibility of lysozyme is reported at -7.0 × 10^{-7} emu g^{-1} [9], the magnetic susceptibility gradient is estimated to be -2.20 × 10^{-4} m^{-1}.

Substituting eq. (6) into eq. (4) gives the following equation.

$$F_{MS} = \frac{1}{2}\mu_0 \chi \frac{dc}{dz} V H^2 \tag{7}$$

When the magnetic flux density is 15 T, the force per unit volume, F_{MS}/V, is estimated to be -1.97 × 10^4 N/m^3, that is, -1.97 × 10^{-2} N/cm^3. This force is enough to affect convection or transportation of solute in the solution, because this is comparable with gravity force on water (9.8 × 10^{-3} N/cm^3). Moreover, the direction of the force is determined by the sign of a magnetic susceptibility gradient, not the direction of the magnetic field. Therefore the isotropic force works on the crystal interface. Since the distribution of concentration gradient around a crystal nucleus is pseudo-spherical, the crystal will grow spherically (Fig. 3(b)).

We reported that three-dimensional silver dendrites produced via the reaction between silver ion and copper metal were drastically affected by the magnetic field. In the absence of the magnetic field, branches of metallic silver grew in dendrite with metallic color. In the presence of the magnetic field, dendrites are black in color and almost spherical in shape [10,11]. It was found that increasing in the yield and growing rate of the silver dendrite were mainly caused by a magnetic force on silver ion.

However, the reason of the morphology change was unclear. This morphology change will be based on the magnetic susceptibility force from the result of this paper.

3. Conclusions

The force caused by the magnetic susceptibility gradient affected the morphology of lysozyme crystal. The magnetic susceptibility force works generally at the interface between different phases or materials, *e.g.* solid/solid, solid/liquid, and so forth, even though the system only contains diamagnetic species. This shows the possibility of a new type of magnetic force.

Acknowledgements

This work was partially supported by Grant-In-Aid of Scientific Research for Priority Area (Area 767, No. 15085208 and 15085205) from MEXT of Japan, and Grant-in-Aid for Scientific Research (B), 16350007, 2004.

References

[1] W. Duan, M. Fujiwara, Y. Tanimoto, *In situ* observation of laser-induced convection of benzene solution of photochromic compound in high magnetic field, Jpn. J. Appl. Phys. 43, (2004) 8213-8216.

[2] F. Tang, A. Katsuki, Y. Tanimoto, Effect of High Magnetic Field on a Quasi-3D Silver Dendrite Growing System, Mol. Phys. *in press*.

[3] Y. Tanimoto, "Magneto-science: -Magnetic Fundamentals and Applications of Field Effects on Materials-," ed. by M. Yamaguchi and Y. Tanimoto, Kodansha/Springer, Tokyo, 2005, Chap. 2-4.

[4] G. Sazaki, E. Yoshida, H. Komatsu, T. Nakada, S. Miyashita, K. Watanabe, Effects of a magnetic field on the nucleation and growth of protein crystals, J. Crystal Growth 173, (1997) 231-234.

[5] M. Ataka, E. Katoh, N. I. Wakayama, Magnetic orientation as a tool to study the initial stage of crystallization of lysozyme, J. Crystal Growth 173, (1997) 592-596.

[6] J. P. Chopart, L. Rabah, J. Douglade, J. Amblard, f. Debray, A. Harrach, Comparison of magnetic forces acting on electrochemical systems, International Symposium on Magneto-Science Nov. 14-17 (2005) Yokohama, Japan.

[7] M. Uhlemann, A. Krause, A. Gebert, L. Schultz, The effect of magnetic fields on the electrodeposition of Cu and Co, International Symposium on Magneto-Science Nov. 14-17 (2005) Yokohama, Japan.

[8] M. Sueda, A. Katsuki, Y. Fujiwara, Y. Tanimoto, Influences of high magnetic field on the glycine crystal growth, Science and Technology of Advanced Materials, *submitted*.

[9] C. M. Sorensen, F. R. Fickett, R. C. Mockler, W. J. O'Sullivan, J. F. Scott, On lysozyme as a possible high-temperature superconductor, J.Phys. C: Solid State Phys. 9, (1976) L251-L254.

[10] A. Katsuki, I. Uechi, M. Fujiwara, Y. Tanimoto, High Magnetic Field Effect on the Growth of 3-Dimensional Silver Dendrites, Chem. Lett. (2002) 1186-1187.

[11] A. Katsuki, I. Uechi, Y. Tanimoto, Effects of a high magnetic field on the growth of 3-dimensional silver dendrites, Bull. Chem. Soc. Jpn. 77 (2004) 275-279.

Figure captions

Figure 1. The distribution of the vertical magnetic flux density $B(z)$ (solid line) and the product of magnetic flux density and the flux gradient, $(\mathrm{d}B(z)/\mathrm{d}z)B(z)$ (broken line). z is the distance from the center of the magnetic field (15 T) along the magnetic field axis. The dot lines show the area of the magnetic fields where the sample vessels were placed. These positions are called “top”, “middle”, and “bottom” from the top of the vertical bore in this paper.

Figure 2. The photographs of the lysozyme crystals. (a) the outside of the bore tube (control < 0.0005 T), (b) the top position (9.87 T, -1500 T^2/m), (c) the middle position (15.0 T, +50 T^2/m), (d) the bottom position (11.5 T, +1230 T^2/m). (a’) and (b’) are the enlargement of (a) and (b), respectively (× 2). White broken ring are reflection of illuminants.

Figure 3. Illustration of a magnetic susceptibility force at a diffusion layer (a) and growth of a round-shape crystal nucleus due to isotropic magnetic susceptibility force (b).

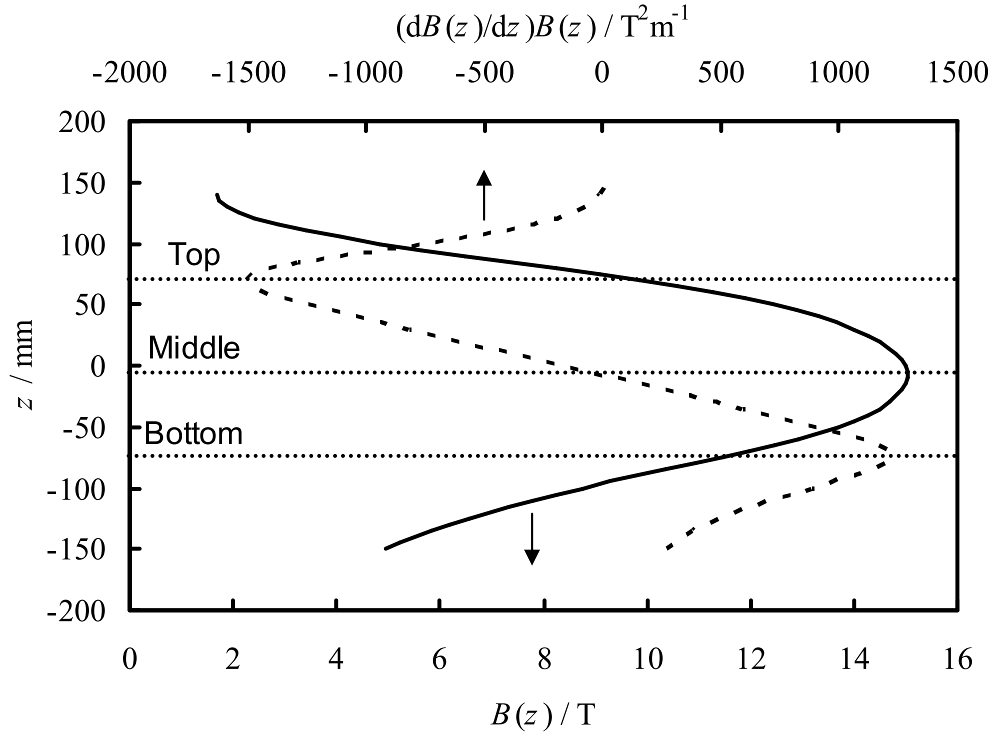

Fig. 1 A. Katsuki et al.

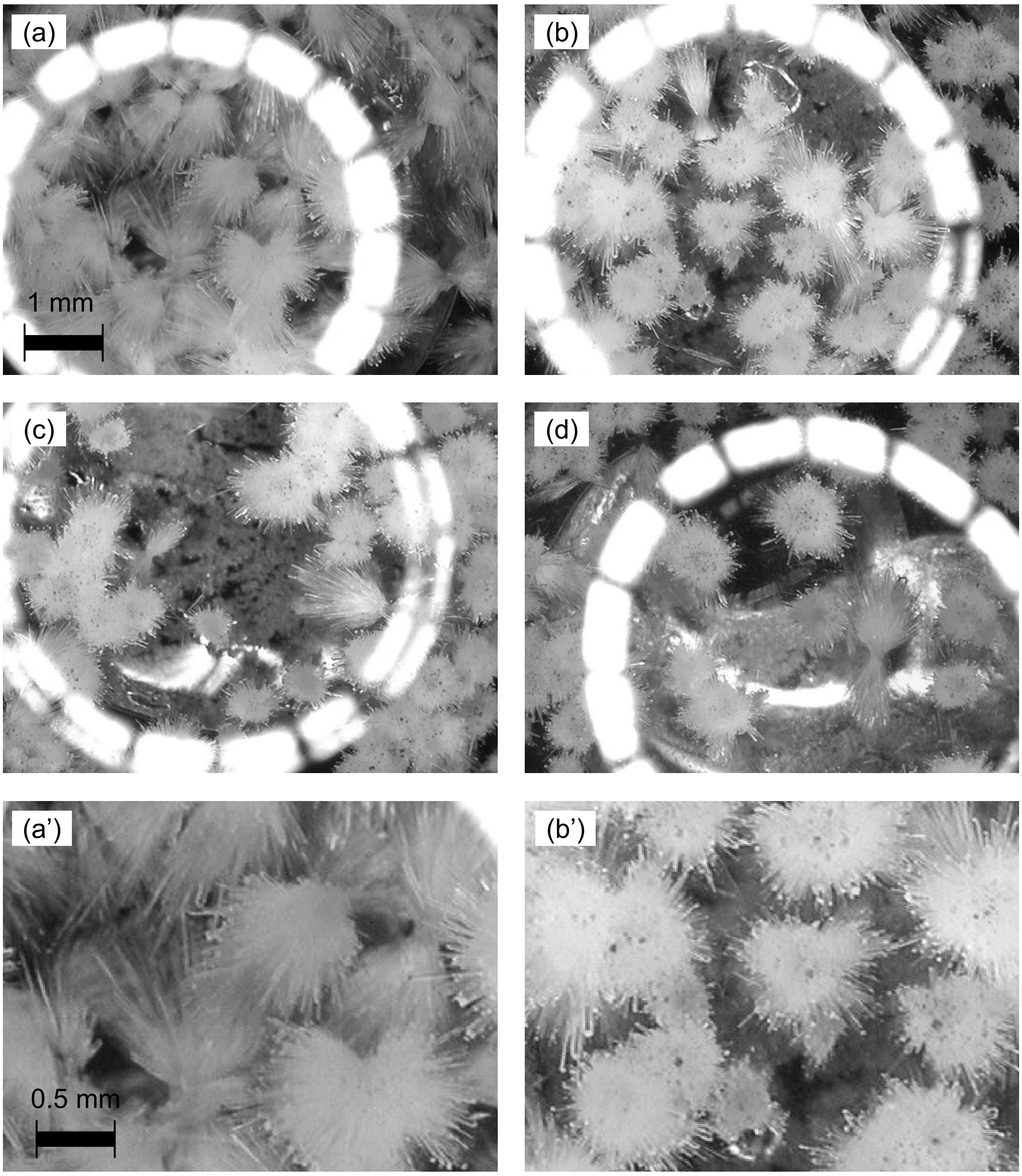

Fig. 2 A. Katsuki, et al.

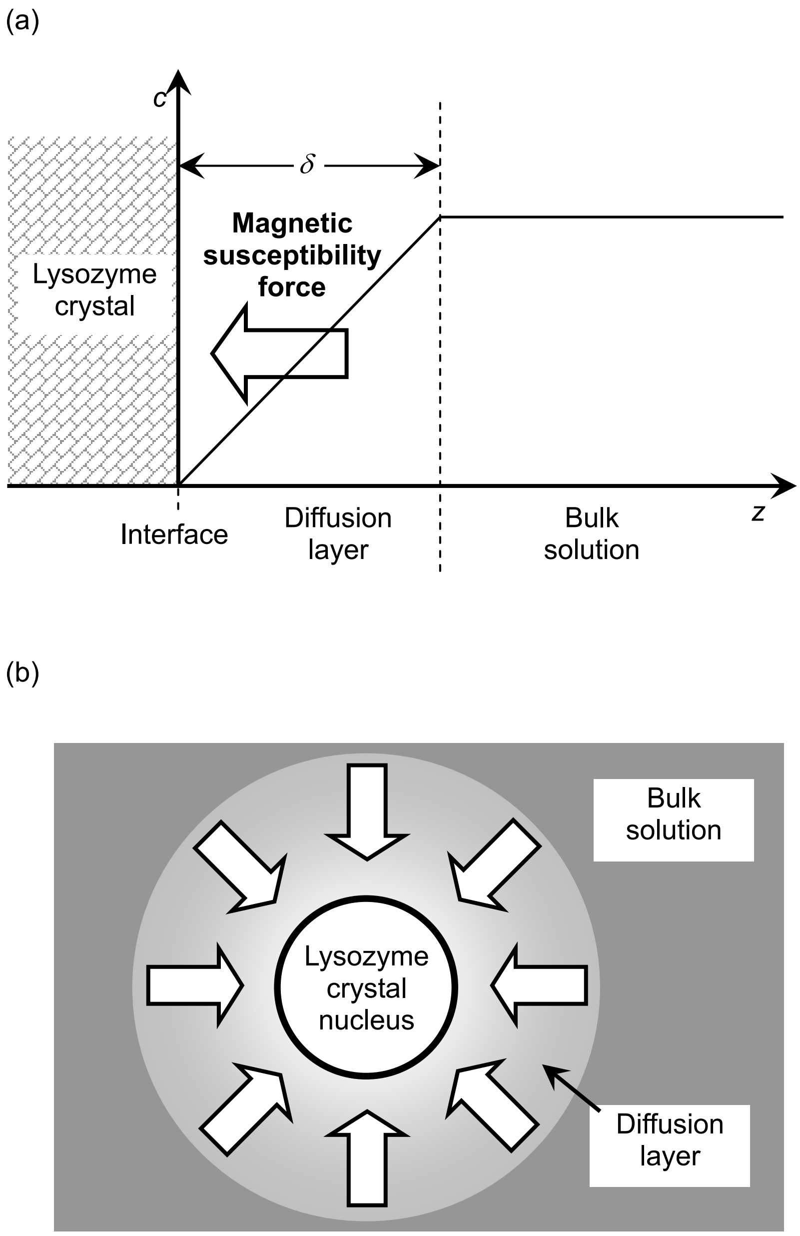

Fig. 3 A. Katsuki, et al.