

# Crystal Growth of Potassium Nitrate in a Magnetic Field of 80 kOe

M. Fujiwara, R. Tokunaga, and Y. Tanimoto\*

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526, Japan

Received: March 30, 1998

The crystal growth of  $\text{KNO}_3$  (diamagnetism) has been investigated in a magnetic field of 80 kOe. The crystallographic axes are determined by X-ray diffraction and compared with the magnetic axes. The crystals grow so that the magnetic  $\chi_a$  axis is perpendicular to the direction of the field. The orientation is explained by the magnetic susceptibility anisotropy ( $\chi_a < \chi_b \sim \chi_c$ ) of the crystals. Since the magnetic energy has a minimum when the  $\chi_a$  axis is perpendicular to the field, the crystals containing a considerable number of unit cells can be stabilized by rotating in this direction against thermal disordering.

## 1. Introduction

Aggregates of diamagnetic organic molecules, such as liquid crystals, crystals, and proteins, are known to be oriented in magnetic fields. The magnetic orientation is considered to take place by the magnetic susceptibility anisotropies. For liquid crystals, organic molecules that are magnetically anisotropic are arranged in orientational order, and the orientation in magnetic fields is characterized by the Freedericksz transition. Crystals of aromatic molecules have rigid and ordered structures that exhibit large magnetic anisotropies ( $>10^{-5} \text{ cm}^3 \text{ mol}^{-1}$ ) originating in benzene rings, and the orientation takes place on growth.<sup>1,2</sup> Proteins are giant molecules including  $\alpha$ -helix and  $\beta$ -sheet structures from which magnetic anisotropies are produced, and the orientation occurs on polymerization and crystallization.<sup>3–6</sup>

With respect to crystals of diamagnetic inorganic molecules, the orientation in magnetic fields has not been reported. Crystals of inorganic molecules have small magnetic anisotropies ( $\sim 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ ). However, when crystals grow large with a large number of molecules, the magnitude of the magnetic anisotropy energies becomes large, and the magnetic orientation is expected.

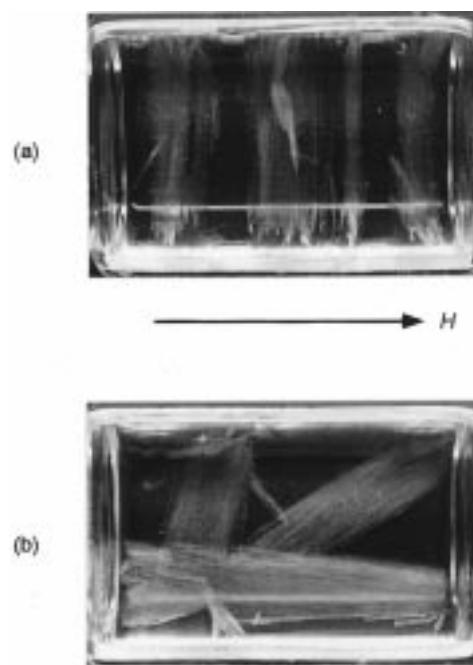
The present paper deals with the crystal growth of potassium nitrate (diamagnetism) in a magnetic field of 80 kOe. The magnetic orientation is observed. The crystallographic axes are determined by X-ray diffraction and compared with the magnetic axes. The relationship between the magnetic orientation and the magnetic axes is discussed.

## 2. Experimental Methods

$\text{KNO}_3$  (Nacalai Tesque, >99%) was dissolved in hot water to prepare  $3.2 \text{ mol dm}^{-3}$  solution. The crystals were obtained after the solution ( $10 \text{ cm}^3$ ) was allowed to stand in a glass cell ( $50 \times 35 \times 25 \text{ mm}$ ). The temperature of the cell was lowered from 313 to 278 K over 2 h by passing water from a circulator (Advantec LP-3100) around it.

The magnetic field of 80 kOe was applied by a superconducting magnet (Oxford Spectromag 1000). The field direction was horizontal.

The orientation of the crystals was followed by a fiberscope (Olympus R100-095-090-50) and a camera (Olympus SC35-



**Figure 1.** Photographs of  $\text{KNO}_3$  crystals growing in (a) 80 kOe and (b) zero fields for 2 h. Field direction is shown with an arrow.

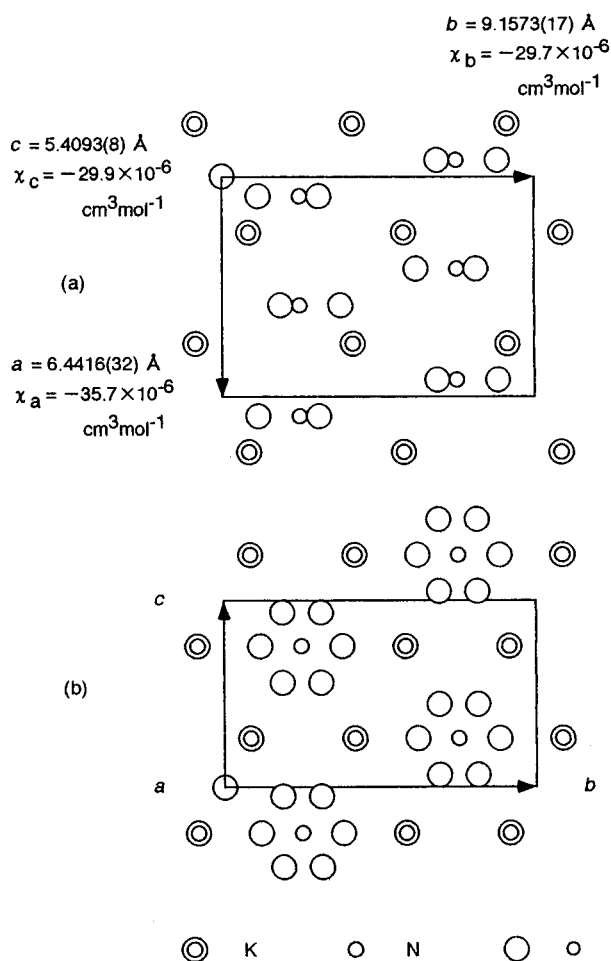
15) in the magnet and recorded by a camera (Nikon Nikomat FTN) after taking the glass cell out of the magnet.

The X-ray diffraction measurements were performed on a four-circle diffractometer (Mac Science MXC 3) with  $\text{Cu K}\alpha$  radiation ( $1.54178 \text{ \AA}$ ) at 293 K. The cell dimensions were determined by a least-squares analysis of 31 reflections. A single crystal ( $1.5 \times 0.6 \times 0.3 \text{ mm}$ ) was used for data collection.

## 3. Results

**3.1. Magnetic Orientation.** The  $\text{KNO}_3$  crystals, shown in Figure 1a, are obtained in a magnetic field of 80 kOe after standing for 2 h. The crystals are of a form of columns lying horizontal. The typical crystal dimensions are  $30 \times 2 \times 2 \text{ mm}$ . The crystals are oriented so that the direction of the growth is perpendicular to the direction of the field.

The growing process of the crystals is followed at 80 kOe. The crystals of lengths of 1 mm, which are at the limit of



**Figure 2.** Projections of molecular arrangement along orthorhombic (a) *c*- and (b) *a*-axes for  $\text{KNO}_3$  crystals.

observation in the present experiment, separate out perpendicularly to the direction of the field.

The crystals shown in Figure 1b are obtained in zero field. The crystal form and dimensions are the same as in the field of 80 kOe, but the crystals are oriented randomly.

**3.2. Crystallographic and Magnetic Axes.** The crystallographic axes are determined for the crystals growing in a magnetic field of 80 kOe. The crystal system is orthorhombic. The cell dimensions are  $a = 6.4416(32)$ ,  $b = 9.1573(17)$ , and  $c = 5.4093(8)$  Å with  $Z = 4$ . These data are in agreement with the previous ones of  $a = 6.4255$ ,  $b = 9.1709$ , and  $c = 5.4175$  Å with  $Z = 4$ .<sup>7</sup> The magnetic field is not found to affect the cell dimensions. With regard to the orientation of the crystals, the direction of the growth is the *a*-axis. The directions of the *b*- and *c*-axes in the field cannot be determined.

The magnetic susceptibilities are reported to be  $\chi_a = -35.6 \times 10^{-6}$ ,  $\chi_b = -29.7 \times 10^{-6}$ , and  $\chi_c = -29.9 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>.<sup>8,9</sup> After determination of the crystallographic axes, it is clear that the crystals are oriented as the  $\chi_a$  axis is perpendicular to the direction of the field.

## 4. Discussion

**4.1. Crystal Magnetic Anisotropy.** For the crystals of aromatic molecules, the magnetic anisotropy is considered to originate from arrangement of the benzene rings. In benzene (diamagnetism), the magnetic anisotropy is large; the susceptibility normal to its plane is much less than the susceptibilities in its plane ( $K_{\parallel} - K_{\perp} = 59.7 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>).<sup>10</sup> Thus, the

large magnetic anisotropy is observed for the organic crystals. For the crystals of inorganic molecules, which possess no benzene rings as their components, the origin of the magnetic anisotropy may be explained somewhat differently.

The structure of the  $\text{KNO}_3$  crystal is of space group *Pnam* and pseudo-hexagonal along the *a*-axis (see Figure 2).<sup>7</sup> The number of molecules in the unit cell is 4. The  $\text{NO}_3^-$  ion, which is a planar equilateral triangle with  $\text{N-O} \sim 1.21$  Å, is perpendicular to the *a*-axis. The data of the crystal structure suggest that the crystal is regarded as magnetically uniaxial along the *a*-axis and that the crystal susceptibilities  $\chi_b$  and  $\chi_c$  are equal. Furthermore, the ground-state configuration of the molecular orbitals of the  $\text{NO}_3^-$  ion, which has  $D_{3h}$  symmetry, is  $(4a_1')^2(1a_2'')^2(3e')^4(4e')^4(1e'')^4(1a_2'')^2$ .<sup>11,12</sup> The  $1a_2''$  orbital corresponds to the  $\pi$  bond between the N and O atoms. The  $1e''$  orbitals are lone pair orbitals of  $\pi$  symmetry on the O atoms. If the electrons on the  $1a_2''$  and  $1e''$  orbitals of the  $\text{NO}_3^-$  ion induce a diamagnetic current against the magnetic field perpendicular to its plane, and if the electrons on the  $\text{K}^+$  ion are oriented isotropically to contribute negligibly to the magnetic anisotropy, the susceptibility  $\chi_a$  normal to this plane will be less than that  $\chi_b$  or  $\chi_c$  in this plane. Thus, the susceptibilities are expected to bear a relation of  $\chi_a < \chi_b \sim \chi_c$ . The expectation is consistent with the data of the susceptibilities:  $\chi_a = -35.6 \times 10^{-6}$ ,  $\chi_b = -29.7 \times 10^{-6}$ , and  $\chi_c = -29.9 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>.<sup>8</sup> The susceptibilities parallel and perpendicular to the *a*-axis, i.e., the axis of magnetic symmetry, are given by  $\chi_{\parallel} = \chi_a = -35.6 \times 10^{-6}$ ,  $\chi_{\perp} = (\chi_b + \chi_c)/2 = -29.8 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>, respectively. In this way, the small magnetic anisotropy is explained to originate from the  $\text{NO}_3^-$  ion for the  $\text{KNO}_3$  crystal.

**4.2. Magnetic Anisotropy Energy.** Suppose a crystal is composed of *n* moles of molecules and has an axis *Z* of magnetic symmetry. When the crystal is placed in a magnetic field *H*, the magnetic anisotropy energy is expressed by

$$E(\theta) = -(n/2)[\chi_{\perp} + (\chi_{\parallel} - \chi_{\perp}) \cos^2 \theta] H^2$$

$\chi_{\parallel}$  and  $\chi_{\perp}$  are the molar magnetic susceptibilities parallel and perpendicular to the *Z*-axis, respectively.  $\theta$  is the angle between the *Z*-axis and the *H*-direction. If  $\chi_{\parallel} < \chi_{\perp}$ , the magnetic energy  $E(\theta)$  has a minimum value and the crystal is stabilized when the *Z*-axis is perpendicular to the *H*-direction ( $\theta = \pi/2$ ). As the crystal grows larger with a larger *n* value, the difference of the magnetic energies  $E(\theta) - E(\pi/2)$  between any direction ( $\theta$ ) and the direction perpendicular to the field ( $\theta = \pi/2$ ) becomes larger. When the difference of the magnetic energies exceeds the thermal energy, the crystal will be oriented so that the *Z*-axis is perpendicular to the *H*-direction.

Owing to gravity, the  $\text{KNO}_3$  crystals grow horizontal; the *a*-axis, which is the axis of magnetic symmetry, lies horizontal. Since the direction of the magnetic field is horizontal, this enables the field to affect the direction of the *a*-axis. From the relation of  $\chi_{\parallel} < \chi_{\perp}$ , the magnetic energy is a minimum and the crystals are stable when the *a*-axis is perpendicular to the direction of the field. The present observation shows that the crystals are oriented to satisfy the requirement of the magnetic energy. The difference of the magnetic energies between the directions parallel ( $\theta = 0$ ) and perpendicular ( $\theta = \pi/2$ ) to the field at 80 kOe is calculated to be  $1.9 \times 10^{-3}$  J mol<sup>-1</sup>. The thermal energy at 278 K is  $3.8 \times 10^{-21}$  J. Since the unit cell contains four molecules, the number of the unit cells required for the orientation of the crystals against thermal disordering can be estimated to be  $> 3.1 \times 10^5$ .

**4.3. Comparison with Organic Crystals.** The orientation of the benzophenone<sup>1a</sup> and *trans*-azobenzene<sup>1b</sup> crystals has been found in the magnetic field of 80 kOe.

For the benzophenone crystals, the crystal system is orthorhombic. The magnetic susceptibilities are  $\chi_a = -88.0 \times 10^{-6}$ ,  $\chi_b = -88.6 \times 10^{-6}$ , and  $\chi_c = -149.3 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .<sup>13</sup> The crystals are columns elongated along the *c*-axis. The crystals grow so that the *c*-axis is perpendicular to the direction of the field. The directions of the *a*- and *b*-axes in the field are not determined. Since  $\chi_c < \chi_a \sim \chi_b$ , the magnetic energy has a minimum and the crystals are stabilized when the *c*-axis is perpendicular to the field. Thus, the magnetic orientation is explained to result from stabilization by minimization of the magnetic energy. The difference of  $61.0 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  between the susceptibilities  $\chi_c$  and  $\chi_a \sim \chi_b$  for the benzophenone crystals is 1 order of magnitude larger than that of  $5.8 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  between the susceptibilities  $\chi_a$  and  $\chi_b \sim \chi_c$  for the KNO<sub>3</sub> crystals. The larger magnetic anisotropy for the benzophenone crystals originates from existence of the benzene rings. The orientation may be easier for the benzophenone crystals than for the KNO<sub>3</sub> crystals.

For the *trans*-azobenzene crystals, the crystal system is monoclinic. The magnetic susceptibilities are  $\chi_1 = -87.5 \times 10^{-6}$ ,  $\chi_2 = -130.2 \times 10^{-6}$ , and  $\chi_3 = -83.1 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .<sup>13</sup> The crystals are tabular rhombuses, the rhombic planes corresponding to the  $\chi_1\chi_3$  plane and the diagonal lines that bisect the obtuse angles of the rhombuses parallel to the  $\chi_3$ -axis. The crystals are oriented as the  $\chi_3$ -axis is parallel to the direction of the field. From  $\chi_2 < \chi_1 < \chi_3$ , the magnetic energy is a minimum and the crystals are stable when the  $\chi_3$ -axis is parallel to the field. The magnetic orientation is explained in terms of the magnetic energy. The difference of  $4.4 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  between the susceptibilities  $\chi_1$  and  $\chi_3$  for the *trans*-azobenzene crystals is similar to that between the susceptibilities  $\chi_a$  and  $\chi_b \sim \chi_c$  for the KNO<sub>3</sub> crystals. The relatively small magnetic anisotropy between  $\chi_1$  and  $\chi_3$  for the *trans*-azobenzene crystals results from the fact that the benzene rings occupy a larger area on the projection along the  $\chi_2$ -axis than along the  $\chi_1$ - or  $\chi_3$ -axis. The *trans*-azobenzene and KNO<sub>3</sub> crystals may be oriented when they grow to contain a similar number of molecules.

## 5. Conclusion

The KNO<sub>3</sub> crystals grow as the magnetic *a*-axis is perpendicular to the direction of the magnetic field. The orientation is explained by the magnetic anisotropy ( $\chi_a < \chi_b \sim \chi_c$ ) of the crystals. Since the anisotropy energy is a minimum when the *a*-axis is perpendicular to the field, the crystals containing a considerable number of unit cells are stabilized by rotating in this direction against thermal disordering.

**Acknowledgment.** The authors thank Prof. K. Akiba, Dr. Y. Yamamoto, and Dr. M. Minoura for the use of the four-circle diffractometer and Dr. A. Katsuki for the discussion on the crystallographic axes. The work was supported partly by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture (07NP0101, 09874157) and from the Iwatani Naoji Foundation.

## References and Notes

- (1) (a) Katsuki, A.; Tokunaga, R.; Watanabe, S.; Tanimoto, Y. *Chem. Lett.* **1996**, 607. (b) Fujiwara, M.; Chidiwa, T.; Tokunaga, R.; Tanimoto, Y. *J. Phys. Chem. B* **1998**, 102, 3417.
- (2) Tsuboi, Y.; Akita, H.; Yamada, K.; Itaya, A. *Jpn. J. Appl. Phys.* **1997**, 36, 1048.
- (3) Torbet, J. *Biochemistry* **1986**, 25, 5309.
- (4) Yamagishi, A.; Takeuchi, T.; Higashi, T.; Date, M. *Physica B* **1990**, 164, 222.
- (5) Sazaki, G.; Yoshida, E.; Komatsu, H.; Nakada, T.; Miyashita, S.; Watanabe, K. *J. Cryst. Growth* **1997**, 173, 231.
- (6) Ataka, M.; Katoh, E.; Wakayama, N. I. *J. Cryst. Growth* **1997**, 173, 592.
- (7) Wyckoff, R. W. G. *Crystal Structures*; John Wiley & Sons: New York, 1964; Vol. 2, Chapter VIIA.
- (8) Krishnan, K. S.; Raman, C. V. *Proc. R. Soc. London* **1927**, A115, 549.
- (9) The present unit cell is chosen differently from that of the magnetic data;<sup>8</sup> the present *a*- and *c*-axes correspond, respectively, to the *c*- and *a*-axes of the magnetic data.
- (10) Gupta, R. R. *Landolt-Börnstein*; Hellwege, K.-H., Hellwege, A. W., Eds.; Springer-Verlag: Berlin, Heidelberg, 1986; Vol. II/16, Chapter 8.
- (11) Harris, L. E. *J. Chem. Phys.* **1973**, 58, 5615.
- (12) Loew, L. M.; MacArthur, W. R. *J. Am. Chem. Soc.* **1977**, 99, 1019.
- (13) Krishnan, K. S.; Guha, B. C.; Banerjee, S. *Philos. Trans. R. Soc. London* **1933**, A231, 235.