

Magnetic Orientation of Benzophenone Crystals in Fields up to 80.0 KOe

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The magnetic orientation of benzophenone crystals (diamagnetism) has been studied in various intensities of fields (0.0–80.0 kOe). As the field intensity is increased, the proportion of oriented crystals increases. The orientation is found to follow the Boltzmann distribution for crystals possessing different magnetic energies.

1. Introduction

Aggregates of diamagnetic molecules with ordered structures, such as liquid crystals, crystals,^{1–3} and polymers,^{4,5} are known to be oriented in magnetic fields. The magnetic orientation is believed to take place by the susceptibility anisotropies. When aggregates are formed by arrangement of anisotropic molecules, the magnetic energies are explained to become large enough for them to be oriented against the thermal disordering.

However, there have been only a few reports^{4,5} that clarify quantitatively the relationship between the magnetic and thermal energies in the orientation. To know the roles of the magnetic and thermal energies, the distribution of the directions of aggregates must be analyzed in various magnetic–thermal conditions.

The present work investigates the crystal growth of benzophenone (diamagnetism) in various intensities of magnetic fields. As the field intensity is increased, the probability that crystals are oriented becomes higher and the distribution of crystals near the orientation becomes sharper. The phenomenon is interpreted as the Boltzmann distribution for crystals possessing different magnetic energies.

2. Theory

Suppose a crystal is composed of a mole number n of molecules and has an axis Z of magnetic symmetry (see Figure 1). When the crystal is placed in a magnetic field H , the magnetic anisotropy energy is expressed by

$$E(\theta, H) = -(n/2)[\chi_{\perp} + (\chi_{\parallel} - \chi_{\perp}) \cos^2 \theta]H^2 \quad (1)$$

where θ is the angle between the axis Z and the field H and χ_{\parallel} and χ_{\perp} are the molar magnetic susceptibilities parallel and perpendicular to the axis Z , respectively. For a crystal bearing a relation of $\chi_{\parallel} < \chi_{\perp}$, the anisotropy energy $E(\theta, H)$ has a minimum value and the crystal is stabilized when the axis Z is perpendicular to the field H ($\theta = \pi/2$). As the crystal grows larger with a larger value of the mole number n , the difference of the magnetic energies $E(\theta, H) - E(\pi/2, H)$ between any direction (θ) 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 axis Z is perpendicular to the field H .

The simple case is one in which both the axis Z and the field H are restricted in a given plane such as the horizontal plane. In this instance, the axis Z moves in the two-dimensional space and the degree of freedom is 1 for the crystal direction, which

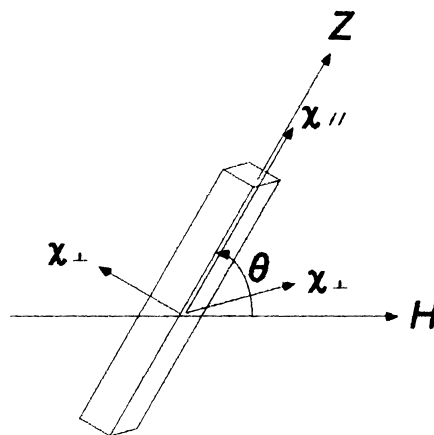


Figure 1. Diagram of a crystal possessing an axis Z of magnetic symmetry in an external magnetic field H . Susceptibilities χ_{\parallel} and χ_{\perp} are ones parallel and perpendicular to an axis Z , respectively. An angle θ is measured between an axis Z and a field H .

is represented by the angle θ . The energy $E(\theta, H)$ is a continuous function of the variable θ . The crystal direction follows the Boltzmann statistics and the probability that the crystal exists between the angles θ and $\theta + d\theta$ at the temperature T is written as

$$P(\theta, H) d\theta = \frac{\exp[-E(\theta, H)/kT] d\theta}{\int_0^{\pi} \exp[-E(\theta, H)/kT] d\theta} \quad (2)$$

with k being the Boltzmann constant.

The order parameter in the two-dimensional space is given by

$$S(H) = \int_0^{\pi} [2 \cos^2(\theta - \pi/2) - 1] P(\theta, H) d\theta \quad (3)$$

The order parameter is equal to 1 when all the crystals take the orientation perpendicular to the field H ($\theta = \pi/2$). It is -1 when all the crystals have the orientation parallel to the field H ($\theta = 0, \pi$). It becomes 0 for the random orientation.

The experiment measures the probability $P(\theta, H)$ that the crystal is directed to the angle θ at the field H . Then, the simulation of the experimental results is made using eqs 1 and 2 as functions of the variables θ and H . The parameter n is the only one involved in eqs 1 and 2 and is to be determined by the simulation. The order parameter $S(H)$ is calculated using eq 3, after the probability $P(\theta, H)$ is obtained by the experiment or simulation.

3. Experiment

Benzophenone (Tokyo Chemical, >99.0%) was dissolved in hot *n*-hexane (Nacalai Tesque, >96.0%) to prepare 0.50 mol dm⁻³ solution. The crystals (~80 pieces) grew after the solution (10 cm³) was allowed to stand in a glass vessel (50 mm length × 35 mm width × 25 mm height) for 5 h. The temperature of the glass vessel was kept at 281 K by passing water from a circulator (Advantec LP-3100) around it.

The magnetic fields up to 80.0 kOe were applied by a superconducting magnet (Oxford Spectromag 1000). The field direction was horizontal.

While the crystals were growing, the orientation was followed with a fiberscope (Olympus R100-095-090-50) and a camera (Olympus SC35-15) in the magnet. The spatial resolution of the fiberscope was ~1 mm.

After the crystals had grown, the orientation was recorded with a camera (Nikon Nikomat FTN) by taking the glass vessel out of the magnet. The angle between the growth and field directions was measured on the photograph. The angle measurement was performed for 300–500 crystals at each field intensity.

For the crystals that completed the growth, were mobile, and were directed randomly, the effect of the magnetic field on the direction was examined. The crystals obtained in zero field were picked up from the saturated solution and placed in the glass vessel along with the filtered solution. Then, the magnetic field was applied to the crystals and the change of the direction was observed with the fiberscope in situ.

4. Results

4.1. Orientation of Crystals in Magnetic Fields. The orientation was recorded for the benzophenone crystals that had grown in a 80.0 kOe magnetic field. As shown in Figure 2a, the crystals are column-shaped with dimensions of ~10 × 1 × 1 mm and fixed to each other, to the wall, and to the bottom in the glass vessel. They lie horizontal to be oriented so that the *c* axis is perpendicular to the field (see below).^{1a}

The crystals, in Figure 2b, were obtained in a 4.8 kOe field. The crystals are partially oriented as the *c* axis is perpendicular to the field.

The crystals, in Figure 2c, were obtained in zero field. The crystals are directed randomly.

The growing process of the crystals was followed in a 80.0 kOe field. The crystals with length of ~1 mm, which were at the limit of observation, precipitated with the *c* axis perpendicular to the field.

The change of the crystal directions by the effect of a 80.0 kOe magnetic field was followed for the mobile and randomly directed crystals that were obtained in zero field, separated from the saturated solution, and placed in the glass vessel with the filtered solution. On application of the field, the crystals rotated on the bottom of the glass vessel in the direction that the *c* axis was perpendicular to the field.

The crystallographic data have shown that the cell dimensions are *a* = 10.30, *b* = 12.15, and *c* = 8.00 Å and that the space group is *P*2₁2₁2₁ with *Z* = 4.⁶ By the X-ray diffraction measurement of the crystals growing in a 80.0 kOe field, the cell dimensions have been found to be the same as the reported ones and the direction of the growth has been identified as the *c* axis.^{1a} It is shown that the crystals grow so that the *c* axis is perpendicular to the field. The direction of the *a* or *b* axis in the field cannot be distinguished.

The magnetic susceptibilities have been reported to be $\chi_a = -88.0 \times 10^{-6}$, $\chi_b = -88.6 \times 10^{-6}$, and $\chi_c = -149.3 \times 10^{-6}$ cm³ mol⁻¹.^{7,8} The susceptibilities parallel and perpendicular to

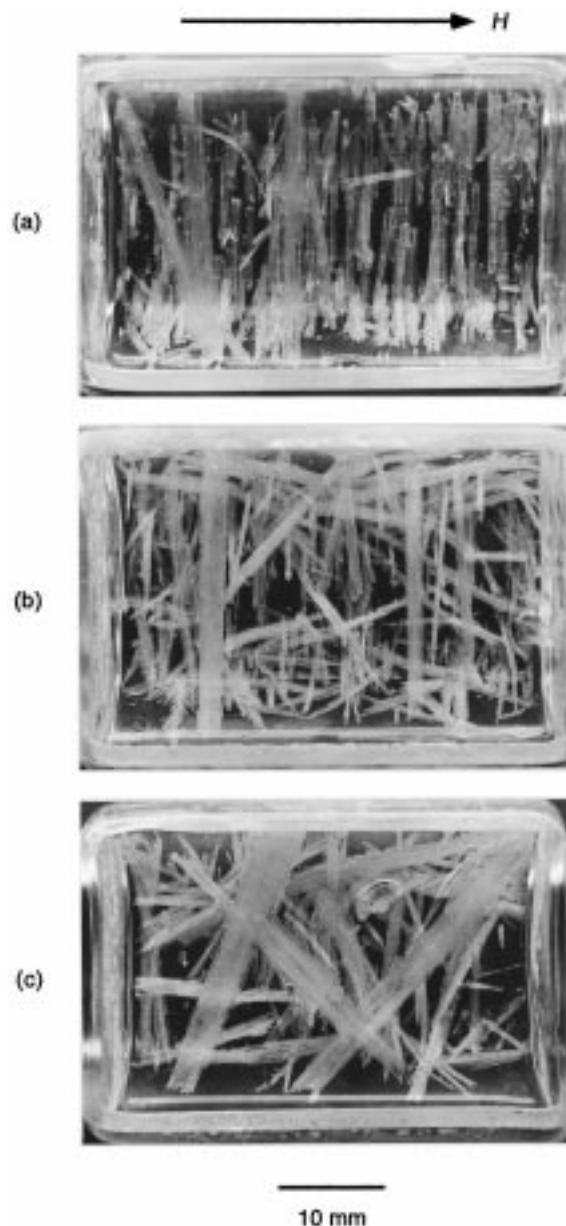


Figure 2. Photographs (top views) of benzophenone crystals growing in magnetic fields. Field direction is shown with an arrow. Field intensity (kOe): (a) 80.0; (b) 4.8; (c) 0.0.

the *c* axis, i.e., the axis of magnetic symmetry, are given by $\chi_{||} = \chi_c = -149.3 \times 10^{-6}$ and $\chi_{\perp} = (\chi_a + \chi_b)/2 = -88.3 \times 10^{-6}$ cm³ mol⁻¹. Since the relation of $\chi_{||} < \chi_{\perp}$ holds, the magnetic energy is a minimum and the crystals are stable when the *c* axis is perpendicular to the field ($\theta = \pi/2$). Thus, the magnetic orientation is explained qualitatively by the magnetic energy.^{1a}

4.2. Distribution of Directions of Crystals in Magnetic Fields. The benzophenone crystals were obtained at various intensities (0.0–80.0 kOe) of magnetic fields. The quantity of the precipitating crystals did not vary with the field intensity. The crystal form or dimensions did not change either. Only the proportion of the oriented crystals depended upon the field intensity.

The distribution of the angles of the crystallographic *c* axis in magnetic fields is shown in Figure 3. At zero field, the directions of the crystals are random. On increasing the field intensity, the fraction of the crystals oriented perpendicularly to the field ($\theta = \pi/2$) increases and the width of the distribution near the perpendicular orientation narrows. At a 38.0 kOe field,

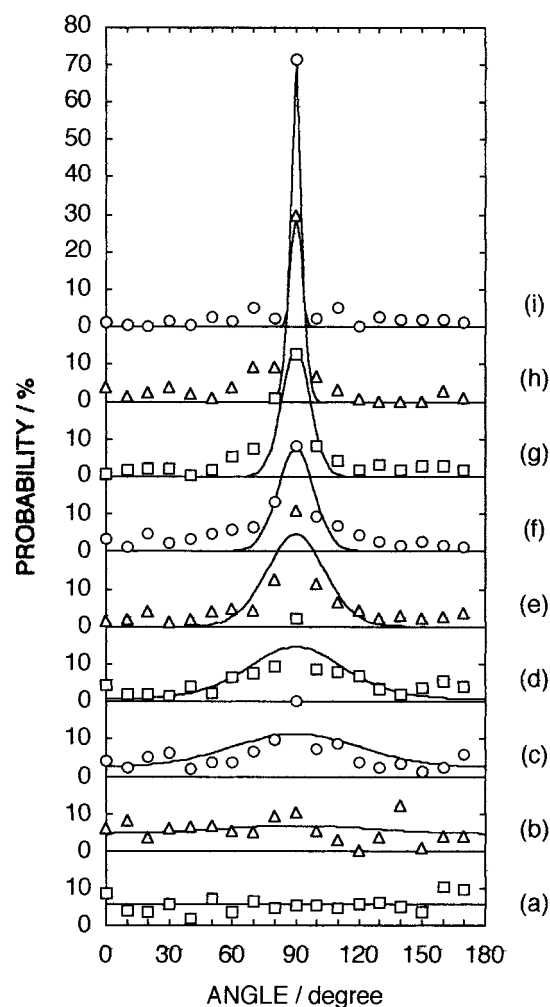


Figure 3. Observed (circles, triangles, squares) and calculated (curves) distribution charts for directions of benzophenone crystals in magnetic fields. An abscissa represents an angle between a crystallographic c axis and a field. An ordinate shows the proportion (in percent) of crystals directed to each angle. Field intensity (kOe): (a) 0.0; (b) 1.0; (c) 1.9; (d) 2.9; (e) 4.8; (f) 7.7; (g) 9.6; (h) 19.0; (i) 38.0.

most of the crystals are oriented perpendicularly to the field. To simulate the angle distribution, the calculation was made with the mole number n of molecules treated as a parameter. The calculated distribution is also shown in Figure 3, where $n = (4.9 \pm 2.2) \times 10^{-16}$ mol corresponds to 7.4×10^7 unit cells. Simulation reproduces the experimental results well, showing that the magnetic orientation is governed by the Boltzmann distribution.

The order parameter for the orientation of the crystals in magnetic fields is given in Figure 4. The order parameter increases from 0.0 at zero field to ~ 1.0 at a 10.0 kOe field. It does not change above a 10.0 kOe field. The calculated order parameters are also given in Figure 4. The calculation describes the experimental results, when the direction of a crystal containing 7.4×10^7 unit cells is assumed to be affected by fields. The calculation does not fit the experimental results, when 7.4×10^6 or 7.4×10^8 unit cells are assumed to be required for the effect of fields. It is inferred that the estimate of the number of unit cells of 7.4×10^7 is suitable.

5. Discussion

5.1. Movement of a Crystal in a Two-Dimensional Plane.

The model assumes that a crystal of given dimensions is placed

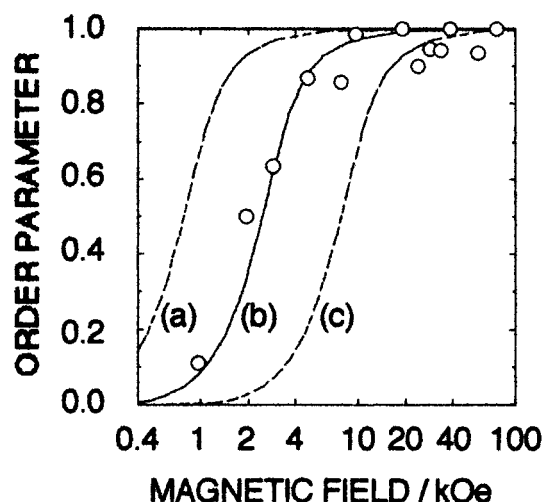


Figure 4. Observed (circles) and calculated (curves) order parameters for orientation of benzophenone crystals in magnetic fields. Assumed number of unit cells in a crystal: (a) 7.4×10^8 ; (b) 7.4×10^7 ; (c) 7.4×10^6 .

in a two-dimensional plane and affected by a magnetic field H . The direction of the crystal is specified by a rotation angle θ around the axis perpendicular to that plane. Then, the magnetic energy is a function of the variables θ and H . Experimentally, the crystal is column-shaped and lies horizontal on the bottom of the glass vessel owing to gravity. Moreover, the mobile and randomly directed crystal rotates to be oriented on the bottom of the glass vessel, when it is affected by a 80.0 kOe field. Therefore, the assumption of movement in the two-dimensional plane seems to be reasonable. The crystal of dimensions smaller than $\sim 1.9 \times 0.2 \times 0.2 \mu\text{m}$ (see section 5.4) will rotate by the thermal and magnetic energies, while it is in solution and after it settles to the bottom of the glass vessel.

5.2. Distribution of Directions of Crystals. The magnetic energy is minimized and a crystal is stabilized for the direction where it is perpendicular to the field ($\theta = \pi/2$). However, while the crystal is small, the difference of the magnetic energies between any direction (θ) and the stable direction ($\theta = \pi/2$) is small and the orientation is disordered to be random by the thermal energy. As the crystal grows larger, the difference of the magnetic energies becomes larger and the probability is higher that it is oriented in the stable direction. If thermal equilibrium is maintained during the growth, the probability that the crystal is directed to any direction follows the Boltzmann statistics. The calculation reproduces the observed distribution of the directions of the crystals. This justifies the model that the orientation is governed by the Boltzmann distribution for the crystals possessing different magnetic energies.

5.3. Cessation of Rotation of a Crystal. Since the magnetic energy is proportional to the dimensions of a crystal, the probability that it is oriented perpendicularly to the field ($\theta = \pi/2$) increases as it grows larger. The crystal would be oriented perfectly even at a low field intensity if it continued to grow. However, the experiment shows that the distribution of the crystals near the perpendicular orientation has a width, which is reproduced by the calculation. This implies that the rotation is interrupted and the direction is frozen for the crystal while it is growing on the bottom of the glass vessel. Indeed, the observation is that the crystal is fixed after the growth is completed. What begins to make the crystal with dimensions of $\sim 1.9 \times 0.2 \times 0.2 \mu\text{m}$ (see section 5.4) fixed in the course of the growth cannot be determined at present. Adhesion by an

increase of friction to the neighboring crystals or to the bottom in the glass vessel may stop the rotation during the growth.

In this relation, it is notable to refer to a recent discussion on the orientation and sedimentation of a lysozyme crystal growing for 24 h.³ When the protein solution was placed in a 16 kOe field for 8 h immediately after preparation, 68% of the crystals were oriented. For the protein solution placed in a 16 kOe field after standing in zero field for 8 h, only 14% of the crystals were oriented. From these results, the protein crystal was suggested to be first affected by the magnetic field in solution and to be then fixed after sedimentation. The protein crystal may be fixed, due to its stickiness, by contact with the bottom of the glass vessel.

5.4. Crystal Dimensions and a Susceptibility Anisotropy Required for Orientation. The model requires that a certain number of unit cells must assemble for the direction of a crystal to be affected by a magnetic field against the disordering by the thermal motion. The model does not allow for variation of dimensions among crystals. The number of unit cells is estimated to be 7.4×10^7 by fitting the experimental results with the Boltzmann distribution. The value is considered to be one when the crystal is fixed on the bottom of the glass vessel, and corresponds to crystal dimensions of $\sim 1.9 \times 0.2 \times 0.2 \mu\text{m}$ and a susceptibility anisotropy $n |\chi_{\parallel} - \chi_{\perp}|$ of $3.0 \times 10^{-20} \text{ cm}^3 \text{ crystal}^{-1}$.

An alternative estimate for the number of unit cells of 3×10^4 has been made, by setting the difference between the maximum ($\theta = 0$) and minimum ($\theta = \pi/2$) for the magnetic energies at 80.0 kOe to be equal to the thermal energy at 282 K.^{1a} However, when the difference of the magnetic energies is equal to the thermal energy, the ratio of the probabilities that the crystal takes the unstable ($\theta = 0$) and stable ($\theta = \pi/2$) directions is 1/e. Such distribution is observed at ~ 1.9 kOe (Figure 3c), and most of the crystals are found to be oriented in the stable direction at 38.0 kOe (Figure 3i). Hence, the value of the number of unit cells obtained in this way is much underestimated.

The magnetic orientation was investigated for erythrocyte and platelet cells in fields up to 80 kOe.^{5b} Erythrocyte and platelet cells are of an oblate shape. The susceptibility anisotropy for

an erythrocyte cell was estimated to be $8.2 \times 10^{-22} \text{ cm}^3 \text{ cell}^{-1}$ and that for a platelet cell to be $1.2 \times 10^{-21} \text{ cm}^3 \text{ cell}^{-1}$.⁹ The order parameters for erythrocyte and platelet cells were found to become ~ 1.0 at a 40 kOe field. The susceptibility anisotropy of $3.0 \times 10^{-20} \text{ cm}^3 \text{ crystal}^{-1}$ for the benzophenone crystal is 1–2 orders of magnitude larger than the anisotropies for the erythrocyte and platelet cells. The difference of the magnitude of the susceptibility anisotropies may explain the difference of the degrees of the orientation. The order parameter for the crystal becomes ~ 1.0 at a 10.0 kOe field, whereas the blood cells are only partially oriented at the same field intensity.

6. Conclusion

The proportion of benzophenone crystals oriented magnetically depends on the field intensity. The orientation follows the Boltzmann distribution for crystals having different magnetic energies.

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- (9) A term "cell⁻¹" means "per erythrocyte cell" or "per platelet cell".