Alignment of nonmagnetic solid grains that essentially require high magnetic field; alignment of hexagonal ice $I_h$

C Uyeda and T Abe
Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan, E-mail: uyeda@ess.sci.osaka-u.ac.jp

Abstract. Minimum field intensity required to achieve alignment of solid grains, which possess small diamagnetic anisotropy ($\chi_{\text{DIA}}$), is discussed based on observed values of hexagonal ice $I_h$; the field intensity is about 6 Tesla at $T = 273K$ for ice $I_h$ crystal with 1.0 $\mu$m in diameter. Grain alignment essentially require strong magnetic field above several Tesla when $\chi_{\text{DIA}}$ is in the level of $10^{-10}$ emu/g. $\chi_{\text{DIA}}$ arises from preferential orientation of individual chemical bond with respect to a magnetic principle axis of the solid body. Hence $\chi_{\text{DIA}}$ is negligibly small for materials with high crystal symmetry, such as crystals having a rutile, wurtzite or perovskite structure. Alignment should be studied intensively in high magnetic-field for these types of materials. Whereas alignment occurs below $B = 2T$ for most of the unmeasured diamagnetic crystals with lower symmetry, since their $\chi_{\text{DIA}}$ values are expected to exceed $1 \times 10^{-9}$ emu/g according to the above-mentioned model; this field is produced by an ordinary electromagnet.

1. Introduction
It is generally accepted that magnetically stable axes of micron-sized particles, dispersed in a fluid medium at temperature $T$, align almost parallel to $B$ when an anisotropy energy $(1/2)M\Delta\chi B^2$ induced in the particle is one order of magnitude larger compared to the energy of Brownian motion $(1/2)k_B T$ [1], according to a mechanism proposed by Langevin and Curie [2]; here $M$ and $\Delta\chi$ denote the weight and magnetic anisotropy of the particle, respectively. Considerations were often neglected on the minimum field intensity required to achieve alignment; the alignments were usually studied at field intensities above several Tesla [1,2]. This was because the magnitude of $\Delta\chi$ value was not discussed quantitatively for most of the materials; the magnitude was considered to range below the detection limit. Consequently, magnetic effects due to $\Delta\chi$ are investigated for a limited number of materials. Relationship between degree of grain alignment and field intensity were studied previously on some materials, such as on liquid crystal molecules [1], blood cells [3], mica and clay minerals [4], agalose [5], lythozyme crystal [6] or graphite grains [7]. The relationships were obtained for the first time on inorganic materials by measuring various ceramic materials [4] such as talc, kaotinite and muscovite as well as graphite grains [7]; it was pointed out that minimum field intensity required to achieve alignment can be calculated prior to the measurement provided that the numerical values are given for three parameters, namely for $\Delta\chi$, $M$ and $T$ [3,4,7].

Small $(\Delta\chi)_{\text{DIA}}$ values of inorganic oxide were accumulated effectively by introducing a simple setup to measure $\Delta\chi$ [8]. $(\Delta\chi)_{\text{DIA}}$ was obtained for oxides with different types of crystal structure such as corundum, forsterite, KDP, gypsum, muscovite, talc, Mg(OH)$_2$ and AlOOH [7]. The values ranged between $10^{-7}$ and $10^{-9}$ emu/g, which indicated that most of the unmeasured materials posses similar amount of $(\Delta\chi)_{\text{DIA}}$ value. Almost full alignment is expected below 2 Tesla for micron-sized grains at room temperature when $\Delta\chi$ is above $1 \times 10^{-9}$ emu/g [7] according to the above mentioned analysis.
Origin of published \( \Delta \chi \) values was discussed for the inorganic oxides [7]. The \( \Delta \chi \) values were explained quantitatively by assigning a constant uniaxial \( \Delta \chi \) tensor to the individual bond orbital [9]. The anisotropy assigned to a single bond had the order of \( 10^{-30} \) emu with its magnetically unstable axis being parallel to bond direction. This assignment was compatible with the fact that a spatial electron distribution is spread preferentially in the direction perpendicular to the bond direction. It is deduced from the above mentioned model that \( \Delta \chi \) should be negligibly small for materials which have high crystal symmetry. In the case of hexagonal ice \( I_h \) that have a structure similar to that of a wurtzite crystal, the tetrahedral configuration in the crystal hold regular symmetry, so that the \( \Delta \chi \) tensors of individual bonds in a unit cell cancel out. However, finite amount of \( \Delta \chi \) was reported previously on ice \( I_h \) [10]. The value was \( 3.3 \times 10^{-9} \) emu/g which was an order of magnitude smaller compared to other inorganic materials; it was concluded at that time that the small \( \Delta \chi \) value derived from its high crystal symmetry.

\( T \)-\( \Delta \chi \) measurement of ice \( I_h \) below \( T = 273K \) is realized in the present work, in order to determine the exact \( \Delta \chi \) by excluding the contribution of paramagnetic anisotropy \( \Delta \chi_{\text{PARA}} \). The above-mentioned published value of ice \( I_h \) was considerably small, which can be easily altered by \( \Delta \chi \) caused by a small amount of impurity ions. It is shown that a exact \( \Delta \chi \) value is essential in understanding the driving force of an alignment process in high magnetic fields.

2. Experimental Procedure and Measured Results

A setup was developed to measure \( \Delta \chi \) - \( T \) relationship of ice \( I_h \) in the low temperature regions [12]. A sample was suspended inside a copper cell contained with \( N_2 \) gas. Temperature of the sample was reduced using liquid \( N_2 \) filled in Dewar vessels surrounding the cell. The temperature, monitored by a thermo-couple set near the sample, was adjusted to a setting temperature by controlling a current supplied to the heater coil, which was placed around the sample cell. A thin fiber suspended the crystal in a horizontal magnetic field \( B \); the direction of magnetically stable and unstable axes rotated in the horizontal plane. In case of ice \( I_h \), the unstable axis was identical to the c-axis and the stable axis was in an arbitrary direction in the c-plane as shown in the insert of fig.1. The direction of stable axis of the crystal showed rotational oscillation with respect to \( B \) which follows an equation described as

\[
I \left( \frac{d^2 \Theta}{dt^2} \right) = -B^2 M \Delta \chi \Theta,
\]

where \( \Theta \) denote the angle of stable axis with respect to \( B \). Here the restoration torque of the fiber suspending the sample should be negligible compared to the torque caused by field-induced anisotropy energy [8]; It is deduced from eq. (1) that \( \Delta \chi \) is obtained from the gradient of the proportional \( \tau^1 \)-\( B \) relationship \( \tau^1 = 2\pi \left( \frac{L}{M} \Delta \chi \right)^{1/2} B \) without the effect of the torque of fiber. \( \Delta \chi \) of the level of \( 1 \times 10^{-9} \) emu/g was previously reported from mm-sized samples in terms of this method [7,8].

It is seen in fig.1 that \( \tau^1 \) is proportional to \( B \) in the high field regions; small \( \Delta \chi \) of the level of \( 10^{-10} \) emu/g is obtained for the first time in terms of this method. A polyaramid fiber of 12\( \mu \)m diameter was used in order to fulfil the above mentioned condition. The \( B-\tau^1 \) relationship of ice deviates from the proportional line below 1.2T, which is caused by the above-mentioned restoration torque of the fiber. It is seen in the figure that the effect of this torque is relatively low for a corundum crystal, which has similar \( I/M \) and a larger \( \Delta \chi \) of \( 1.0 \times 10^{-9} \)emu/g. These data indicate that the \( \Delta \chi \) value obtained for ice \( I_h \) is just above the detection limit of the present setup. Measurement using microgravity was performed to improve sensitivity. Here the fiber was completely excluded from the system [11]; sensitivity can be improved to \( 10^{-15} \)emu/g in an orbital laboratory.

Measured \( \Delta \chi \) - \( T \) relationship of ice \( I_h \) is described in fig.2. \( \Delta \chi \) is almost constant with respect to temperature; no evidence of temperature dependence due to paramagnetic anisotropy was observed.
\(\Delta \chi\) of ice Ih was determined as \(2.9 \times 10^{-10}\text{emu/g}\) from the average of the \(\Delta \chi\) values. This value is about 9% of the published value reported by Lonsdale.

4. Discussions

\(\Delta \chi\) - \(T\) data shown in fig.2 had a minimum point at about \(T = 230\ K\). This pattern of \(\Delta \chi\) variation with respect to temperature is similar to that of the c/a ratio of lattice constants reported previously [13]. The above-mentioned tetrahedral unit may cause a slight deformation from regular symmetry by the variation of c/a ratio, which may be the cause the observed \((\Delta \chi)_{\text{DIA}}; \Delta \chi\) - \(T\) measurement at lower temperatures is now in progress, in order to confirm whether the temperature dependence of \(\Delta \chi\) has definite correlation with that of the a/c ratio which is obtained at temperatures below \(T=200\ K\).

As mentioned before, relationship between the degree of alignment <\(m\)> and field intensity \(B\) of micron-sized crystals dispersed in liquid are determined by three parameters, \(\Delta \chi\), \(M\) and \(T\) [4,7]. Typical examples of such relationships measured at \(T=300\ K\) are shown in fig.3 for three mica minerals having similar crystal structures but different values; value increases with the concentration of paramagnetic ions [14,15]. For example magnetic anisotropy of biotite having high magnetic susceptibility of \(\chi = 4.4 \times 10^{-5}\text{emu/g}\), was as large as \(\Delta \chi = 1.2 \times 10^{-5}\text{emu/g}\). Whereas was \(5.0 \times 10^{-8}\text{emu/g}\) for phlogopite which had smaller magnetic susceptibility of \(\chi = 1.2 \times 10^{-6}\text{emu/g}\). Magnitude of \(\Delta \chi\) was below the detection limit for synthetic phlogopite free of paramagnetic ions; \(\Delta \chi\) was probably at a level of \(10^{-11}\text{emu/g}\) according to the observed <\(m\)> - \(B\) curve [15]. It is seen that the large variation in field intensity required to achieve alignment among the three curves are caused mainly by the difference of \(\Delta \chi\) values, since the three materials have

- similar \(M\) values (with sizes of several microns in diameter) and are all measured at room temperature. <\(m\)> - \(B\) curves were calculated independently from the observed values of \(T\), \(M\) and \(\Delta \chi\); the results are consistent with the <\(m\)> - \(B\) data described in fig.3 for biotite and phlogopite.

Calculated <\(m\)> reaches 0.8 above 6.3 Tesla for spherical ice (Ih) crystal of 1.0 \(\mu\)m in diameter at \(T=273\ K\); the calculation is based on the \((\Delta \chi)_{\text{DIA}}\) value obtained in fig.2. It is noted that magnetic alignment of various materials with high crystal symmetry, such as materials that have a rutile, wurtzite or perovskite structure, is expected to occur above several Tesla as well. Experiments on alignment should be performed intensively at high magnetic-field laboratories for this type of materials; it is necessary to improve sensitivity of measurement up to the level of \(10^{-11}\text{emu/g}\) in order
to realize quantitative analysis on the alignment process, as seen in the case of synthetic phlogopite described in fig.3. As mentioned before, the analysis is essential in understanding the driving force of alignment in high magnetic field.

![Fig.3](image_url)  
**Fig.3** Relationship between the degree of alignment and field intensity $B$ observed for micron-sized crystals of mica[14,15]. Degree of alignment is described by an order parameter $<m> = \frac{(3\cos^2 \theta - 1)/2}{},$ where $\theta$ is the angle between magnetically stable-axis of a particle and $B$ [3,4]. $<m> = 0$ and 1 correspond to a completely random and an ordered state of the particles, respectively. Measured data are shown by symbols. Theoretical fit to the measured data are shown by solid curves.

On the other hand, most of the unmeasured diamagnetic crystals are expected to possess a $(\Delta \chi)_{DIA}$ above $1 \times 10^{-9}$ emu/g, and alignment is achieved below 2 Tesla for the micron-sized crystals as mentioned before [7]; this field intensity is produced by an ordinary electromagnet or a permanent magnet. The possibility of producing new magnetic devises may increase considerably when magnetically active materials at low field intensity is expanded to solid materials in general; experiments can be carried out in various research fields, when alignment is easily performed by a low-cost field generator.

References
[1] Malet G & Dransfeld G, 1985 *Topics in App. Phys.*, 57 144; various papers appearing in *Proc. Int. Symp. New Magneto-Sci. Tsukuba*, (Jpn. Sci. & Tec. Corp., NIMS, 1999)
[2] Langevin M.P & Curie P, 1910 *C.R.Acad. Sci.Paris* 151 475
[3] Yamagishi A, Takeuchi T, Higashi H & Date M, 1989 *J.Phys.Soc.Jpn.* 58 2280
[4] Uyeda C, Takeuchi T, Yamagishi A & Date M, 1991, *J.Phys.Soc.Jpn.*, 60 3234
[5] Yamamoto I, Matsumoto Y, Yamaguchi M, Shimazu Y and Ishizuka F, 1998, *Physica B*, 246-247 408
[6] Sazaki G, Yoshida E, Komatsu H, Nakada T, Mityashita S and Watanabe K, 1996, *J.Cryst. Growth* 173 1243
[7] Uyeda C, Tanaka K, Takashima R and Sakakibara M, 2005, *Appl.Phys.Lett.* 86 094103
[8] Uyeda C, 1993, *Jpn.J.App.Phys.* 32 L268
[9] Uyeda C, 1993, *Jpn.J.App.Phys.* 32 L268
[10] Lonsdale K, 1949 *Nature* 164 101
[11] Uyeda C, Mamiya M, Takashima R, Abe T and Okutani T, 2006 *Jpn.J.App.Phys.* 45 L124
[12] Abe T, Takashima R and Uyeda C *Proc. ISMS 2005 Yokohama* p69
[13] Röttger K, Endriss A and Ihringer J, 1994, *ActaCryst.* B50 644
[14] Uyeda C, Takashima R and Hiraoka K, 2005, *Jpn.J.App.Phys.,* 44 L371
[15] Uyeda C, Takeuchi T, Yamagishi A, Tsuchiyama A, Yamanaka T, and Date M, 1993, *Phys. Chem. Minerals* 20 369