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Efficiency of Magnetic Alignment Detected for Non-magnetic Oxide Crystals Deriving from Individual Bonding Orbital

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The possibility of realizing magnetic alignment of diamagnetic nonmetal in general is studied based on experimental data of diamagnetic anisotropy ($\Delta\chi$)$_{DIA}$. The values of basic inorganic oxides, such as corundum, forsterite, muscovite, gypsum, orthoclase, apophylite, KDP, ADP, $Mg(OH)_2$, $Al(OH)_3$ and AlOOH were detected using a method developed by the present authors for this purpose. The restoring force of a fiber suspending the sample in the magnetic field, which had been the standard in measuring $\Delta\chi$, was extracted in the new system. The origin of obtained ($\Delta\chi$)$_{DIA}$ values were explained quantitatively by assigning a constant amount of anisotropy to individual bonding orbital composing the crystal. The ($\Delta\chi$)$_{DIA}$ value deriving from a single orbital was determined for a T-O bond of the $[TO_4]$ block, for a M-O bond of the $[MO_6]$ block as well as for a hydrogen bond. Accordingly many of the nonmagnetic oxides are expected to cause alignment at a finite field intensity; the majority of inorganic oxides are composed of the three types of bonds.

Key words: diamagnetic anisotropy deriving from single chemical bond, magneto-rotation of diamagnetic nonmetal, inorganic oxides, efficiency of magnetic alignment of diamagnetic nonmetals

1. INTRODUCTION

A ceramic material is known to cause magnetic alignment when it possesses a finite amount of diamagnetic anisotropy ($\Delta\chi$)$_{DIA}$ even if it contains no ferromagnetic moments[1,2]. The magnetically stable axes of a micron-sized solid-body is aligned almost parallel to the field direction when the anisotropy energy induced in the body is an order of magnitude large compared to the energy of rotational Brownian motion; this energy randomizes the direction of the bodies according to the conventional Langevin theory on magnetic alignment[3]. The magnetic anisotropy which cause the magnetic alignment arise from the intrinsic diamagnetic anisotropy ($\Delta\chi$)$_{DIA}$ of the material as well as from the paramagnetic anisotropy ($\Delta\chi$)$_{PARA}$ caused by the impurity ions[1,2]. This type of alignment was studied intensively on organic material.

Accumulations of ($\Delta\chi$)$_{DIA}$ values were carried out by Krichnann and Banarge[4]. The large ($\Delta\chi$)$_{DIA}$ values observed for the organic crystals were interpreted by Pauling to arise from the large spatial anisotropy of the molecular orbital[5]. Studies of the alignments process were performed mainly on organic material since then, which usually required strong field intensity above several Tesla[1,2]. The reports on inorganic materials were limited in numbers, because their ($\Delta\chi$)$_{DIA}$ values were too small to be detected by the conventional methods of $\Delta\chi$ measurements[4,6]; reports on ceramic materials have been made on kaolin, talc[7], phlogopite, muscovite[8], graphite[9] potassium nitrate[10] and Al_2O_3 [11].

The published ($\Delta\chi$)$_{DIA}$ data of inorganic oxides increased considerably for nonmetallic oxides recently due to the development of a new method to detect small $\Delta\chi$ values. Data was obtained for basic materials such as forsterite[12], corundum, Mg(OH)2, $Al(OH)_3$, AlOOH, muscovite[13], orthoclase, apophilite, petalite, scapolite[14], ADP, KDP and gypsum[15]. A preliminary model, in which the anisotropy was assigned to the individual bonding orbital composing the material, was effective in interpreting the origin of the measured ($\Delta\chi$)$_{DIA}$ values[12,15,16]. The present paper concerns the significance of the above-mentioned model on practical applications of magnetic-alignment process observed for diamagnetic nonmetals.

2. DETECTION OF SMALL DIAMGNETIC ANISOTROPY

The principle of the conventional torque methods in measuring magnetic anisotropy is generally based on a rotational equation of a bulk crystal suspended in a horizontal field, in which the direction of the magnetically stable-axis may rotate freely in the horizontal plane[4]. The equation is described as, $I(d^2\theta/dt^2) = - B^2 m\Delta\chi \sin 2\theta - (D/\ell)\theta$ where the term $- B^2 m\Delta\chi \sin 2\theta$ denote the torque due to the field-induced anisotropy energy; the angle of stable-axis with respect to B is described as θ. The term $(D/\ell)\theta$ denote the torque due to the restoring force of the fiber; D and ℓ, shows the tensional rigidity and the length of the fiber, respectively. $\Delta\chi$ is detected by achieving the balance between $- B^2 m\Delta\chi \sin 2\theta$ and $(D/\ell)\theta$ in the above equation. The sensitivity of the measurable $\Delta\chi$ value was hence limited by the values of D and ℓ.

The present authors have improved the sensitivity by controlling the second term to be negligible compared to the first term[17]. The direction of the stable-axis showed rotational oscillation with respect to the field direction in the improved method, and $\Delta\chi$ was obtained from the period of oscillation without the use of D and ℓ. The

paramagnetic anisotropy due to the impurity ions were extracted effectively by performing $\Delta\chi$-T measurements in the above-mentioned measurements [13,14,16]. Most of the natural and synthetic inorganic-oxides showed the temperature dependence obeying the Curie law. Origin of diamagnetic anisotropy was evaluated in terms of the published $(\Delta\chi)_{DIA}$ data obtained by the improved method. The values are listed in Table I.

The fiber itself was removed from the system for the purpose of improving of sensitivity using micro-gravity condition. The consistency between the measured and calculated periods indicated that factors other than the magnetic torque can be neglected as the cause of the observed rotational-oscillation, and that magnetic anisotropy can be detected from the newly proposed principle with limitless sensitivity [18,19]. Further accumulation of $(\Delta\chi)_{DIA}$ data are required to confirm the sufficiency of above-mentioned model on $(\Delta\chi)_{DIA}$, however, the improved sensitivity obtained at terrestrial-gravity is not high enough to detect the small $(\Delta\chi)_{DIA}$ values in many cases.

Table I Measured Diamagnetic Anisotropy of Inorganic Oxides[16,21]

Materials	$(\Delta\chi)_{DIA}$ values [x 10^{-9} emu/g]
Graphite	20000
α-quartz	2.0±0.2
Muscovite	11±2
Orthoclase	2.1±2
Alumina	0.7±0.1
Forsterite	9.6±0.2
Calcite	8.3±0.3
Gypsum	9.6±0.2
KDP	8.3±0.3
ADP	11±0.5
$Mg(OH)_2$	1.4±0.2
$Al(OH)_3$	2.6±0.2
AlOOH	4.2±0.3

3. CORRELATION BETWEEN $(\Delta\chi)_{DIA}$ AND BOND DIRECTION

Diamagnetic anisotropy were generally considered to derive from the spatial anisotropy of electron distribution for the organic materials[5]. In the case of inorganic oxides, the amount of spatial anisotropy was expected to be considerably small compared to those of organic materials. The fact that the advanced "Pascal's law" explains the published diamagnetic susceptibility χ_{DIA} fairly well[6], indicates that χ_{DIA} is approximately equivalent to the simple summation of the susceptibility assigned to the individual orbital consisting the material. This treatment on diamagnetic susceptibility can be expressed by a 3-demensinal χ-tensor of a material, assuming that each orbital posseses an constant $(\Delta\chi)_{DIA}$ value with the bond direction being the principle axis[12,15,16]. The field-induced free energy $U(B)$ of an orbital is calculated as, $U(B) = -(1/2)B^2 \{ \chi_{BO}\perp + \Delta\chi_{BO}(a^2\alpha^2 + b^2\beta^2 + c^2\gamma^2)\}$. The anisotropy of an orbital is defined as $\Delta\chi_{BO} = \chi_{BO}\parallel - \chi_{BO}\perp$ in the above equation, where $\chi_{BO}\parallel$ and $\chi_{BO}\perp$ denote the susceptibilities parallel and perpendicular to the bond direction, respectively. The direction cosines of B and bond direction are denoted as (a,b,c) and (α,β,γ), respectively. $(\Delta\chi)_{DIA}$ values between x-y, y-z and z-x axes should be proportional to, $\Sigma\alpha^2 - \Sigma\beta^2$, $\Sigma\beta^2 - \Sigma\gamma^2$ and $\Sigma\gamma^2 - \Sigma\alpha^2$, respectively. All the bonds consisting the crystal(per mol) are included in the summations $\Sigma\alpha^2$, $\Sigma\beta^2$ and $\Sigma\gamma^2$. The correlation assumed above were examined for three types of chemical bonds, namely for the T-O bonds of the tetrahedral [TO_4] units[20], for the hydrogen bonds[15] and for the M-O bonds of the [MO_6] units[16]. Published data listed in Table I were used in the calculation. The regressions between experimental and calculated anisotropy were obtained separately for the three types of bonds and described in Fig.I. The regression lines are obtained as

O-H bond:

$$(\Delta\chi)_{DIA} = -2.2\,(\Delta\Sigma) + 0.06 \quad [\times 10^{-6}\text{emu/mol}]$$

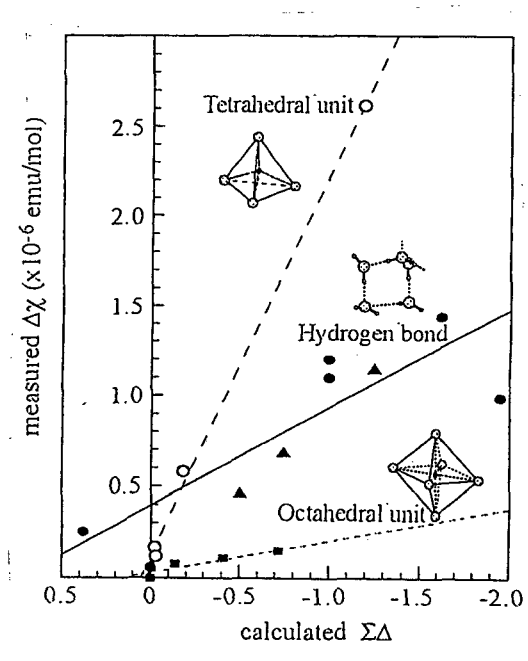
T-O bond:

$$(\Delta\chi)_{DIA} = -0.63(\Delta\Sigma) + 0.23 \quad [\times 10^{-6}\text{emu/mol}]$$

M-Obond:

$$(\Delta\chi)_{DIA} = -0.19(\Delta\Sigma) + 0.03 \quad [\times 10^{-6}\text{emu/mol}]$$

Fig.I Relationship Between Diamagnetic Anisotropy and Bond Direction[16,21]



where $\Delta\Sigma$ denote the differences between $\Sigma\alpha^2$, $\Sigma\beta^2$ and $\Sigma\gamma^2$ described in the above equations. Clear positive correlations are seen for the three types of chemical bonds. It is noted that the chemical bonds are the major categories of bonding orbital composing the oxides of light elements. Many of the oxides may hence have the potential of possessing a finite amount of diamagnetic anisotropy, which can be the cause of magnetic alignment[16].

4. Discussion

It is expected from the conventional Langevin theory on magnetic grain-alignment that the process is controlled by three parameters, namely the mole number of the particle N, magnetic anisotropy (per mol) $\Delta\chi$, and temperature T of the suspension[7,18]. The effects of these parameters were not examined, partly because most of the experiments on magnetic alignment were performed on organic and biological particles.

The field intensity to achieve alignment is expected to decrease with temperature, since the process proceeds by the balance between the anisotropy energy induced in the crystals and the thermal agitation energy that randomize the direction of the crystal as mentioned before. This tendency was examined experimentally for micron-sized single- crystals of synthesized graphite dispersed in liquid ethanol. The results measured between T = 273K and 180K was consistent with the above-mentioned Langevin theory[9]. The field intensity to achieve magnetic alignment of diamagnetic inorganic-insulator grains was considered to exceed 10 tesla previously. The observed results on graphite micro-crystals indicate that the magnetic alignment may be achieved at a practical low field intensity for the inorganic oxides discussed above by reducing temperature[21,22]. The effect is applicable as well on organic and biological materials provided that the particles do not deform by temperature alterations.

References

[1] G.Malet and K.Dransfeld, Topics in App. Phys., **57**, 144, (1985).
[2] *for example various paper appearing in*, Proc.Intern.Symp. New Magneto-Science (Jpn.Sci. Tec.Corp.1999)
[3] M.P.Langevin and P.Curie, C R.Acad. Sci. Paris, **151**, 475 (1910).
[4] K.S.Krichnann and S.Banerjee, Phi. Trans. Roy. Soc. London, **A231**, 235 (1933).
[5] L.Pauling, J. Chem. Phys. **4**, 672 (1936).
[6]R.Guputa: *Diamagnetism*, "Landort Bornstein" New Series II (1983) 445.
[7] C.Uyeda, T.Yamanaka and M.Date, J.Phys.Soc.Jpn., **20**, 82 (1991).
[8]C.Uyeda, T.Takeuchi, A.Yamagishi, A.Tsuchiyama, T.Yamanaka and M.Date, Phys. Chem. Minerals **20**, 369 (1993).
[9] H.Chihara C.Uyeda, A.Tsuchiyama and T.Yamanaka, Publ. Astron. Soc. Jpn. **50**, 149 (1998)
[10] M.Fujiwara, R.Tokunaga and Y.Tanimoto, J.Phys.Chem.B **102**, 102 (1998).
[11] S.Suzuki, Y.Sakka and K.Kitazawa, Adv.Eng.Mater. **3**, 490 (2001).
[12] C.Uyeda, Phys. Chem. Minerals **20**, 77 (1993).
[13] C.Uyeda, K.Ohtawa, and K.Okita, Jpn.J.App.Phys. **39**, L514 (2000).
[14] C.Uyeda, K.Ohtawa and K.Okita, J.Phys.Soc.Jpn. **69**, 1019 (2000).
[15] C.Uyeda, K.Ohtawa, K.Okita and N.Uyeda, Jpn. J. App. Phys. **39**, 1234 (2000).
[16] C.Uyeda and K.Tanaka: J.Phys.Soc.Jpn. **72**, 2334 (2003).
[17] C.Uyeda, Jpn. J. App. Phys.**32**, L268 (1993)
[18] C.Uyeda, K.Tanaka and R.Takashima, Jpn. J. App. Phys. **42**, L1226 (2003)
[19] K.Tanaka, R.Takashima and C.Uyeda, appearing in present volume
[20] C.Uyeda, K.Ohtawa, K.Okita and N.Uyeda, J. Phys.Soc.Jpn, **70**, 889 (2001).
[21] C.Uyeda, K.Tanaka and R.Takashima, Jpn. J. App. Phys.43 (2004) in print
[22] R.Takashima, K.Tanaka and C.Uyeda, appearing in present volume

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