Attempt to Detect Diamagnetic Anisotropy of Oxides with Isotropic Crystal Structure by Measuring Its Rotational Oscillation in Strong Magnetic Field

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Abstract. Sensitivity to detect diamagnetic anisotropy $\Delta\chi_{\text{DIA}}$ of inorganic oxides was improved by increasing intensity of horizontal field from 1.6 T to 5.0 Tesla. The field induced a rotational oscillation of a magnetically stable axis of a sample, which was suspended with a thin fiber. Accurate $\Delta\chi$ values are obtained when restoration torque of the fiber is negligibly small compared to torque due to magnetic anisotropy. Accordingly, $\Delta\chi$ value at a level of $5\times10^{-10}$ emu/g can be acquired, even if the mass of the sample is relatively small (0.318 g). Necessity of realizing $\Delta\chi$ measurement at low temperature is discussed, which realizes separation of $\Delta\chi_{\text{DIA}}$ from a paramagnetic anisotropy caused by isolated magnetic ions.

1. Introduction

Magnetic alignment of solid materials without spontaneous magnetic moment has been effectively applied in various research areas [1, 2, 3]. Intrinsic value of magnetic anisotropy $\Delta\chi$ is essential for investigating origin of magnetic alignment. Recently, small $\Delta\chi_{\text{DIA}}$ values of many popular inorganic oxides have been detected by a method using harmonic-oscillation of a sample in a horizontal magnetic field of 1.6 T [4]. This oscillation is achieved in a condition where restoration torque of a fiber suspending a sample is much small compared to torque due to magnetic anisotropy. The sensitivity to detect $\Delta\chi$ in the above method is about $1\times10^{-9}$ emu/g.

The origin of diamagnetic anisotropy was studied quantitatively based on published $\Delta\chi_{\text{DIA}}$ values recently obtained for popular oxides, namely corundum, forsterite, orthoclase, muscovite, gypsum, KDP, ADP, talc, apophirite, Mg(OH)$_2$ and Al(OH)$_3$ [5, 6]. The published values were consistently explained by assuming a constant $\Delta\chi$ tensor on individual bonding orbital composing the material [7]; here anisotropy of a single bond $\Delta\chi_{\text{BD}}$ was assumed to have a anisotropy at a level of $10^{-30}$emu/g. Accordingly, $\Delta\chi_{\text{DIA}}$ of an unmeasured material can be predicted from the $\Delta\chi_{\text{BD}}$ values, and it was expected that $\Delta\chi_{\text{DIA}}$ is smaller than $1\times10^{-9}$ emu/g for materials with high crystal symmetry. In case of wurtzite structure for example, the tetrahedral configuration in the crystal is very close to regular symmetry, so that the summation of the above-mentioned $\Delta\chi$ tensors of individual bonds in a unit cell
cancels out [8]. An ideal $\Delta\chi_{\text{DIA}}$ value of a crystal with cubic symmetry is expected to be zero according to this model. Hence it is essential to improve $\Delta\chi$ sensitivity in order to understand an overall tendency on diamagnetic anisotropy of oxides.

In a previous report, $\Delta\chi$ above $1 \times 10^{-9}$ emu/g were measurable even if field intensity was as small as 0.1 T, provided that a thin polyaramid fiber having a small $D$ value was introduced [9]. It is implicated that sensitivity of $\Delta\chi$ measurement using this fiber would be considerably improved by increasing field intensity. In the present study, rotational oscillation was observed in static horizontal field of 5.0 T using a cryogen-free magnet. A new apparatus was developed for the purpose of realizing the detection of $\Delta\chi$ below $1 \times 10^{-9}$ emu/g.

2. Experimental

A bulk sample is suspended in a horizontal field $B$ by the above-mentioned polyaramid fiber that has a diameter of $1.2 \times 10^{-5}$ m and a length of $3.0 \times 10^{-2}$ m; the directions of two principal axes of a sample are in the horizontal plane. The direction of magnetically stable axis shows rotational harmonic-oscillation with respect to $B$, which follows the equation described as

$$I \frac{d^2\theta}{dt^2} = -\frac{1}{2} B^2 N\Delta\chi \sin 2\theta - \frac{D}{I} \theta$$

(1)

where $\theta$ is an angle of magnetically stable axis with respect to field $B$. $I$ denote moment of inertia of a crystal. $N$ is mass of a sample. $D$ and $l$ are tensional rigidity and length of the fiber, respectively. The evaluated $D/l$ value of the fiber was $(1.1 \pm 0.4) \times 10^{-9}$ Nm which was two orders of magnitude smaller compared to magnetic term in EQ.(1) [9]. Hence, the restoration torque of the fiber is negligibly small with respect to that of magnetic anisotropy in the present condition. The period of oscillation $\tau$ of a sample is deduced theoretically from eq.(1) as

$$\tau = \frac{2\pi}{\sqrt{\frac{I}{N\Delta\chi}} B^{-1} \left\{ 1 + \frac{1}{4} \sin \theta \frac{\theta}{2} + \ldots \right\}}.$$

(2)

Here $\theta_0$ is the angle of amplitude, which is below 15 degree in this study. $\Delta\chi$ value of the sample is determined from the gradient of measured $\tau^{-1}$-$B$ relationship [9].

Experimental setup developed in the present work is shown schematically in figure. 1. A cryogen-free superconducting magnet (JMTD-6T100) produced a maximum magnetic field of 5.0 T. The inhomogeneity of the field was less than 1 % in a spherical area of 10 mm in diameter at field center. The sample with fiber was put inside a glass tube at center of the homogeneous magnetic field. The rotational motion was observed through a flat mirror and recorded by a video camera (Panasonic HDC-SD3) as shown in Fig.1. A standard sample was prepared in the present experiment so as to examine the reliability of the achieved sensitivity of this system using 5.0 T. The sample, which was made from blocks of $\alpha$-quartz single crystal, was expected to have $\Delta\chi_{\text{DIA}}$ value of $5.75 \times 10^{-10}$ emu/g. The size of the sample was 0.50 cm square and 0.48 cm depth, and its mass was 0.318 g. Center of top plane was determined by geometrical measurement of the sample, and fiber was attached to this point. Value of $I$ measured by rotational oscillation at $B=0$ condition generally agree fairly well with $I$ value calculated from the above geometrical condition.
3. Results and Discussion

Observed $\tau^{-1}$–$B$ relationship of above-mentioned standard sample was shown in Fig 2. The obtained $\Delta \chi$ value was $5.2 \times 10^{-10}$ emu/g, it showed good agreement with the expected value of $5.75 \times 10^{-10}$ emu/g. It was confirmed that $\Delta \chi$ value at a level of $5 \times 10^{-10}$ emu/g could be detected using the present setup. Origin of intercept of regression line (Fig 2.) is qualitatively explained by adding a term of viscous drag caused by air to eq.(1). Contribution of this term may be quantitatively evaluated by performing experiment in a diffused condition.

Inorganic crystals generally contain paramagnetic impurity ions that cause anisotropy of paramagnetic susceptibility $\Delta \chi_{\text{PARA}}$, and it is important to distinguish quantitative amount of $\Delta \chi_{\text{PARA}}$ in order to obtain an exact $\Delta \chi_{\text{DIA}}$. Paramagnetic susceptibility and its anisotropy are proportional to temperature $T$ according to a Curie's law, whereas diamagnetic $\Delta \chi_{\text{DIA}}$ is independent of temperature. Previous experiments revealed that a $\Delta \chi$-$T^{-1}$ relationship is effective to obtain $\Delta \chi_{\text{DIA}}$ value [6, 10, 11, 12]; here intercept of the $\Delta \chi$-$T^{-1}$ regression line with the $T=0$ axis was adopted as a $\Delta \chi_{\text{DIA}}$ value. However when concentration of paramagnetic ion was high, the obtained $\Delta \chi_{\text{DIA}}$ value contained large amount of uncertainty. This is because deviation of measured $\Delta \chi$-$T^{-1}$ data with respect to regression line was not negligible. In order to obtain a reliable $\Delta \chi_{\text{DIA}}$ value, high sensitive $\Delta \chi$-$T^{-1}$ measurements should be performed on samples with high purity. By following the above-mentioned procedure, $\Delta \chi_{\text{DIA}}$ may be obtained for oxides with high crystal symmetry as described before.

Recently, micro-gravity experiments were conducted in order to improve sensitivity of $\Delta \chi$. Here the fiber was completely excluded from the system [13]. Experiments were recently performed at MGLAB [Micro gravity laboratory of Japan]; here a highly-qualified $\mu$G condition of $2.0 \times 10^{-3}$ Gal was produced for 4.5 sec. According to eq.(2), it is essential to increase duration of $\mu$G in order to increase sensitivity of $\Delta \chi$[8]. When rotational oscillation is realized in orbital laboratory, sensitivity of $\Delta \chi$ measurement will be increased almost limitlessly. Hence, $\Delta \chi_{\text{DIA}}$ value may be obtained for most of the highly-symmetrical crystals in $\mu$G condition. However it is also important to develop high-sensitive $\Delta \chi$ measurement in normal-gravity condition, because the method is far easier to perform compared to the measurements in $\mu$G. It is noted that compiling of $\Delta \chi_{\text{DIA}}$ data at a level of $10^{-10}$ emu/g may proceed rapidly by adopting the present method.

An upper limit of available field intensity has increased considerably during the last several decades [14]. Novel applications on diamagnetic alignment may be realized when small $\Delta \chi$ values of inorganic materials with highly symmetric structures are obtained.

![Figure 1. Schematic view of apparatus (left hand) and geometrical relations of a sample (right hand).](image-url)
4. Conclusion
An experiment to determine $\Delta \chi$ values using magnetic field of 5.0 T was realized by setting a conventional apparatus to observe harmonic-oscillation of a sample in a cryogen-free magnet. High sensitivity of $\Delta \chi$ measurement was achieved; $\Delta \chi$ value of $5 \times 10^{-10}$ emu/g was accurately detected. A setup for low temperature experiment is now being developed in order to separate the contribution of $\Delta \chi_{\text{DIA}}$ from $\Delta \chi_{\text{PARA}}$. The presented system is effective for investigating $\Delta \chi_{\text{DIA}}$ values of symmetric crystals, which are expected to be smaller than $1 \times 10^{-9}$ emu/g.

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