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ORIGINAL PAPER

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Temperature dependence of the magnetic rotation process of kaolinite microcrystals containing paramagnetic impurity ions dispersed in liquid medium

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Abstract Temperature dependencies of magnetic rotation were measured in micron-sized silicates dispersed in ethanol for two different samples of kaolinite. Magnetic rotation proceeded by balance between thermal agitation energy and magnetic anisotropy energy. Measurements were performed between 195 and 343 K. The field intensity required to achieve magnetic alignment of microcrystals increases with temperature, because of the temperature dependence of paramagnetic anisotropy, and the temperature dependence of thermal agitation energy. The results indicate that the values of magnetic anisotropy of nonmagnetic materials might partially derive from the paramagnetic moments, which derive from paramagnetic impurity ions. The present experiment provides a technical basis for determining the precise values of diamagnetic anisotropy $(\Delta\chi)_{DIA}$ from minerals which have a concentration of paramagnetic ions and do not form a single crystal large enough to allow bulk $\Delta\chi$ measurements. The values of $(\Delta\chi)_{DIA}$ can be obtained by extrapolating the $\Delta\chi$–T relations, which follow the Curie law, to the temperature limits.

Keywords Magnetic alignment · Diamagnetic anisotropy · Kaolinite · Sheet-silicate · Paramagnetic anisotropy · Micron-sized crystal · Ceramic material

Introduction

Values of diamagnetic anisotropy $(\Delta\chi)_{DIA}$ for various inorganic oxides have been measured by a newly developed method that is more sensitive than the conventional torque method (Uyeda 1993; Uyeda et al. 1993a). The anisotropy was obtained from the period of field-induced harmonic oscillation of the crystal under a strong field where the restoration force of a string suspending the crystal was negligible as compared with the anisotropy energy. This improvement-enhanced measurement sensitivity to 1.3×10^{-12} emu /sample^{-1} (Uyeda et al. 1998). The $(\Delta\chi)_{DIA}$ values of forsterite, talc, calcite, corundum, and quartz were examined by this method. Diamagnetic anisotropies of inorganic oxides are considered to be negligibly small as compared to those of organic materials, and only limited data are published (e.g., Gupta 1983). The origin of anisotropy in inorganic oxides is not discussed in detail.

In addition to poor sensitivity, a major problem in accumulating $(\Delta\chi)_{DIA}$ values lies in paramagnetic impurities that are generally contained in diamagnetic materials. The $(\Delta\chi)_{DIA}$ values reported previously were obtained from crystals that are free of paramagnetic impurities, and at present only limited numbers of such oxide species are known. T–$\Delta\chi$ measurements from room temperature to 800 K were performed in order to determine precise $(\Delta\chi)_{DIA}$ values from natural samples containing paramagnetic ions. The T–$\Delta\chi$ relations follow the Curie law, which originates from the paramagnetic ions isolated in the diamagnetic crystals. The $(\Delta\chi)_{DIA}$ values of the materials were obtained from the high temperature limit. This method was employed to obtain the diamagnetic anisotropy of basic oxides, such as orthoclase and apophyrite (Uyeda et al. 2000a); gibbsite, brucite, corundum and muscovite (Uyeda et al. 2000b); and KDP, ADP, and gypsum (Uyeda et al. 2000c). These observations revealed that the anisotropy originating from paramagnetic moments at room temperature often exceeds the intrinsic $(\Delta\chi)_{DIA}$ value of the material.

Another difficulty in accumulating the $(\Delta\chi)_{DIA}$ values is that the above-mentioned measurements cannot be performed when the size of single crystals is smaller than several millimeters in diameter. In such cases, observation of magneto-rotation on micron-sized single crystals suspended in liquid medium was the only available method for estimating the $(\Delta\chi)_{DIA}$ values. Measurements were performed intensively on organic or biological

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particles, and the $(\Delta\chi)_{DIA}$ values were obtained from observations at a fixed temperature (e.g., Maret and Dansfeld 1985). Measurements for inorganic microcrystals were performed on sheet silicates, namely, kaolin and talc (Uyeda et al. 1991), and phlogopite, muscovite, and lepidorite (Uyeda et al. 1993a). The $\Delta\chi$–T observation on bulk samples mentioned above revealed that, in determining precise $(\Delta\chi)_{DIA}$ values, the paramagnetic $\Delta\chi$ component of the impurity ion should be evaluated quantitatively. Paramagnetic anisotropy was studied intensively for some of the rock-forming minerals in investigating the origin of magnetic anisotropy observed in rock samples (e.g., Ballet and Coey 1981).

Accumulations of inorganic $(\Delta\chi)_{DIA}$ values could serve as the basis for reconsidering the mechanism of interstellar dust alignment caused by the cosmic field. The local field of a star formation area is generally estimated by observation of dust alignment (e.g., Spitzer 1978). According to recent investigations of dust disks or bipolar flows that are commonly observed around protostars, the cosmic field is considered to play a major role in star and planetary evolution. The standard model for interpreting dust alignment, i.e., on the basis of paramagnetic relaxation of magnetic moments included in a grain, is not applicable in the star formation region (e.g., Whittet 1992). The major elements composing the grains are nonmagnetic, in accordance with the elemental abundance. The existence of interstellar grains composed of basic rock-forming minerals, such as corundum or enstatite, has been discussed on the basis of recent infrared observations. Magnetic ions of the grains are considered to be of low concentration, since they are likely to be condensates of high-temperature gas. Hence, the overall characteristics of diamagnetic anisotropy, now commonly observed for oxide minerals, should be clarified in order to evaluate the effect of diamagnetic anisotropy energy on interstellar dust alignment.

In the present work, the temperature dependencies of the magnetic rotation process for micron-sized crystals of kaolinite $[Al_4Si_4O_{10}(OH)_8]$ containing paramagnetic impurity ions was measured, in order to establish a method for determining precise $(\Delta\chi)_{DIA}$ values from micron-sized crystals. At present, many of the inorganic oxides cannot be obtained in the form of single crystals that are sufficiently large to perform bulk measurements. Also, the oxides generally contain a finite amount of magnetic impurities. These two conditions prevent the determination of precise $(\Delta\chi)_{DIA}$ values by the conventional methods.

Experimental

Figure 1 shows a schematic view of the experimental setup used in the present study, which is a modified system of an apparatus developed to detect the temperature dependence of magnetic rotation of graphite microcrystals (Chihara et al. 1998). The suspension of interest was contained in a cell which has a volume of 10 cm^3 and is surrounded by a heat bath. A pair of thermocouples

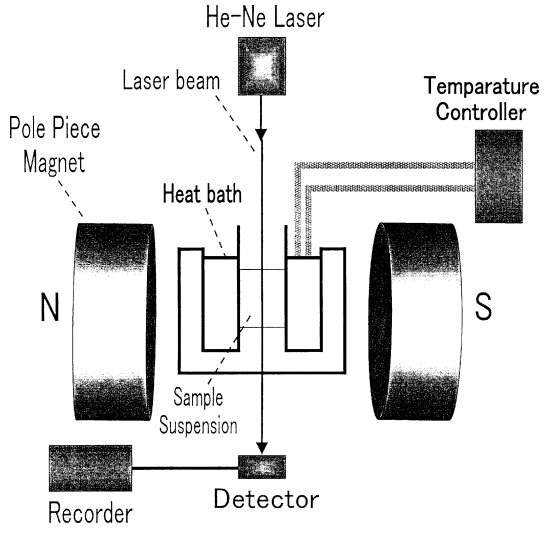

Fig. 1 Experimental setup for measuring the temperature dependence of the magnetic rotation process in microcrystals dispersed in a liquid medium. The direction of the magnetic field is perpendicular to that of the light path

placed inside the inner cell monitored the temperature of the sample suspension. The temperature of the suspension was varied between 197 and 343 K with an accuracy of 0.1 K by controlling the temperature of the heat bath. The cell was attached at the center of a pole-piece magnet, which produced a horizontal magnetic field up to 1.45 T within a spherical area of 40 mm diameter at the pole-piece center, the spatial inhomogeniety of the field being less than 200 ppm. The sphere enclosed the sample cell.

The degree of grain alignment was observed by means of the optical method conventionally used to analyze the magnetic rotation of small particles (e.g., Maret and Dansfeld 1985). The relation between the field intensity (B_i) applied to the suspension and the intensity of the He–Ne laser beam transmitted through the suspension was determined. The variation in beam intensity attributable to the application of the field was monitored, and is denoted as $\Delta I_i = I_i - I_0$, where I_i and I_0 represent the transmitted light intensity with and without the magnetic field B_i, respectively. The field intensity was increased stepwise until the alignment was completed and ΔI_i was saturated to a constant value ΔI_S. The degree of grain alignment could be monitored quantitatively, since the principal magnetic axis of the disk-shaped grain coincided with the principal optical axis. Visual observation has confirmed that μm-sized crystals of kaolinite have a quasi-uniaxial type of magnetic anisotropy, with the unstable axis being identical to the c-axis (Uyeda et al. 1991). As was also confirmed, the transmitted light intensity was minimized when the crystals were aligned parallel to the field.

The magnetic state of the samples was examined by chemical analysis as well as by the vibrating sample magnetization system (VSM). Table 1 lists the results for the two samples measured in the present work, kaolinite-1 and kaolinite-2. The upper limits of χ values estimated from the chemical concentrations of the magnetic ions were 1150×10^{-6} emu mol^{-1} for kaolinite-1 and 530×10^{-6} emu mol^{-1} for kaolinite-2. All the iron and titanium ions in the calculation were assumed to occupy the Fe^{+3} or the Ti^{+3} state according to which have the largest effective Bohr magneton numbers p_{eff} (Fe^{+3} : $p_{eff} \simeq 5.9$ and Ti^{+3} : $p_{eff} \simeq 1.8$). The estimated χ values are both large compared to the measured χ values using the VSM method, which indicates that many of the iron and titanium ions are in ionic states with lower p_{eff} values. The magnetic ions are considered to occupy an isolated paramagnetic site in both samples according to the values of the VSM measurements. No minor crystal phases were detected by X-ray diffraction analysis or VSM measurement. The samples were dispersed in liquid ethanol. The grain sizes were controlled by a precipitation method described

Table 1 Chemical, geometric, and magnetic data for the measured samples

Sample[a]	Magnetic ions[b] (wt%)			χ^c ($\times 10^{-6}$ emu mol^{-1})	Average size[d]	
	Fe	Mn	Ti		S(μm^2)	h(μm)
Kaolinite-1	1.00	–	–	190	2.2	0.2
Kaolinite-2	0.30	–	1.44	72	4.3	0.3

[a]Kaolinite-1 and -2 are products of Sanderville, Georgia, USA, and Bath, South Carolina, USA, respectively
[b]The *bars in the table* indicate that the concentration was below the detection limit of 0.01%
[c]Measured paramagnetic susceptibility at 298 K
[d]Average area and thickness of the samples obtained by the SEM images are denoted as listed $S(\mu m^2)$ and $h(\mu m)$, respectively. The average N values are calculated from S and h by use of the published value of density $\rho = 2.6$ g cm^{-3} for kaolinite

previously (Chihara et al. 1998). Table 1 lists the average sizes of the grain samples as analyzed by a scanning electron microscope (JEOL Super Probe 733, Osaka University).

Results

Figure 2 shows typical relations observed between the degree of grain alignment and field intensity in the kaolinite-1 sample. In the figure, the degree of grain alignment is expressed by an order parameter $\langle m \rangle$, which is a Boltzmann average of the function $(3\cos^2\theta - 1)/2$ over the dispersed crystals. Here θ denotes the angle between the field and the magnetically stable axis of the crystal. The value of $\langle m \rangle$ varies from zero to unity, corresponding to the random state and the ordered state, respectively.

In the experimental results, measurements at $T = 197$ K and $T = 343$ K are shown by solid circles. As shown in the figure, when the temperature is lowered, magnetic alignment is achieved at lower field intensity. The experimental $\langle m \rangle$ values are obtained in terms of the relation $\langle m \rangle = \Delta I_i / \Delta I_S$, where ΔI_i and ΔI_S are obtained from the measurements described in the previous section. This relation was deduced theoretically (Twersky 1969; Yamagishi et al. 1989; Maret and Dansfeld 1985), and confirmed experimentally by measuring the magnetic rotation of microcrystals which had published $(\Delta\chi)_{\mathrm{DIA}}$ values determined from bulk measurements (Chihara et al. 1998). Theoretical $\langle m \rangle$-B relations for $T = 197$ K and $T = 343$ K are described by solid and broken curves, respectively. The curves were deduced by a theory first proposed by Langevin (1910) and later extended by other researchers. In the proposed theory, thermal agitation from the liquid molecules is assumed to randomize the grain direction. The Boltzmann average of the function $(3\cos^2\theta - 1)/2$ at a given temperature T is calculated from the free energy U induced in a single disk-shaped crystal in the presence of a magnetic field B,

$$U = -(NB^2/2)\{\chi_\perp + \Delta\chi \cos^2\theta\} \quad . \tag{1}$$

In the above equation, N denotes the mole number of the grain, and $\Delta\chi$ denotes diamagnetic anisotropy, which is defined as $\Delta_\chi = \chi_\parallel - \chi_\perp$. Here $\chi_\parallel$ and $\chi_\perp$ denote the molar susceptibilities parallel and perpendicular to the c-plane, respectively. An arbitrary $\langle m \rangle$-B relation is determined by three parameters, namely, N, $\Delta\chi$, and T. The theoretical curves of Fig. 2 are calculated by adopting $\Delta\chi$ values which yield the best fit to the measured data for the experimental temperatures. The values of N are obtained from the SEM observation mentioned above.

The relationships between the $\Delta\chi$ and T values obtained above are compiled in Fig. 3. The linear $\Delta\chi$–$1/T$ relations of each sample are attributed to the Curie dependence of paramagnetic anisotropy caused by impurity ions. The data of each sample follow different $\Delta\chi$–$1/T$ lines, depending on the concentration of para- magnetic ions and on the local fields of the impurity sites. The intercepts of the lines denoted $(\Delta\chi)_{T=\infty}$ correspond to the diamagnetic anisotropy of the respective samples. The $(\Delta\chi)_{T=\infty}$ values are obtained as $(5.8 \pm 7.5) \times 10^{-6}$ emu mol^{-1} for kaolinite-1 and $(10 \pm 3.5) \times 10^{-6}$ emu mol^{-1} for kaolinite-2 according to the regression analysis on the measured data of each sample, as is described in solid lines in the figure.

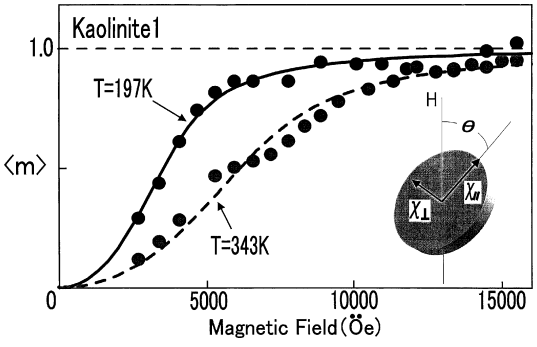

Fig. 2 Observed and calculated relations between field intensity B and the order parameter $\langle m \rangle = < (3\cos^2\theta - 1)/2 >$, indicating the degree of grain orientation for the kaolinite-1. *Solid and dashed curves* denote the theoretical fits to the measured data observed at $T = 197$ K and $T = 343$ K, respectively. The efficiency of the theory on grain alignment was examined experimentally by examining the expected dependences of the three parameters $\Delta\chi$, N, and T. The results for $T^{1/2}$ dependence are described in the text. The $N^{-1/2}$ dependence was examined by comparing the B_S value of grain suspensions of the same material with different size distributions. The $\Delta\chi$ dependences were examined by measuring five ceramic materials with different $\Delta\chi$ values (Uyeda et al. 1991, 1993a; Chihara et al. 1998)

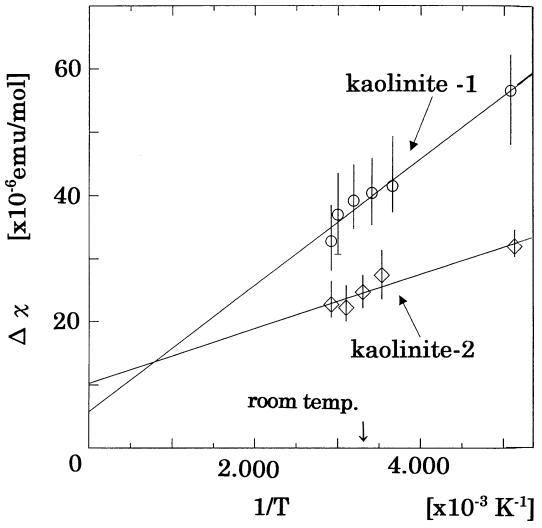

Fig. 3 The $\Delta\chi$–T relations obtained from measurements of kaolinite-1 (*open circles*) and kaolinite-2 (*open squares*). The *solid lines* denote the regressions to the measured data of each samples, calculated as $\Delta\chi = 9830(1/T) + 5.8$ [$\times 10^{-6}$ emu mol^{-1}] (correlation factor: 0.98) for kaolinite-1 and $\Delta\chi = 4120(1/T) + 10.3$ [$\times 10^{-6}$ emu mol^{-1}] (correlation factor: 0.95) for kaolinite-2

Discussion

To date, experiments on magnetic rotation of micron-sized materials have typically been performed at fixed room temperature, since the investigations were focused mainly on organic or biological material. To the best of our knowledge, the results plotted in Fig. 3 represent the first measurements of paramagnetic temperature dependence of magnetic rotation for ceramic microcrystals. Note that the $(\Delta\chi)_{\mathrm{DIA}}$ values depart significantly from the $\Delta\chi$ values measured at room temperature, indicating that evaluation of paramagnetic anisotropy is essential for elucidating the driving force of the magnetic rotation process. The paramagnetic and diamagnetic components of magnetic anisotropy in the micron-sized samples can be distinguished by performing precise $\Delta\chi$–T measurements. The $\Delta\chi$ values assumed from measurement at fixed temperature, which have often been interpreted as diamagnetic anisotropy of the material, may have included a finite amount of paramagnetic anisotropy. The $(\Delta\chi)_{\mathrm{DIA}}$ values of two kaolinite samples reported previously (Uyeda et al. 1993a) in terms of measurements at a fixed room temperature, were 32×10^{-6} emu mol^{-1} (Macon, Georgia) and 42×10^{-6} emu mol^{-1} (Mesa Alta, New Mexico). The values are comparable to those of kaolinite-1 and -2 measured at room temperature as seen in Fig.3, indicating that the major portion of the $(\Delta\chi)_{\mathrm{DIA}}$ values reported previously derive from the paramagnetic impurity ions.

The upper limit of the paramagnetic concentration at which the paramagnetic anisotropy becomes negligible as compared with the diamagnetic anisotropy may depend on the local crystal field of the paramagnetic site. For example, according to the $\Delta\chi$–T above-mentioned measurements by harmonic oscillation (Uyeda et al. 2000a), the paramagnetic $\Delta\chi$ component of a brucite sample (product of Ethel Mine, Zimbabwe) at room temperature is comparable to that of the diamagnetic component even when the molar concentration of paramagnetic ions is as low as 10 ppm. In contrast, paramagnetic anisotropy was negligible for a different brucite sample (product of Ural, Russia), which had a paramagnetic molar concentration (7 ppm) comparable to that of the brucite from Zimbabwe. The paramagnetic $\Delta\chi$ components of individual samples should be evaluated quantitatively by performing $\Delta\chi$–T measurements or by performing magnetic analysis of individual local sites by ESR measurements (e.g., Ballet and Coey 1981).

The difference between the $(\Delta\chi)_{T=\infty}$ values observed for the two kaolinite samples is too large for determining an intrinsic $(\Delta\chi)_{\mathrm{DIA}}$ value for pure kaolinite. The harmonic-oscillation measurements (Uyeda et al. 2000a,b) yield $(\Delta\chi)_{T=\infty}$ values that converge to an approximately singular value with a deviation of less than $+10\%$, and the average of the $(\Delta\chi)_{T=\infty}$ values is adopted as the intrinsic $(\Delta\chi)_{\mathrm{DIA}}$ value of the material. The major cause of the scattering observed in the present study on kaolinite derives from the small temperature range of the experiments, which according to Fig. 3 was about 150 K. This range is much smaller than that adopted in the bulk measurements in the high-temperature region, which has a width of nearly 500 K (Uyeda et al. 2000a, b). The uncertainty in the gradient of the $\Delta\chi$ $-1/T$ line increases with reduction of the temperature range, which may cause the scattering of $(\Delta\chi)_{T=\infty}$ values. Note that the present experimental procedure cannot be used for rotation measurements of microcrystals at temperatures above the boiling point of ethanol (348 K). Inert gases are candidate-dispersing mediums that might preserve the suspended grains up to $T = 800$ K. The magnetic grain alignments of diamagnetic grains dispersed in Ar gas at room temperature was recently realized for the first time (Uyeda and Sakakibara 2001), and serves as a technical basis for developing a system to detect the precise $\Delta\chi$–$1/T$ relation of microcrystals in the high-temperature region. Note that conducting the experiments in the gas phase also enables $\Delta\chi$–T measurements below the melting point of ethanol ($T = 158$ K), which provides the basis for reproducing interstellar dust alignment.

The origin of diamagnetic anisotropy has been studied mainly in organic materials since Pauling (1936) gave theoretical explanations of the large anisotropies observed in simple aromatic materials. The anisotropy was attributed to an anisotropic spatial distribution of electrons in organic molecules. A preliminary model assumed for the purpose of investigating the origin of the observed $(\Delta\chi)_{\mathrm{DIA}}$ values in oxide minerals was proposed on the basis of the spatial anisotropy of individual bonding orbital between oxygen atoms and their near neighbors (Uyeda 1993c; Uyeda et al. 2000b, 2001). Individual orbital was assumed to possess finite amounts of uni-axial diamagnetic anisotropy. This model was effective in

interpreting the magnitudes of measured $(\Delta\chi)_{DIA}$ values and the directions of magnetically stable axes in individual oxides. The $(\Delta\chi)_{DIA}$ values assigned to a chemical bond were $(\Delta\chi)_{OH} = 0.7 \times 10^{-30}$ emu for a hydrogen bond, and $(\Delta\chi)_{TO} = 3.5 \times 10^{-30}$ emu for a T–O bond composing the tetrahedral [TO_4] blocks. For both types of orbital the bond direction is the magnetically unstable axis. These results indicate that noncubic oxide minerals generally possess a finite diamagnetic anisotropy. Further $(\Delta\chi)_{DIA}$ values are required in order to evaluate this model quantitatively. Measurements of $(\Delta\chi)_{DIA}$ values are required especially for oxides belonging to sheet silicates and zeolite groups, because they are expected to exhibit anisotropic spatial distributions of bonding orbitals that are significantly larger than those in oxides with higher symmetry. Contemporary methods cannot perform $\Delta\chi$ measurements for many of the oxides belonging to these types of oxides, because of their minute crystal sizes and the existence of paramagnetic impurity ions. A method for measuring the $(\Delta\chi)_{DIA}$ values from microcrystal grains is essential for obtaining an overall view of diamagnetic anisotropies in inorganic oxides.

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