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Effective Parameters on the Magnetic Alignment Process of Nonmagnetic Inorganic Micro-Crystals Dispersed in a Fluid Medium Including the Inert Gas

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The effective parameters, which control the process of magnetic alignment, are discussed quantitatively for the diamagnetic inorganic micro-crystals dispersed in the fluid medium. It is deduced from the Langevin theory that the process is controlled by three parameters, namely temperature T, mole number of the crystal N and the magnetic anisotropy of the crystal per moll $\Delta\chi$. The possibility of decreasing the field intensity to achieve magnetic alignment is discussed based on the experimental examination of the effects of three parameters, which may increase the possibility of developing new material processing procedure in terms of diamagnetic grain alignment. An apparatus to observe magnetic orientation of grains dispersed in the gas medium is developed as a technical step forward to realize magneto-rotation in the high and low temperature region, where the fluid medium is not preserved. The field intensity to achieve magnetic alignment is expected to reduce considerably with the decreasing temperature.

Key words: diamagnetic anisotropy, inorganic material, magneto-rotation, magnetic alignment, gas, cryogenic condition

1. INTRODUCTION

Solid materials generally possess an efficiency of magneto-rotation due to the anisotropy of diamagnetic susceptibility. Krishnann and Banarjee[1] studied the magnetic anisotropy of various materials systematically in the 1930's on both magnetic and non-magnetic materials. The diamagnetic anisotropy$(\Delta\chi)_{DIA}$ of aromatic molecular crystals were more than three orders of magnitudes larger compared to those of inorganic oxides such as quartz or calcite. The origin of the large anisotropies found in the aromatic molecules were explained by Pauling[2] in terms of the spatial anisotropies of the molecular orbital, which became the concept for interpreting the observed $(\Delta\chi)_{DIA}$ values of insulators. The experiments on magneto-rotation have been carried out mainly on organic materials.[3-5] At first the effect has been applied on material processing such as polymerization or crystal growth for organic and biological materials[5].

The experiments on magnetic-rotation had been performed for diamagnetic particles dispersed in a liquid medium. The relation between the field intensity and the degree of orientation was expected to depend explicitly on temperature T, since the balance between the field-induced anisotropy energy and the thermal agitation energy was assumed to drive the process. The experiments were preformed mainly at room temperature partly because the biological materials might deform by large temperature alteration.[3-7] The effect of other parameters which control the magnetic-alignment process, namely the moll number of the particle N and the magnetic anisotropy of the material per moll $\Delta\chi$, has not been studied on organic materials as well.

Magneto-rotation was not studied intensively for the inorganic diamagnetic materials because their $(\Delta\chi)_{DIA}$ values were considered to be much smaller compared to the organic materials. Field intensities to achieve magneto-rotation of inorganic materials such as kaolin, talc,[8] lepidolite, phlogopite, muscovite,[9] graphite,[10] Al_2O_3[11] and various inorganic materials[12] usually exceeded several tesla. The small $(\Delta\chi)_{DIA}$ values of various inorganic oxides were obtained by the present author from bulk crystal measurements by introducing a method based on the field-induced rotational harmonic-oscillation of the sample in the high-field condition.[13] The sensitivity as high as 1.3x 10^{-12}emu/sample was achieved by this method.[14] The $(\Delta\chi)_{DIA}$ values were newly obtained for some basic oxides such as forsterite [Mg_2SiO_4],[15] corundum[Al_2O_3], bruccite[$Mg(OH)_2$], gibbsite[$Al(OH)_3$], diaspore[$AlOOH$][16] muscovite[$KAl_2Si_3AlO_{10}(OH)_2$],[16] orthoclase[$KAlSi_3O_8$],apophylite,scapolite,[17] gypsum [$CaSO_4 2H_2O$], ADP and KDP.[18] The measured data were explained quantitatively by assuming that the individual chemical bond consisting the material possessed a constant amount of diamagnetic anisotropy.[15,18]

The results of the experimental examinations on the effects of the three parameters are compiled in the present paper. It is deduced from the measured results that the field intensity to achieve magnetic-alignment is reduced considerably by controlling the T, N and $\Delta\chi$ values.[19,20] The reduction of the field intensity increases the possibility of developing a new procedure on material processing due to diamagnetic alignment.

2. MECHANIZM OF MAGNETIC ALIGNMENT OF GRAINS DISPERSED IN A FLUID MEDIUM

The degree of grain alignment at a field intensity B had been analyzed by a formula first proposed by Langevin,[21] which was extended later by Beams[22], Buckingham et al.[23], Peterlin et al.[24], Twersky[25], Maret et al[4] and Yamagishi et al.[26] The free energy U of single grain induced in the field is described as,

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

where θ denotes the angle between the field B and the magnetically stable axis of the particle. The mole number of the particle is given by N in eq.(1). The anisotropy of molar magnetic susceptibility is described as $\Delta\chi=\chi_{//}-\chi_{\perp}$ where $\chi_{//}$ and $\chi_{\perp}$ denote the susceptibility in the direction parallel and perpendicular to the magnetically stable axis, respectively. The measured micron-sized single-crystal possessed an uniaxial-type of diamagnetic anisotropy. Its magnetically principal axis (c-axis) of the crystal grain is normal to the disk plane of the grains. The degree of orientation is described by an order-parameter $<m>$, which is commonly used to describe the state of molecular orientation in the liquid crystals. The parameter is calculated numerically from the Boltzmann average of a function $(3\cos^2\theta-1)/2$ at a given temperature T in terms of the free energy U expressed in eq.(1).,

$$<m>=<(3\cos^2\theta-1)/2>, \qquad (2)$$

Here $<m>=0$ and 1 correspond to completely random state and to the completely ordered state of the grains, respectively. It is deduced from eqs. (1) and (2) that a $<m>$-B relation is dominated by three parameters, namely T, $\Delta\chi$ and N. The theoretical fit to the experimental $<m>$-B relation was calculated generally by the use of eq.(2) by adopting the $N\Delta\chi$ values showing the best fit to the experimental data.

The field of full orientation, denoted as B_S, was introduced tentatively for the purpose of proceeding quantitative analysis on the $<m>$-B relation. B_S was defined as the field intensity at which $<m>=0.8$ is achieved. The state of full orientation, corresponding to $<m>=1$, cannot be obtained at a finite field intensity. B_S was calculated as,[8,9,19,20]

$$B_S=(15k_BT/N\Delta\chi)^{1/2} \qquad (3).$$

The dependences of the parameters T, $\Delta\chi$ and N mentioned above on the $<m>$-B relation are expressed explicitly in the above equation. The field to achieve magnetic alignment is expected to decrease by the increase of $\Delta\chi$ and N, and by the decrease of T.

3. EFFECTS OF THE PARAMETERS $\Delta\chi$, N, and T ON THE MAGNETIC ALIGNMENT PROCESS

Experimental examinations of the Langevin theory was carried out by varying the three parameters N, $\Delta\chi$ and T. A He-Ne laser beam was transmitted through sample suspension in a direction parallel to the magnetic field. The degree of orientation $<m>$ can be obtained from the observed relation between B_i and the variation of light intensity $\Delta I(B_i)$ transmitted through the grain-suspended medium. This is because the optical principal axis of the disk- shaped grain coincides with that of the magnetic principle axis.

The contribution of parameter N was examined by comparing the B_S value of grain suspensions with different size distributions of the same material.[8,9] The $N^{1/2}$ dependence of B_S was confirmed in the range of 10^{-10} to 10^{-12}mole. The measurement was performed for several kinds of materials having different orders of $\Delta\chi$ values.[8,9] The results revealed that the $\Delta\chi$ values of individual materials dominate the B_S values as well.

The temperature dependence of magnetic grain alignment was measured between room temperature and 175K for graphite grains dispersed in liquid ethanol[19]. This medium was effective to realize the experiment since it can disperse the graphite grains and also remain as the dispersing liquid below room temperature. It was adopted as a dispersing medium after many trials on different types of liquid. The theoretical fit to the experimental $<m>$-B relation were given by the calculation based on eq.(2). The $N\Delta\chi$ value adopted in the calculation was consistent with the values calculated from the grain size observed by the Scanning Electron Microscope (SEM) and the published $\Delta\chi$ values of graphite. It is seen that the trend of the experimental B_S values follows the theoretically expected $T^{1/2}$ dependence as expected in eq.(3). The observed temperature dependences demonstrated directly for the first time that the process of magnetic alignment is controlled by the Brownian thermal rotation

4. MAGNETIC ALIGNMENT IN THE GAS MEDIUM

The magneto-rotation of diamagnetic material dispersed in the gas medium has been detected quantitatively for the first time by the present authors.[26] The experimental setup was based on the optical methods to detect magnetic alignment of small particles dispersed in liquid as mentioned before.[8,9] Two improvements were necessary to realize the experiment. Firstly, the inner size of the sample chamber in which the grain-dispersed gas was contained was increased to be as large as 200mm in diameter and 400mm in height. The reduction rate of the grain population in the gas medium was serious when the chamber was smaller than this size, since grains were removed from the gas medium rapidly by its attachment to the inner wall. The chamber was placed at the center of a Helmholtz-coil system having a size large enough to produce homogeneous field up to 0.05T within the spherical area of 500mm in diameter at the center of the system. Consequently the two equivalent coils of the Helmholtz system had the inner diameter as large as 1000mm separated 570mm with each other.

The second improvement was made to preserve the $\Delta I(B_i)$ intensity. The population density of the grain in the gas medium is considerably small compared to the conventional systems for measuring grains dispersed in liquid. Quantitative measurement was difficult by using the conventional laser beam section.[8,9,19] The diameter of the beam section is hence widened to ϕ 100mm. The laser beam was formed into a wide parallel beam by a convex lens and transmitted through the gas suspension. The beam reflected by a flat mirror was transmitted through the suspension again and is focused on a detector by the convex lens.

The $\langle m \rangle$-B curve was calculated by eq.(2) which gives the best fit to experimental values. The agreement between observed and calculated $\langle m \rangle$-B curve confirms that the balance between the thermal agitation and the diamagnetic anisotropy energy determines the process of magnetic orientation in the gas medium, although the viscosity of the medium is two orders of magnitude smaller compared to the previous experiments done in the liquid medium.[8,9] The orientation was achieved at a low field intensity of B_s =0.014T since the $(\Delta\chi)_{DIA}$ value of graphite was exceptionally large compared to other inorganic insulators.[27] The B_s value is expected to decrease even more when the temperature is reduced considerably, which can be realized only in the gas phase as discussed in the next section.

5. DISCUSSION

The observed temperature dependences of magnetic grain alignment indicate the field intensity to achieve magnetic orientation is reduced even more at temperatures below the melting point of ethanol. Cryogenic liquids such as N_2 or He could not be used as a dispersing medium since micron-sized grains in general do not disperse efficiently in these medium. The only possible dispersing medium below T=100K is the inert gas.

A preliminary model was proposed to explain the origin of the diamagnetic anisotropies, based on the accumulated $(\Delta\chi)_{DIA}$ values mentioned above.[16,17] It was assumed in the model that the spatial anisotropy of individual bonding orbital between the O^{2} ion and the cations possesses a finite amount of diamagnetic anisotropy, and that the principal axis of the anisotropy was identical to the bond direction. The model gave a quantitative explanation to the experimental values as well as to the observed magnetic principal-axes of the material.

Further data accumulation was required to evaluate the efficiency of the model, especially for the oxides with low crystal symmetry. However, the compiling could not be carried out for materials such as the sheet-silicates and the zeolite materials because single-crystals large enough to perform bulk $\Delta\chi$ measurements were difficult to obtain for these materials in many cases. Bulk $\Delta\chi$ measurements are difficult when the size of the obtainable single-crystal is smaller than one millimeter in diameter. The magneto-rotation measurement on micro-crystals suspended in the fluid medium had been the unique method to estimate the $(\Delta\chi)_{DIA}$ values in such cases. It has become clear that the evaluation of paramagnetic anisotropy due to the impurity ions are essential in determining the exact $(\Delta\chi)_{DIA}$ values. The $\Delta\chi$-$1/T$ relation of the Curie law should be measured in the high temperature near T= 1000K, since the interference due to the Weiss-field becomes significant in the low temperature region. It is obvious that the measurement cannot be performed at temperatures above the boiling point of ethanol or other liquid medium by means of the conventional system. One solution to this problem is to disperse the particles in the gas medium and control the temperature of the gas. The experimental setups to realize the magnetic grain orientation in the high and low temperature regions are now being developed separately.

The measured results demonstrates that the magnetic alignment can be achieved a low field intensity by controlling the three parameters, T, N and Δ. The possibility of developing new procedure on material processing may increase considerably when the Bs value is reduced to the order below 1 tesla.

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