Anomalous magnetic properties of heavily Tb-doped glasses

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Tb-doped glasses usually show a paramagnetic character. Recently, glasses have been successfully doped with Tb^{3+} ions in heavy concentrations of more than 10 at. %. These glasses show magnetic properties different from the conventional paramagnetic behavior. However the mechanism of their anomalous magnetic properties has not been clarified yet. In this study, we prepared heavily Tb-doped glasses and investigated their magnetic and magneto-optical properties. We observed some results that indicate a slower relaxation process of more than 1.0 sec.

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I. INTRODUCTION

Rare-earth-doped glasses have been researched intensively regarding their magnetic properties and Faraday effects by many authors. Among those, Tb-doped glasses have the largest Verdet constant.[1,2] In the magnetic and magneto-optical properties, $4f$ electrons play an important role. In the case of a Tb^{3+} ion, the ground state of $4f$ electrons is expressed by $^7F_6$ as a J multiplet. Even in a glass, the electronic property of $^7F_6$ is preserved because $4f$ electrons are well shielded by the outer electrons of $5s$ and $5p$. Therefore, it is considered that in glass, Tb^{3+} ions are well isolated from each other and that there are no exchange or superexchange interactions even among the nearest ions. Here, Tb-doped glasses show paramagnetic behavior and their Faraday effect is proportional to magnetization; this phenomenon is called ''paramagnetic Faraday rotation.''[3] However in a low-temperature range and under high magnetic fields, it was reported that the magnetic and magneto-optical properties of Tb-doped glasses are different from the paramagnetic behavior.[4,5] Recently, magnetic and magneto-optical properties for heavily rare-earth-doped glasses at more than 10 at. % were reported. Yuan and co-workers reported these magnetic properties as ''superparamagnetic'' where magnetic clusters are formed.[6,7] In our investigation, we observed a behavior of heavily Tb-doped glasses that is different from the paramagnetic property, due to random interactions among Tb^{3+} ions.

We prepared a heavily Tb-doped glass with a Tb^{3+} ion concentration of 15.6 at. % and performed measurements of magnetization and Faraday effect under pulsed magnetic fields of up to 15 T in a temperature range between 10–250 K. In addition to these, measurements of temperature dependence of ac susceptibilities under dc magnetic fields were performed. By these measurements, we found that a certain relaxation process is dependent on the magnitude of external magnetic fields. We aim to understand the physical mechanisms of the magnetic properties in heavily Tb-doped glass, where they have never been reported before.

II. EXPERIMENTS

In this study we experimented on several Tb-doped glasses fabricated by SUMITA Optical Glass Manufacturing, Inc. Japan and mainly conducted a series of experiments on a glass that contains 15.6 at. % of Tb^{3+} ions (1.29×10^{28} Tb^{3+}/m^3). From this value, the mean distance between Tb^{3+} ions can be estimated as 4.26 Å. The composition of the glass is as follows: $35Tb_2O_3+20B_2O_3+25SiO_2+19.5Ga_2O_3+0.5Sb_2O_3$.

The samples had a cylindrical shape of 2 mm in diameter and 5 mm in length, and their end surfaces were polished for optical improvement. Pulsed magnetic fields reaching 15 T were produced by discharging currents from a 35-mF condenser bank. The rise up and decay time of the applied magnetic fields are 24 ms and 100 ms, respectively, which are long pulsed fields in comparison to other reported experiments.[4,5] The sample magnetization was detected by time derivatives (dM/dt) with a pickup coil. In Faraday effect measurements, we obtained the light source by using a halogen lamp with monochromatic color filters ranging between 460–700 nm. Light was transmitted to the sample through an optical fiber and irradiated with a linear polarizer. Light coming out from the opposite surface was guided by an optical fiber to a photomultiplier tube. Two optical polarized sheets (HN22 KOYO) were used as the polarizer and analyzer. In these experiments, the ambient temperature was controlled by a closed-cycle refrigerator system in a range between 10–250 K with an accuracy of about ± 0.5 K. Figure 1 shows an example of the Faraday rotation of this glass.

III. RESULTS

The magnetization of the sample was cross checked by using a superconducting quantum interference device

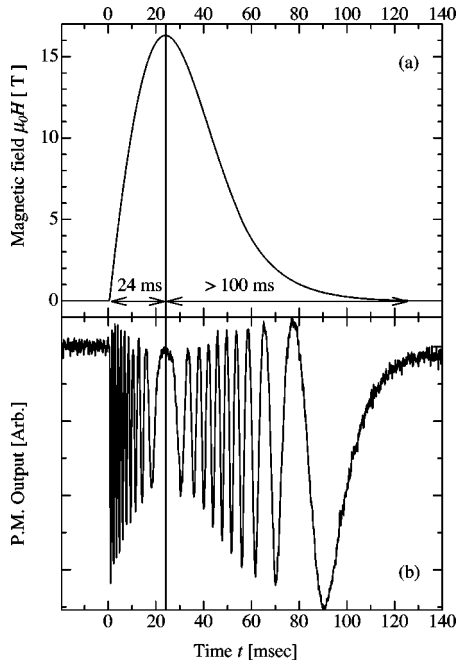

FIG. 1. (a) Wave profile of the pulsed magnetic field. (b) Typical result of the Faraday rotation measurement of the sample.

magnetometer and also the temperature dependence of the magnetization was measured. Figure 2 shows the magnetization curve of the sample under dc magnetic fields at a temperature of 6.5 K, experimental values represented by solid squares. The magnetization became almost saturated under magnetic fields higher than 5.5 T. The solid line in Fig. 2 shows a curve calculated by the Brillouin function for the corresponding ion concentration of the present sample. In this case, the actual sample magnetization was experimentally found to be 0.69 T (550 emu/cm^3), which is about 40% smaller than the value calculated by the single-ion

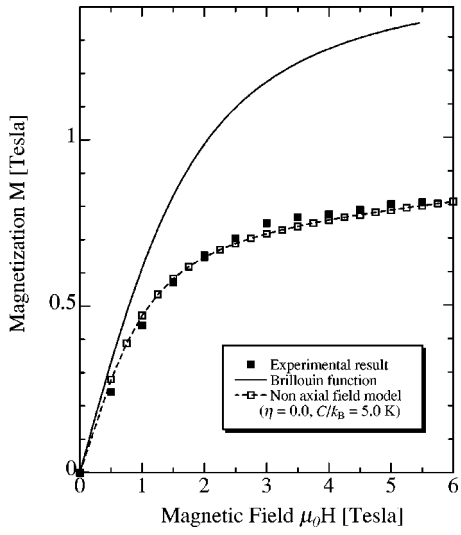

FIG. 2. Magnetization of the sample as a function of the applied dc field at $T=6.5$ K. Experimental result is shown by solid squares; solid line is calculated by the Brillouin function and dashed-squared line indicates the least-squares fit.

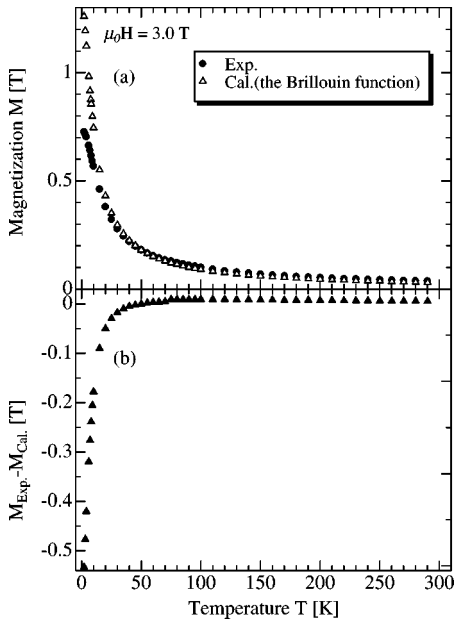

FIG. 3. Magnetization of the sample as a function of temperature at a dc magnetic field of 3.0 T. (a) ● and △ denote the experimental result and the value calculated by the Brillouin function, respectively. (b) Sample's deviation from the calculated value.

model. Here, we adopted the following parameters: Lande's g factor, $g=1.47$; total angular momentum, $J=6$; and the number of Tb^{3+} ions per unit volume, $N=1.29\times10^{28}$ (Tb^{3+}/m^3). On the other hand, the dashed-squared line in the figure shows a fitting result that includes a crystal-field effect. We will discuss its details in a later section. Figure 3(a) shows an experimental result and a result calculated by the Brillouin function as a function of temperature ranging between 4.5–300 K in an applied magnetic field of 3.0 T, and Fig. 3(b) shows its deviation from the calculated value. It shows that the experimental result is well fitted to the Brillouin function in a temperature range higher than 50 K, however for temperatures lower than 40 K, it abruptly deviates from the calculated value as temperature decreases. The results of Figs. 2 and 3, which are different from those of the Tb-doped glasses at usual concentration, mean that the present glasses do not obey a simple paramagnetic behavior.

On the other hand, the dc magnetic susceptibility of this sample in a low magnetic field of 1.0×10^{-3} T obeyed the Curie-Weiss law with a Weiss point of $\theta=-0.7$ K, as shown in Fig. 4. We also measured the temperature dependence of the ac susceptibilities in a frequency range between 10–1 kHz in an applied field with an amplitude of 3.0×10^{-4} T. The results of ac susceptibilities showed the same temperature dependence of the dc susceptibility and no frequency dependence. Furthermore, neither dc nor ac susceptibilities showed the difference between the zero-field-cooled and the field-cooled treatments.

Figure 5 shows experimental results of magnetization versus pulsed magnetic field at three different temperatures, 14 K, 45 K, and 110 K. In this figure, all of them have a nearly linear dependence on the applied magnetic fields. Here we should notice the fact that the magnetization at 14 K is

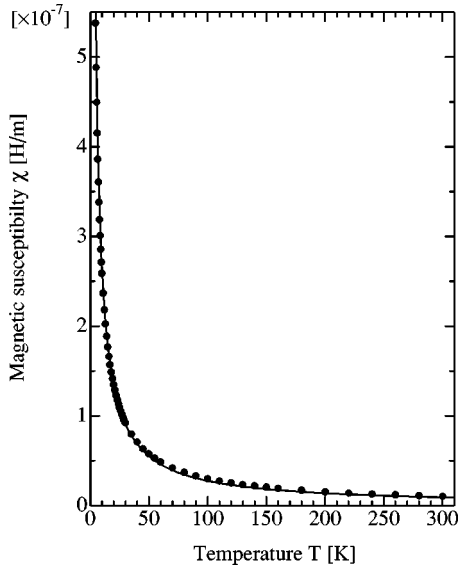

FIG. 4. Magnetic susceptibility of the sample under a low-dc magnetic field of 1.0×10^{-3} T. The solid line in this figure shows a result of the least-squares fit.

smaller than that at 45 K. On that point Fig. 6 shows the temperature dependence of the magnetization under pulsed magnetic fields. The magnetization increases with decreasing temperature in a temperature range higher than 45 K, i.e., a paramagnetic behavior. On the contrary, below 45 K, it decreases with decreasing temperature. Adapting the Curie-Weiss law in the higher-temperature range above 45 K, the Weiss point was estimated at -21 K under an applied field of 3.3 T. Figure 7 shows experimental results of the reciprocal Verdet constant dependence on light wavelength in pulsed fields. As shown in this figure, the reciprocal Verdet

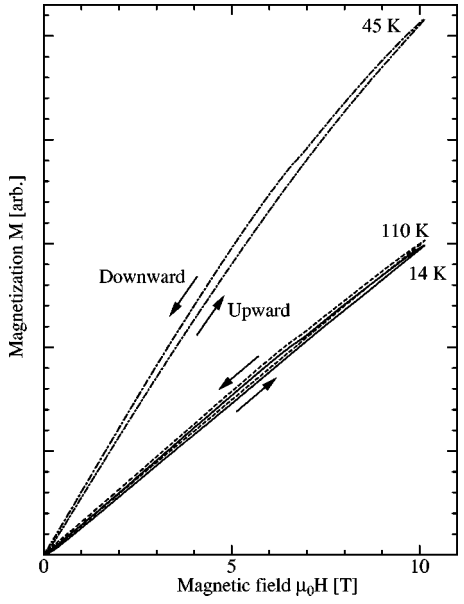

FIG. 5. Magnetization curves of the sample under pulsed magnetic fields at various temperatures. Upward ''→'' and downward ''←'' indicate an increase and a decrease of pulsed magnetic fields, respectively.

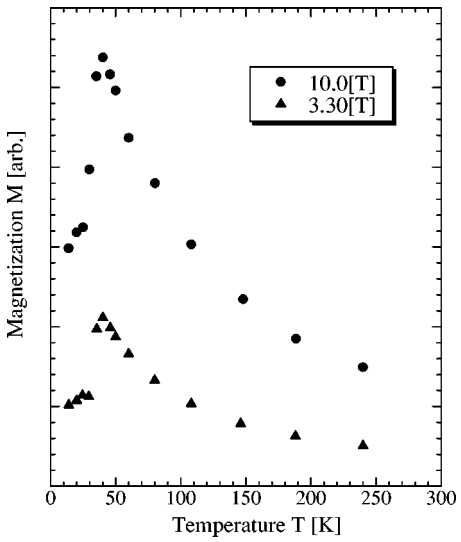

FIG. 6. Temperature dependence of the magnetization under pulsed magnetic fields of 3.3 T and 10.0 T.

constant is proportional to $(\lambda^2-\lambda_0^2)/C$.[3] Here, λ_0 and C denote a resonant wavelength and a proportional constant at an ambient temperature, respectively. From these results, we found no wavelength-dependent anomaly. Figure 8 shows the temperature dependence of the Verdet constant at a wavelength of 460 nm under an applied magnetic field of 3.0 T. It should be noticed that the Verdet constant shows a peak at around 40 K and has a temperature dependence similar to that of the magnetization detected with the pickup coil. We calculated the Weiss point from the result of the Verdet constant and it was found to be -24 K. Here we would like to point out that the temperature dependence of the Verdet constant and that of the magnetization do not obey a paramagnetic character.

We presume that the appearance of these anomalous phenomena observed under pulsed magnetic fields need both high magnetic fields and their time variation. Therefore, to confirm this presumption, ac susceptibility measurements were performed under external dc magnetic fields of

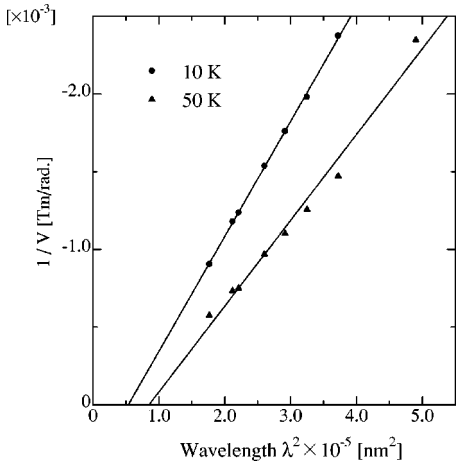

FIG. 7. Wavelength dependence of the reciprocal Verdet constant at two different temperatures, 10 K and 50 K.

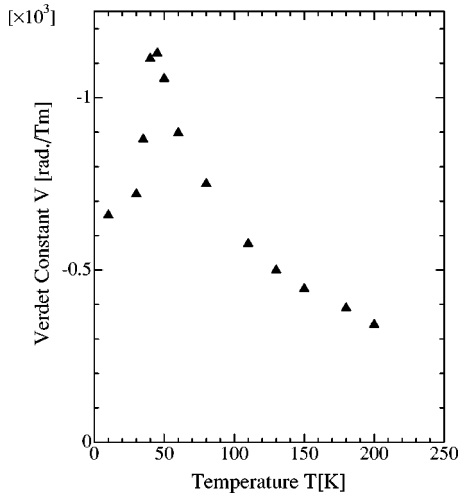

FIG. 8. Temperature dependence of the Verdet constant under a pulsed magnetic field of 3.0 T.

$\mu_0 H_{dc}=0.0$, 0.25, and 1.0 T. The results are shown in Fig. 9. Under $\mu_0 H_{dc}=0.25$ T, in-phase χ' slightly deviates from that without the external dc magnetic fields below 30 K and out-phase χ'' shows a peak at 6.0 K. Under a higher field of $\mu_0 H_{dc}=1.0$ T, χ' shows a noticeable peak at 13 K and the peak of χ'' increases and shifts to the higher temperature of 8.5 K. Figure 10 shows the in-phase χ' and out-phase χ'' under the dc magnetic field of $\mu_0 H_{dc}=1.0$ T at various frequencies of the ac magnetic field: $f=1.0$, 10.0, and 120 Hz. The peak value of χ' increases and its position shifts from 14–13 K while decreasing the frequency from 120–1.0 Hz.

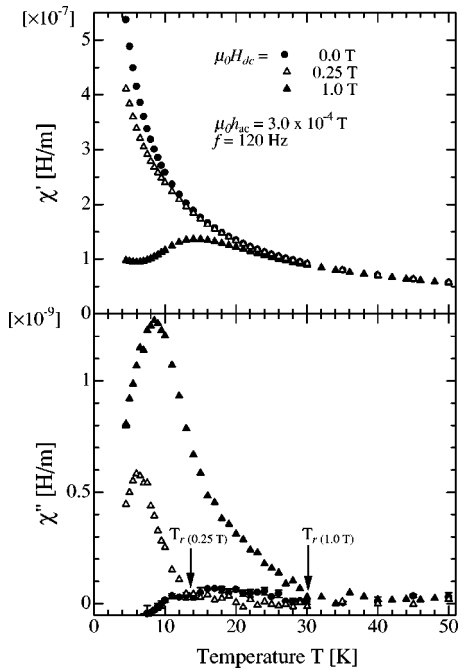

FIG. 9. Ac susceptibilities under various external dc magnetic fields. The applied ac magnetic field has an amplitude of 3.0×10^{-4} T and a frequency of 120 Hz. T_r denotes the temperature below which the increase of χ'' is observed (see text).

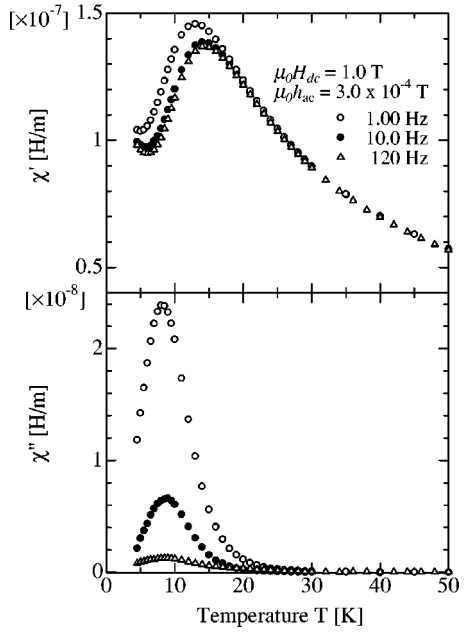

FIG. 10. Ac susceptibilities at various frequencies of an ac magnetic field. The intensity of the dc magnetic field was set at 1.0 T.

The out-phase χ'' begins to increase at about 30 K and shows a peak at 8.5 K, its intensity increasing with decreasing frequency.

IV. DISCUSSION

Slightly Tb-doped glasses show paramagnetic behavior due to isolated and noninteracting Tb^{3+} ions as an aggregation of free ions.[8] Even on our heavily Tb-doped glass, magnetic susceptibilities obey the Curie-Weiss law in low-dc and -ac magnetic fields. However under the high pulsed magnetic fields used in this study, both the magnetization and the Verdet constant showed an anomalous peak in their temperature dependence. Yuan and co-workers have found that their heavily Tb-doped glasses had a large absolute value of Néel temperature and reported the existence of a superparamagnetic structure in which oxygen and terbium ions form clusters.[6,7] At first, we have also tried to explain the anomalous phenomenon of a decrease in the magnetization with decreasing temperature below 45 K as a thermal fluctuation aftereffect caused by a superparamagnetic structure. In general for superparamagnetic materials, the blocking temperature or the difference between the experimental results of FC and ZFC treatments are observed in the temperature dependence of the magnetic susceptibility.[9] However, neither the blocking temperature nor the difference between ZFC and FC measurements were observed for the sample in the present experiment. Nor was observed a frequency dispersion from the results of ac susceptibility measurements in the absence of external dc magnetic fields superposed on ac magnetic fields. Therefore we do not agree with the idea that the anomalous behavior under pulsed magnetic fields is caused by the aftereffect based on a cluster superparamagnetic model. We propose other mechanisms to explain the anomalous results obtained in this study. To discuss their

possibility, we review the ground state of Tb^{3+} ions and, in doing so, we notice that they have a large orbital angular momentum ($L=3$), which in turn leads us to concentrate on the influence of crystal fields.

Here, in our approach to the problem, we adopt a nonaxial crystal field Hamiltonian H_{CF} expressed by Eq. (1), as proposed by Fert and Campbell[10] and Borchi and De Gennaro[11] when treating crystal fields in rare-earth Fe alloys.

$$H_{CF}=\alpha J_{x_i}^2+\beta J_{y_i}^2+\gamma J_{z_i}^2. \tag{1}$$

α, β, and γ are functions of both η and C as follows:

$$\alpha=\frac{3-\eta}{6}C, \quad \beta=\frac{\eta}{3}C, \quad \gamma=-\frac{3+\eta}{6}C. \tag{2}$$

$$(-1\leqslant\eta\leqslant 1). \tag{3}$$

In these expressions, J_{x_i}, J_{y_i}, and J_{z_i} are the angular momentum components of the ith Tb^{3+} ion with respect to the local principal axes, η is the asymmetric parameter, and C is the parameter representing the crystal-field strength. In the case of $\eta=1$, by introducing $J_i^2=J_{x_i}^2+J_{y_i}^2+J_{z_i}^2$, Eq. (1) can be rewritten as $H_{CF}=-CJ_{z_i}^2+\frac{1}{3}CJ_i^2$, which is equal to a uniaxial crystal field under which its ground state becomes the doublet $|J_{z_i}=\pm 6\rangle$. In the opposite case of $\eta=-1$, the equation can be rewritten as $H_{CF}=CJ_{x_i}^2-\frac{1}{3}CJ_i^2$ under which its ground state becomes the singlet $|J_{x_i}=0\rangle$. When applying an external magnetic field H_{ex} to the z axis of the fixed coordinate frame, the Zeeman term is expressed by

$$H_{Zeeman}=-g\mu_B H_{ex}(\cos\theta_i J_{z_i}+\sin\theta_i\cos\phi_i J_{x_i} + \sin\theta_i\sin\phi_i J_{y_i}), \tag{4}$$

where θ_i and ϕ_i are, respectively, the angles measured from the z axis and x axis of the fixed coodinate frame. In this case, the total Hamiltonian becomes $H_{tot}=H_{CF}+H_{Zeeman}$ and then an expectation value of $\langle J_z\rangle_i$ at the ith site can be obtained by the following equation:

$$\langle J_z\rangle_i=\frac{\mathrm{Tr}(J_z\rho)}{\mathrm{Tr}(\rho)}, \tag{5}$$

where ρ is a density operator defined as $\rho\equiv e^{-H_{tot}/k_BT}$. On the assumption that θ_i and ϕ_i are randomly and equally probably distributed, by taking the spatial average over θ_i and ϕ_i, the magnetization of the sample can be obtained.[11] We made this calculation taking into account all crystal-field splitting levels. In this manner, we obtained $C/k_B=5.0$ K and $\eta=0.0$ from the fitting process. The energy level for Tb^{3+} as a function of η is shown in Fig. 11. There, the crystal-field splitting of its ground doublet is $\Delta\epsilon_{CF}/k_B=5.0\times10^{-3}$ K, which can be negligible because it is much smaller than the thermal energy at our experimental temperature ($T=6.5$ K). The first excited state is located at $\Delta E_{CF}/k_B=39$ K above the ground doublet. Therefore we can consider the ground state of the Tb^{3+} ion as a degenerated doublet in this glass.

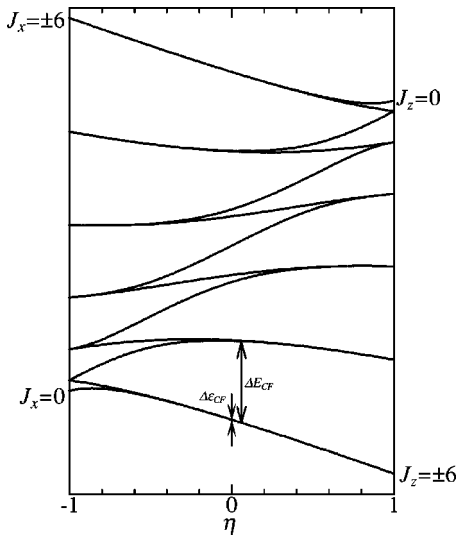

FIG. 11. Energy-level scheme for a Tb^{3+} ion subject to a nonaxial crystal field as a function of η. $\Delta\epsilon_{CF}$ and ΔE_{CF} are, respectively, the energy splitting of the ground doublet and the energy difference between the ground doublet and the first excited state.

On the basis of this consideration, we discuss the dynamic properties of this glass. From the results of ac susceptibility measurements under external dc magnetic fields as shown in Fig. 9, especially those of the χ,'' it is obvious that the relaxation process depends on the magnitude of the external dc magnetic field. We consider that this phenomenon and that observed under the pulsed magnetic fields have the same origin, namely, the relaxation process, though in the temperature-dependence characteristics of χ' ($\mu_0H_{dc}=1.0$ T) and the magnetization under pulsed magnetic fields, their peaks' positions are different (see Figs. 8 and 10). From the results of the frequency dependence of χ' and χ'' under $\mu_0H_{dc}=1.0$ T in Fig. 10, it is observed that their peaks' intensities do increase with decreasing frequency f from 120–1.0 Hz, thus f_c can be lower than 1.0 Hz (f_c is defined as the frequency causing the maximum of the peak's intensity of χ''). Therefore the characteristic relaxation time $\tau=1/\omega_c=\frac{1}{2}\pi f_c$ is expected to be over 1.0 sec at $T=8.5$ K. Integrating the present results, some anomalous magnetic properties of this glass indicate the appearance of a slow relaxation process in a low-temperature range and in the presence of external magnetic fields. From the result of the dc field dependence of the χ'' in Fig. 9, we define the characteristic temperature T_r below which the increase of χ'' is observed. That is to say, the relaxation process takes place when the temperature is decreased below the value T_r. Here the empirical values are estimated as $T_r=12$ K in the case of $\mu_0H_{dc}=0.25$ T and $T_r=30$ K at $\mu_0H_{dc}=1.0$ T.

Regarding the reason why the slow relaxation process appears only in the presence of external magnetic fields: although we are not able to explain its detail at present, we infer that coupling between a disordered crystal structure and magnetic moments of the Tb^{3+} ion plays a part. The short average distance between a Tb^{3+} ion of 4.26 Å due to its heavy concentration and external dc magnetic fields produces the magnetic relaxation observed in this study.

V. CONCLUSIONS

For the conclusions of this study we would like to point out two things. First, from the result of the dc magnetization measurement, we found that in this Tb-doped glass, the ground state of the Tb^{3+} ion in a low-temperature range should be considered as a doublet that is caused by the uniaxial crystal field whose axes are distributed randomly, i.e., the Tb^{3+} ion couples with a disordered crystal structure. Second, under pulsed magnetic fields, the magnetic properties of our glass sample were evidently different from those of paramagnetic or superparamagnetic materials. Both the magnetization and the Verdet constant did not show paramagnetic behavior and showed an anomalous peak at about 45 K. Furthermore the ac susceptibilities were measured under external dc magnetic fields, and it was found that their behavior depends on the field's intensity. Under a dc magnetic field of 1.0 T the in-phase χ' shows a noticeable peak at 14 K, while the out-phase χ'' begins to increase below 30 K and shows a peak at 8.5 K. These results indicate that a certain relaxation process occurs, induced by applying external dc magnetic fields to the glass that has a coupling between a disordered lattice system and the magnetic moments of Tb^{3+} ions at a short average interionic distance.

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