

Novel dynamical magnetic properties in the spin ice compound $\text{Dy}_2\text{Ti}_2\text{O}_7$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 L737

(<http://iopscience.iop.org/0953-8984/13/31/101>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 14:01

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Novel dynamical magnetic properties in the spin ice compound $\text{Dy}_2\text{Ti}_2\text{O}_7$

K Matsuhira^{1,3}, Y Hinatsu¹ and T Sakakibara²

¹ Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

² Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan

E-mail: matuhira@elcs.kyutech.ac.jp

Received 18 May 2001

Published 19 July 2001

Online at stacks.iop.org/JPhysCM/13/L737

Abstract

We found two distinct maxima in the ac magnetic susceptibility χ_{ac} of dysprosium titanate pyrochlore $\text{Dy}_2\text{Ti}_2\text{O}_7$. Their different frequency dependence of χ_{ac} suggest the existence of two different types of dynamical behaviour. One of them, observed below 2 K is the relaxation becoming very slow at lower temperature T , possibly related to a highly degenerate ground state ('spin ice' state). Another slowing down phenomenon is evident above ~ 10 K. Surprisingly, however, there is no anomaly in the dc magnetic susceptibility at this temperature range. Analysing the frequency dependence of χ_{ac} , we found that in spite of a structurally ordered system the magnetic relaxation is well expressed by a Davidson–Cole formula, which is characterized by a wide distribution of the relaxation time τ to the short- τ region and a temperature dependent cut-off, τ_c , in the slow relaxations. The magnetic relaxation of the spin ice compound $\text{Dy}_2\text{Ti}_2\text{O}_7$ is uniquely in contrast with known slow dynamics.

Recently, pyrochlore oxides have attracted much interest because their crystal structures include the corner-sharing tetrahedra whose vertices are occupied by spins [1–4]. When there is a strong single-site anisotropy along the (111) axes in this pyrochlore lattice, even the ferromagnetic interaction can lead to frustration. In the ferromagnetic case, the stable state of a single tetrahedron is given by the configuration of two spins pointing outward and two spins inwards; this problem is topologically equivalent to proton ordering in common water ice [5]. For every tetrahedron there are six ways this spin can configure. Because the ground state is highly degenerate for short range interactions, a static disordered state (so-called 'spin ice' state) is expected down to 0 K without indicating any long-range magnetic ordering in spite of a

³ Present address: Department of Electronics, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan.

structurally ordered system. $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ are known as spin ice compounds [4, 6]. A new spin ice compound $\text{Ho}_2\text{Sn}_2\text{O}_7$ has recently been reported [7].

Ramirez *et al* [6] found that $\text{Dy}_2\text{Ti}_2\text{O}_7$ has residual ground-state entropy which is numerically in agreement with the Pauling entropy for water ice [8]. The spin ice state is surely realized in $\text{Dy}_2\text{Ti}_2\text{O}_7$, although the spin configuration has not yet been examined by neutron scattering experiment. The temperature dependence of specific heat indicates a broad peak at around 1 K, which is due to the short-range ordering characterized by the spin ice configuration. Recent numerical simulations quite well reproduce the experimental result of the specific heat of $\text{Dy}_2\text{Ti}_2\text{O}_7$ [9]. From the result of the simulation, it is suggested that the actual spin ice behaviours of $\text{Dy}_2\text{Ti}_2\text{O}_7$ stems from long-range dipolar interactions as well as nearest-neighbour antiferromagnetic exchange interactions. However, there still remains the question of why long-range dipolar interactions do not actually cause a long-range ordering. It is important to understand how the process spin ice state is formed and stabilized. In an experimental approach for this issue, a study of the dynamical magnetic properties would be important. Since the dynamical magnetic properties of $\text{Dy}_2\text{Ti}_2\text{O}_7$ are, so far, experimentally unclear, as a first step we measured χ_{ac} of $\text{Dy}_2\text{Ti}_2\text{O}_7$ down to 0.1 K with detailed study of the frequency dependence.

Polycrystalline samples were prepared by a standard solid-state reaction. Stoichiometric mixtures of Dy_2O_3 and TiO_2 were heated in air at 1200–1350 °C for three days with intermediate regrinding to ensure complete reaction. By analysing the powder x-ray diffraction patterns, it was confirmed that the reaction products are a single phase with the cubic pyrochlore structure. Ac and dc magnetic susceptibility of the powder samples were measured by a commercial susceptometer (PPMS with ACMS option, Quantum Design Inc.) at temperatures of 1.8–300 K in an ac frequency range of 10 Hz–10 kHz. χ_{ac} down to 0.1 K was measured by a standard Hartshorn-bridge method in an ac field of 5 Oe, using a dilution refrigerator. To facilitate thermal equilibration in the measurement at low temperature T , we prepared a thin plate of a sintered sample. The magnetic field was applied parallel to the plate surface. As will be shown later, demagnetization becomes non-negligible. The data points shown in figures 1–4 are those before the correction.

Figure 1 shows temperature dependence of the ac magnetic susceptibility, χ' (real part) and χ'' (imaginary part) of $\text{Dy}_2\text{Ti}_2\text{O}_7$ below 2.5 K. In this figure, χ' and χ'' are normalized by the maximum. χ' at 10 Hz dramatically drops at 1.2 K and becomes almost zero below 0.5 K. χ'' shows a maximum at 1 K where the decreasing rate of χ' is largest. The behaviour of χ_{ac} depends on the frequency. As the frequency is lower, the peak positions in χ' and χ'' shift toward the lower temperature side, implying that magnetic relaxation becomes very slow at low T . A similar slow dynamics is observed in Ho pyrochlore oxides [7]. In the previous magnetic susceptibility data of $\text{Dy}_2\text{Ti}_2\text{O}_7$ at low T , a discrepancy of the peak temperature can be seen between the ac and dc measurements [10, 11]. This discrepancy can be attributed to the frequency dependent susceptibility (slow magnetic dynamics).

The temperature dependence of χ' and χ'' of $\text{Dy}_2\text{Ti}_2\text{O}_7$ above 1.8 K are shown in figure 2. At 10 kHz, χ' exhibits two maxima, at 2.5 K and 19 K. Two maxima also appear in χ'' , at 2.4 K and 17 K. The maximum on the lower T side is the same as the one shown in figure 1, which is probably related to the formation of the spin ice state. The maximum on the higher T side shifts toward lower T as the frequency decreases. Although this suggests a slowing down of the characteristic relaxation time, there is no anomaly in the dc magnetic susceptibility at this T range. In addition, χ' at high frequency still remains finite. These facts imply a very unique distribution of the relaxation time in this system.

For studying the slow dynamics it is important to examine the temperature dependence of the relaxation time $\tau(T)$. In the case of Debye relaxation with a single dispersion, χ'' at fixed

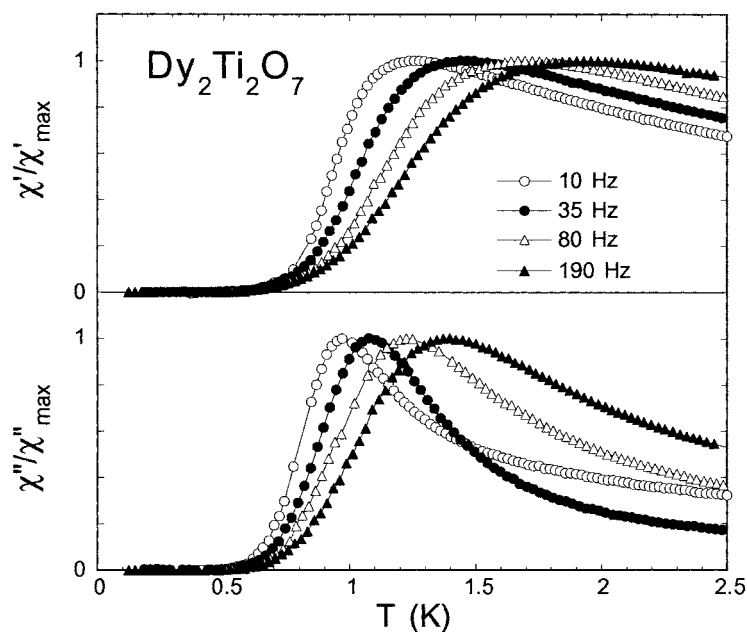


Figure 1. Temperature dependence of χ' and χ'' of $\text{Dy}_2\text{Ti}_2\text{O}_7$ below 2.5 K. χ' and χ'' are normalized by the maximum.

temperature becomes a symmetric function of $\log f$, and exhibits a maximum at the frequency defined by $1/2\pi\tau_0$ where τ_0 is a characteristic relaxation time. The frequency dependence of χ'' at various T are shown in figure 3. In this figure, χ'' is normalized by the isothermal susceptibility χ_0 which is estimated by the dc susceptibility measured at 1 kOe. χ''/χ_0 indicates a single broad peak in the whole T range. The peak position shifts toward the lower frequency side on cooling. As χ''/χ_0 is a nearly symmetric function of $\log f$, $1/2\pi f_m$ where f_m is the position of the maximum in χ''/χ_0 is considered to well represent the mean relaxation time. Therefore, $\tau(T)$ is obtained from the temperature dependence of f_m . However, careful inspection of the data shows that the χ''/χ_0 curve is not perfectly symmetric against $\log f$; it cannot be described by a simple Debye relaxation. We will discuss the asymmetry in the χ''/χ_0 curve later on.

$\tau(T)$ may also be estimated from the peak position of the χ'' against T plots. We define the position of the maximum of χ'' on the lower T side as T_m^L . On the other hand we define T_m^H by the position of maximum of $d(T\chi'')/dT$ on the higher T side because of the ambiguous maximum of χ'' . Frequency dependence of T_m^L and T_m^H and temperature dependence of f_m are summarized in figure 4. Frequency dependence of T_m^H above ~ 2 kHz is consistent with f_m . $\tau(T)$ in this temperature range is almost expressed by the Arrhenius formula $\tau(T) = \tau_0 \exp(E_b/T)$, where E_b is the energy barrier and τ_0 is the characteristic relaxation time, estimated to be 220 K and 5×10^{-11} s, respectively. If $\tau(T)$ obeys this Arrhenius law down to lower T , $\tau(T)$ will then be beyond the characteristic time scale in the dc measurement ($\sim 10^2$ s) below ~ 8 K. In reality, however, there is no anomaly in DC measurements around 8 K. From the behaviour of $f_m(T)$, it seems that a crossover of the dominant relaxation mechanism from the high-frequency region (T_m^H) to the low-frequency region (T_m^L) has occurred at around 10 K. On the other hand, the frequency dependence of T_m^L is not so well expressed by the Arrhenius formula. If the Arrhenius law is applied in the

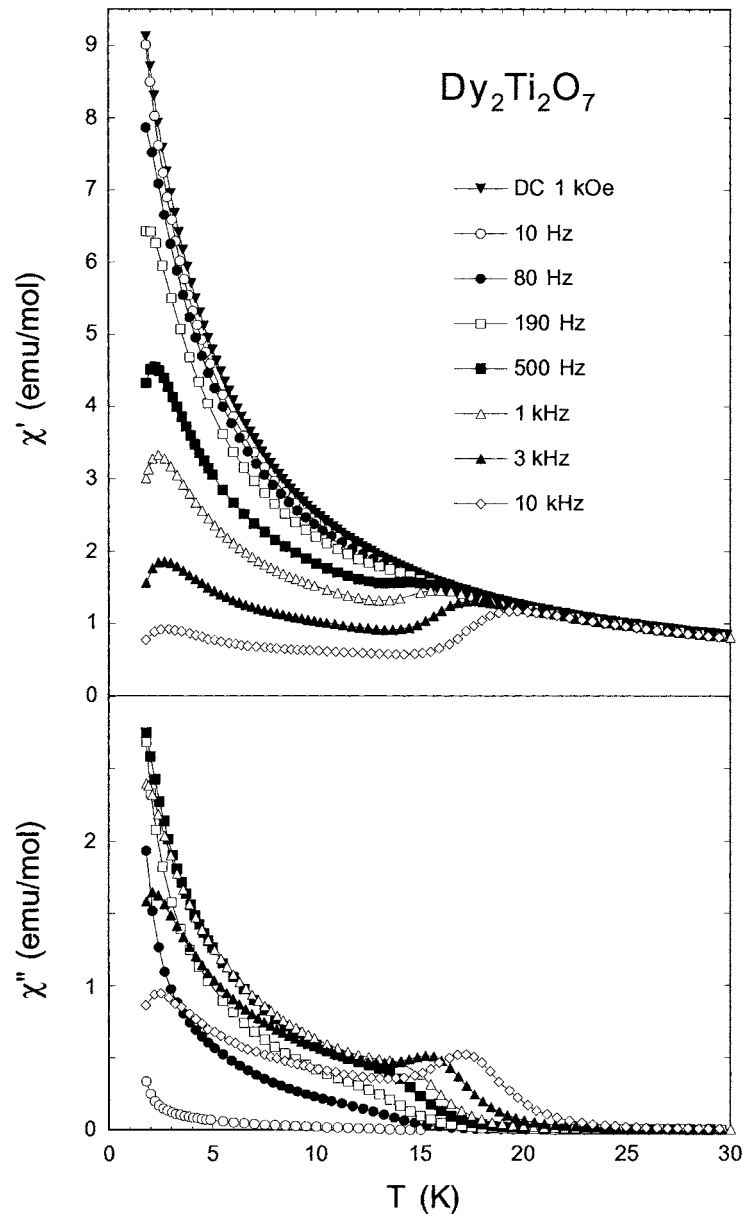


Figure 2. Temperature dependence of χ' and χ'' of $\text{Dy}_2\text{Ti}_2\text{O}_7$ above 1.8 K.

low-frequency region, E_b is estimated to be of the order of 10 K. To say the very least, τ tends to rapidly increase with decreasing T . When τ is beyond the characteristic time scale in the dc measurement, we would observe the magnetic moment frozen in, possibly, the spin ice configuration below 1 K⁴.

⁴ We have measured the dc magnetization of $\text{Dy}_2\text{Ti}_2\text{O}_7$ down to 0.4 K. The temperature dependence of the dc magnetization under low field shows irreversibility between zero field cooling (ZFC) and field cooling below 0.7 K. The ZFC curve indicates a sharp peak at 0.7 K [12].

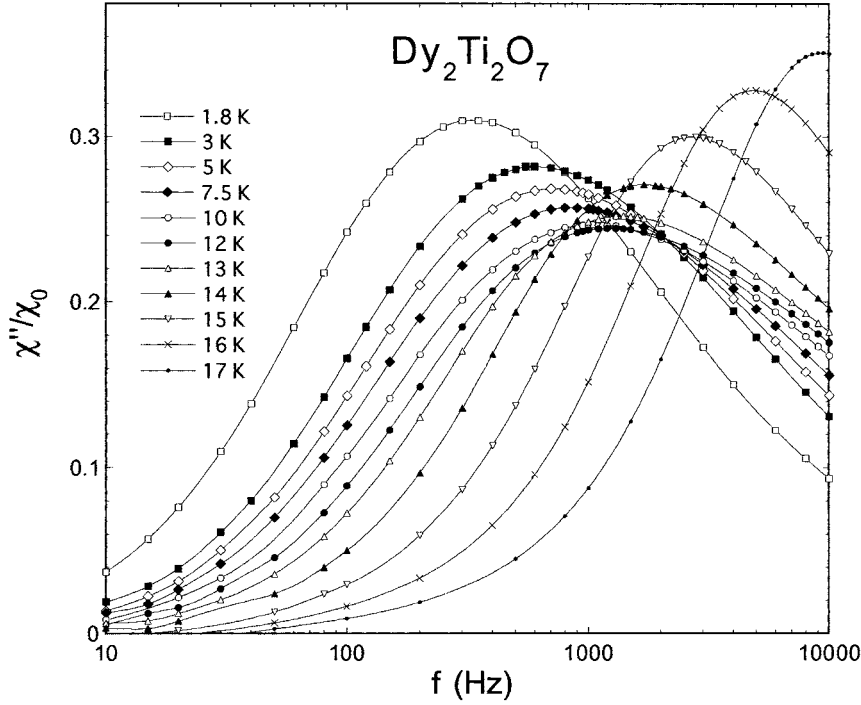


Figure 3. Frequency dependence of χ'' at various T . χ'' is normalized by the isothermal susceptibility χ_0 . The value of χ_0 is estimated by dc susceptibility measured at 1 kOe.

Before the analysis of χ_{ac} , we should make a correction of the demagnetization effect in order to obtain more precise behaviour. In the present compound, this effect is not negligible because of the large magnetic moment. The measured susceptibility $\chi_{meas} = \chi'_{meas} - i\chi''_{meas}$ is converted to the intrinsic susceptibility $\chi_{int} = \chi'_{int} - i\chi''_{int}$ by correcting for the demagnetization as $\chi_{int}^{-1} = \chi_{meas}^{-1} - 4\pi N$, where N is the demagnetization factor [13]. Thus, χ'_{int} and χ''_{int} are expressed as

$$\chi'_{int} = \frac{\chi'_{meas} - 4\pi N(\chi'_{meas}{}^2 + \chi''_{meas}{}^2)}{(1 - 4\pi N\chi'_{meas})^2 + (4\pi N\chi''_{meas})^2} \quad (1)$$

$$\chi''_{int} = \frac{\chi''_{meas}}{(1 - 4\pi N\chi'_{meas})^2 + (4\pi N\chi''_{meas})^2}. \quad (2)$$

We carried out the demagnetization correction using $N = 0.3$ for powder sample data.

We show the loci of $\chi'_{int} - \chi''_{int}$ in the complex plane at various T in figure 5. A deviation from a semi-circle expected in a Debye relaxation is already evident at 15 K (figure 5(c)). The deviation becomes large with decreasing T . This fact suggests a distribution in $\tau(T)$. The slope in the loci of $\chi'_{int} - \chi''_{int}$ makes an angle of 90° against the χ'_{int} axis at the low-frequency limit for all T . On the other hand, it does not seem to intersect the χ'_{int} axis at a right-angle in the high-frequency limit. These features are observed down to 1.8 K. It should be noted that these features are quite different from the slow dynamics seen in systems such as the spin glass [13, 14], critical behaviour in quasi 2D ferromagnets [15] and randomly diluted ferromagnets [16]. In such systems, the magnetic relaxation is described by the well known Cole–Cole formula where the slope angle of the locus of the $\chi' - \chi''$ plot becomes less than 90° against

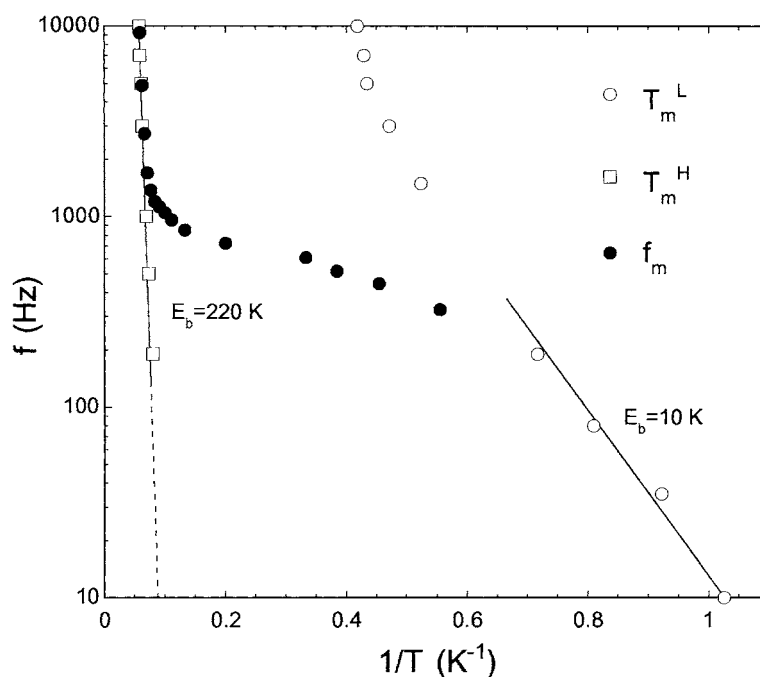


Figure 4. Frequency dependence of T_m^L , T_m^H and temperature dependence of f_m . The full curves represent the Arrhenius law.

the χ' axis at both ends. Instead, we found that the present loci of $\chi' - \chi''$ is very similar to the shape of the dielectric relaxation in glycerine, which is well described by the Davidson–Cole formula [17]. In the following, we will attempt to analyse χ_{ac} of $\text{Dy}_2\text{Ti}_2\text{O}_7$ in terms of this expression.

We apply the Davidson–Cole formalism [17] to the magnetic relaxation:

$$\chi^*/\chi_0 = (\chi' + i\chi'')/\chi_0 = 1/(1 + i\omega\tau_c)^\beta \quad (3)$$

$$\chi'/\chi_0 = (\cos \phi)^\beta \cos \beta\phi \quad (4)$$

$$\chi''/\chi_0 = (\cos \phi)^\beta \sin \beta\phi \quad (5)$$

where τ_c is the relaxation time and $\tan \phi = \omega\tau_c$. As will be shown later, the physical meaning of τ_c is a cut off in the distribution of the relaxation time. β is assumed to be a value between zero and one; the case of $\beta = 1$ corresponds to the Debye relaxation with a single dispersion. In the high-frequency limit ($\omega \rightarrow \infty$), the locus of equation (3) in the complex plane becomes a straight line with an angle $\beta\pi/2$ against the χ' axis. On the other hand, in the low-frequency limit ($\omega \rightarrow 0$), the locus makes an angle $\pi/2$ against the χ' axis. χ'' becomes an asymmetric function of $\log \omega$, pushed up on the high-frequency side; the feature is consistent with the present results in figures 3 and 5. The peak position slightly shifts to a higher frequency side than that expected in Debye relaxation ($\beta = 1$).

We found that the experimental results above 14 K are well fitted by equation (3). The result is shown by full curves in figure 5(c). The best fit at 17 K was obtained with $\beta = 0.544$ and $\tau_c = 2.99 \times 10^{-5}$ s. On cooling, τ_c increases and β tends to decrease. The temperature dependence of τ_c is almost expressed by the Arrhenius formula $\tau_c(T) = \tau_{c0} \exp(E_b/T)$, where $\tau_{c0} = 5.47 \times 10^{-10}$ s and $E_b = 186$ K. Below 14 K, the loci start to deviate from Davidson–Cole

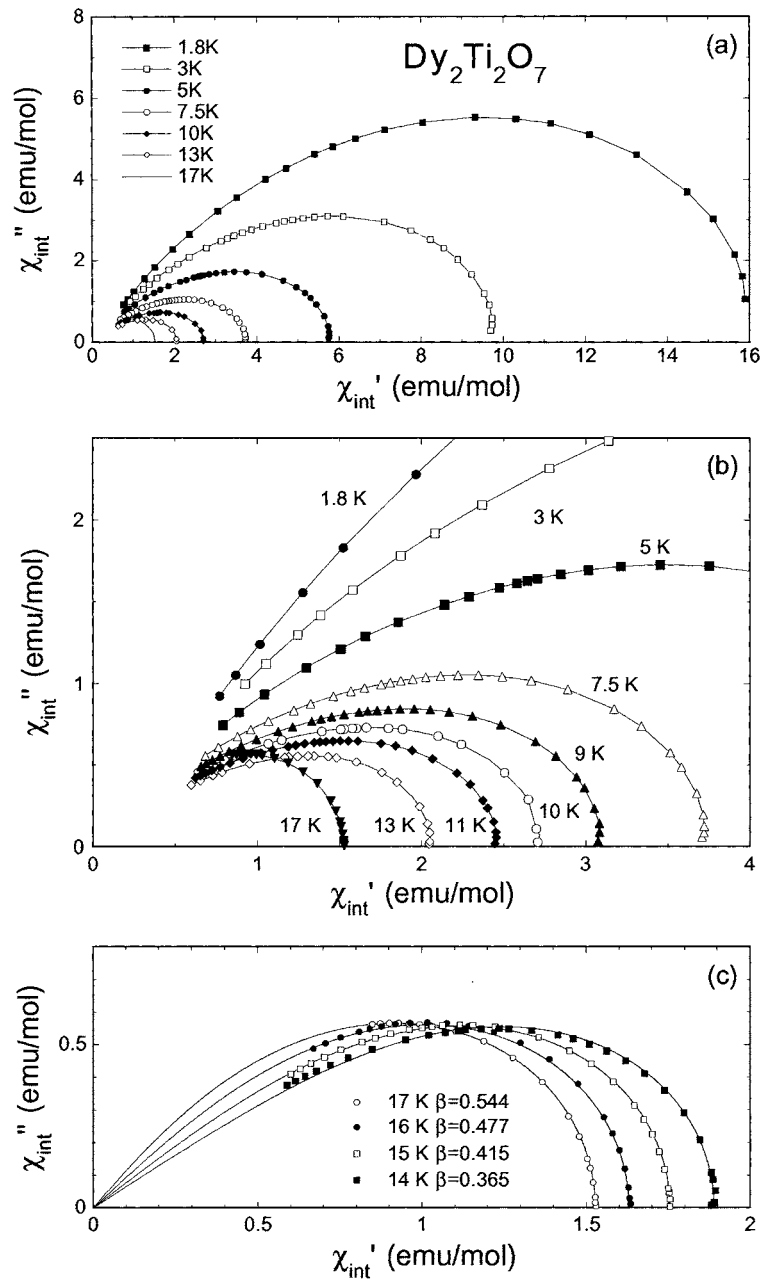


Figure 5. (a) The loci of $\chi'_{\text{int}} - \chi''_{\text{int}}$ for $\text{Dy}_2\text{Ti}_2\text{O}_7$ in a frequency range of 10 Hz–10 kHz. (b) The loci of $\chi'_{\text{int}} - \chi''_{\text{int}}$ around the origin. (c) $\chi'_{\text{int}} - \chi''_{\text{int}}$ fitted by the Davidson–Cole formula. The full curves show the fitting.

behaviour. However, we should note that the locus of $\chi' - \chi''$ still maintains the characteristic feature of the Davidson–Cole formula in the low- and high-frequency limits (figure 5(a)).

The Davidson–Cole formula can be described in terms of a distribution of simple relaxation

processes [17]. Defining a distribution function of the relaxation time $F(\tau/\tau_c)$ in the interval $d \ln(\tau/\tau_c)$, the expression becomes

$$\chi^*/\chi_0 = \int_{-\infty}^{\infty} \frac{F(\tau/\tau_c)}{1 + i\omega\tau} d \ln(\tau/\tau_c). \quad (6)$$

Then, the distribution function F for the χ^* of equation (3) is given by

$$F(\tau/\tau_c) d \ln(\tau/\tau_c) = \begin{cases} \frac{\sin \beta\pi}{\pi} \left(\frac{\tau}{\tau_c - \tau} \right)^\beta d \ln(\tau/\tau_c) & \tau < \tau_c \\ 0 & \tau > \tau_c. \end{cases} \quad (7)$$

The feature is characterized by the existence of a cut-off time τ_c and a long-tail distribution to the very-short- τ region. The fraction $f(\tau/\tau_c)$ of processes with relaxation times less than τ is obtained by integrating $F(\tau/\tau_c) d \ln(\tau/\tau_c)$ as follows:

$$f(\tau/\tau_c) = \int_{-\infty}^{\tau/\tau_c} \frac{\sin \beta\pi}{\pi} \left(\frac{\tau'}{\tau_c - \tau'} \right)^\beta d \ln(\tau'/\tau_c) \quad (9)$$

$$= \begin{cases} \frac{\sin \beta\pi}{\pi} B_{\tau/\tau_c}(\beta, 1 - \beta) & \tau \leq \tau_c \\ 1 & \tau > \tau_c \end{cases} \quad (10)$$

where B is the incomplete beta function. Because of the long-tail distribution, there is significant weight in the short- τ region.

In figure 6, we show the plots of $F(\tau/\tau_c) d \ln(\tau/\tau_c)$ and $f(\tau/\tau_c)$ for the parameters fitted to the experiment. The existence of a broad distribution of τ with a tail to the very short time is remarkable, in spite of a structurally ordered system. Although the distribution around the cut-off time τ_c is surely significant, $F(\tau/\tau_c) d \ln(\tau/\tau_c)$ has a long tail to the short- τ side (figure 6(a)). Therefore, the short- τ components also make a significant contribution (figure 6(b)). These two features of $F(t)$ give rise to the two distinct anomalies (T_m^H and T_m^L) observed in χ_{ac} . The anomaly at T_m^H is caused by the sharp structure and a slowing down of τ_c , whereas the anomaly at T_m^L comes from the long-tail part of F which rapidly decreases in magnitude on cooling. We should pay attention to the slope against the χ' axis in the loci of $\chi' - \chi''$ at the high-frequency limit (figure 5(b)). Although the angle decreases on cooling to 10 K, it begins to increase again below 10 K. This suggests that the weight of F in the short- τ side has shifted to the long- τ side; the distribution of τ becomes narrower as the mean relaxation time becomes longer. The locus of $\chi' - \chi''$ seems to restore the semi-circle with a single dispersion at lower T . This change begins to occur in the crossover region around 10 K, leading to the anomaly around T_m^L .

The low-frequency feature of χ_{ac} at low T is very similar to that of Ho spin ice compounds [7]. It is natural to consider that the very slow dynamics below 10 K comes from the same origin. Therefore, the dominant magnetic relaxation below 10 K will probably be characterized by small ferromagnetic clusters (short-range ordering) formed in the spin ice configuration that is the stable state of a single tetrahedron. The correlation length is expected to be a few tetrahedra by analogy with Ho spin ice compounds [4, 7]. It is reasonable in a structurally ordered system to consider that the distribution for τ become narrow at low T . The origin of the magnetic relaxation dominating above 10 K is, however, unclear. Microscopic measurements will be needed to examine how short-range ordering is realized above 10 K.

In summary, we have reported the dynamical magnetic properties of spin ice compound $\text{Dy}_2\text{Ti}_2\text{O}_7$. We found the crossover of magnetic relaxation occurred around 10 K. Above 10 K, the magnetic relaxation is characterized by the Davidson–Cole formula. Although the origin of crossover is still unclear, the magnetic relaxation is uniquely in contrast with known slow

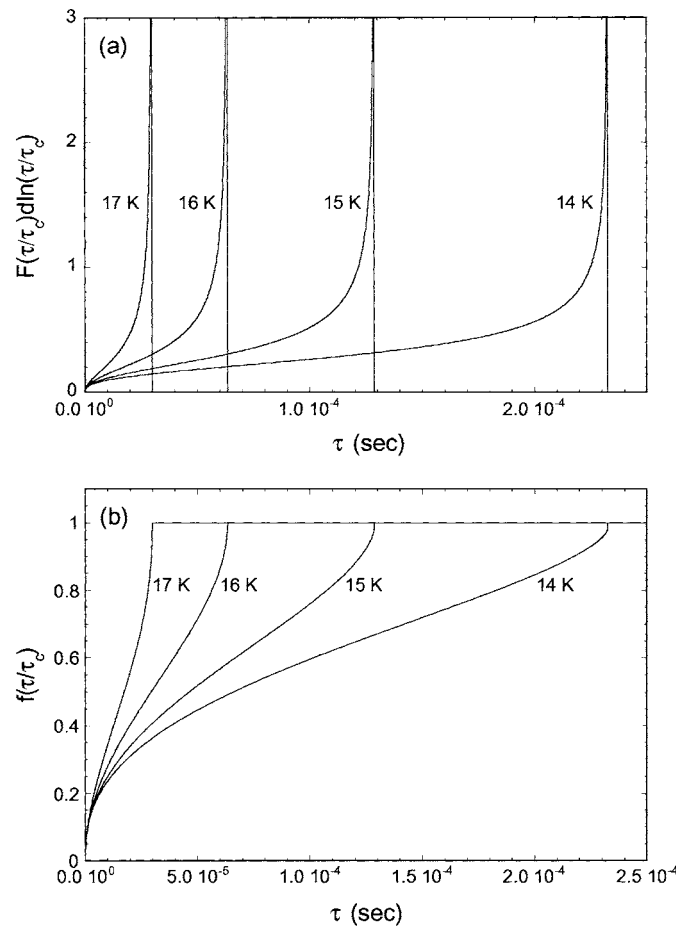


Figure 6. (a) The distribution function of the relaxation time $F(\tau/\tau_c) d\ln(\tau/\tau_c)$ and (b) the fraction $f(\tau/\tau_c)$ of processes with relaxation time less than τ , which are obtained by using the fitting parameters.

dynamics, and probably related to the formation of the spin ice state and to the lack of long-range ordering in $\text{Dy}_2\text{Ti}_2\text{O}_7$.

The authors would like to express thanks to Dr S Chikazawa and Dr K Nemoto for useful discussions. The present work was partly supported by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science, Sports and Culture.

References

- [1] Gaulin B D, Reimers J N, Mason T E, Greedan J E and Tun Z 1992 *Phys. Rev. Lett.* **69** 3244
- [2] Gingras M J P, Stager C V, Raju N P, Gaulin B D and Greedan J E 1997 *Phys. Rev. Lett.* **78** 947
- [3] Shimakawa Y, Kubo Y and Manako T 1996 *Nature* **379** 53
- [4] Harris M J, Bramwell S T, McMorrow D F, Zeiske T and Godfrey K W 1997 *Phys. Rev. Lett.* **79** 2554
- [5] Bramwell S T and Harris M J 1998 *J. Phys.: Condens. Matter* **10** L215
- [6] Ramirez A P, Hayashi A, Cava R J, Siddharthan R and Shastry B S 1999 *Nature* **399** 333
- [7] Matsuhiro K, Hinatsu Y, Tenya K and Sakakibara T 2000 *J. Phys.: Condens. Matter* **12** L649

-
- [8] Pauling L 1945 *The Nature of the Chemical Bond* (Ithaca, NY: Cornell University Press) p 301
- [9] Hertog B C den and Gingras M J P 2000 *Phys. Rev. Lett.* **84** 3430
- [10] Cashion J D, Cooke A H, Leask M J M, Thorp T L and Wells M R 1968 *J. Mater. Sci.* **3** 402
- [11] Blöte H W J, Wielinga R F and Huiskamp W J 1969 *Physica* **43** 549
- [12] Matsuhira K, Hinatsu Y, Tenya K and Sakakibara T, to be published
- [13] Dekker C, Arts A F M, Wijn H W de, Duyneveldt A J van and Mydosh J A 1989 *Phys. Rev. B* **40** 11 243
- [14] Baalbergen J J, Verstelle J C and Duyneveldt A J 1990 *Physica B* **164** 353
- [15] Hashimoto T, Kojima Y and Ikegami T 1980 *J. Magn. Magn. Mater.* **15–18** 1025
- [16] Okuda Y, Matsuura M and Haseda T 1979 *J. Phys. Soc. Japan* **47** 773
- [17] Davidson D W and Cole R H 1950 *J. Chem. Phys.* **18** 1417
Davidson D W and Cole R H 1951 *J. Chem. Phys.* **19** 1484