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LETTER TO THE EDITOR

Low temperature magnetic properties of frustrated pyrochlore ferromagnets $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ K Matsuhira[†], Y Hinatsu[†], K Tenya[‡] and T Sakakibara[§][†] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060–0810, Japan[‡] Division of Physics, Graduate School of Science, Hokkaido University, Sapporo 060–0810, Japan[§] Institute for Solid State Physics, University of Tokyo, Kashiwa 277–8581, Japan

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Abstract. AC and DC magnetic susceptibilities have been measured on frustrated pyrochlore ferromagnets $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ at temperatures down to 100 mK. In the AC magnetic susceptibility, a dramatic drop of χ' (in-phase component) and a single maximum of χ'' (quadrature component) are observed at around 1 K. The frequency dependence of these peak positions indicates the presence of a slow magnetic relaxation at low temperature, whose relaxation time obeys the Arrhenius formula with the energy barrier $E_b = 19.6$ K and 27.5 K for $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, respectively. Strong irreversibility is also observed in the temperature dependence of the DC magnetization of $\text{Ho}_2\text{Sn}_2\text{O}_7$ at 1 kOe below $T_p \sim 0.75$ K; the zero-field-cooling (ZFC) curve indicates a very sharp peak at T_p , whereas the field-cooling curve has no anomaly at T_p and increases monotonically with decreasing T . In the DC magnetization process of the ZFC state at 0.46 K, a steep increase of the moment occurs above 2 kOe, and the irreversibility disappears at around ~ 15 kOe where the moment ferromagnetically saturates. These results indicate a clustering of magnetic moment whose size is of the order of a few tetrahedra, consistent with a recently proposed ‘spin ice’ model.

The pyrochlore oxides have attracted much interest recently because their crystal structures include the corner-sharing tetrahedra [1–3]. As is well known, when the spins occupy the vertices of the tetrahedra, antiferromagnetic interaction can lead to a strong frustration. Interestingly, it has been discovered recently that ferromagnetic interaction can also lead to a frustration when there is a strong single-site anisotropy along the $\langle 111 \rangle$ axes in this pyrochlore lattice [4]. In the ferromagnetic case, the stable state of a single tetrahedron is given by the configuration of two spins pointing outward and two spins pointing inwards. Topologically, this is the same problem as the proton ordering in common water ice. A static disordered state is then expected down to 0 K because this ground state is highly degenerate.

The frustrated pyrochlore ferromagnet was firstly reported in $\text{Ho}_2\text{Ti}_2\text{O}_7$ (space group $Fd\bar{3}m$) [4]. In this compound, the Ho^{3+} ion carries magnetic moment, whereas the Ti^{4+} ion is non-magnetic. It is found by inelastic neutron scattering that the CEF ground state doublet has a $\langle 111 \rangle$ local Ising anisotropy axis [5]. As the Ho^{3+} ion has a large moment, not only the superexchange interaction but also the dipolar interaction is significant [5]. No magnetic long-range order is, however, observed down to 0.35 K in the neutron scattering experiment, except for short-range ferromagnetic correlations [4]. Later, Ramirez *et al* showed that $\text{Dy}_2\text{Ti}_2\text{O}_7$ has residual ground states entropy [6], which is numerically in agreement with the Pauling entropy for water ice [7]. So far only $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ are known as a frustrated pyrochlore ferromagnet ‘spin ice’.

The spin ice behaviour is much more attractive under a magnetic field because the situation is never accessible in water ice. In $\text{Dy}_2\text{Ti}_2\text{O}_7$, a sharp anomaly in the temperature dependence of specific heat appears only under magnetic field [6]. Moreover, an occurrence of a new type of magnetic phase transition is theoretically predicted, which is a kind of a liquid–gas transition [8]. These interesting phenomena should be examined by various experimental methods. However, the magnetization behaviour is still unclear, even at low field, because of its low characteristic temperature. Low temperature magnetization measurement is certainly needed. It is also important to search for new frustrated ferromagnets. Recently, we found by AC magnetic susceptibility measurements that some of tin pyrochlore oxides $\text{Ln}_2\text{Sn}_2\text{O}_7$ (Ln : lanthanides) are new frustrated ferromagnets (spin ice compounds) [9]. In this letter, we report on the first magnetization measurement below 1 K in Ho pyrochlore oxides $\text{Ho}_2\text{Ti}_2\text{O}_7$ and a new spin ice compound $\text{Ho}_2\text{Sn}_2\text{O}_7$, focusing attention on the slow dynamics of the magnetic moment at low temperature. The results indicate the presence of small ferromagnetic clusters in these structurally ordered systems.

Polycrystalline samples were prepared by standard solid state reaction. Stoichiometric mixtures of Ho_2O_3 and SnO_2 or TiO_2 were heated in air at 1200–1400 °C for three days with intermediate regrinding to ensure a complete reaction. By analysing the powder x-ray diffraction patterns in the range $10^\circ \leq 2\theta \leq 120^\circ$ measured at room temperature, it was confirmed that the reaction products are a single phase with the cubic pyrochlore structure. The lattice constants a_0 in the cubic unit cell obtained by powder x-ray diffraction are 10.3762 Å and 10.1059 Å for $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, respectively. The Ho–Ho distance in the tetrahedron given by $(\sqrt{2}/4)a_0$ is 3.6685 Å and 3.5730 Å for $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, respectively.

Magnetic susceptibility of powder samples was measured by a SQUID magnetometer (MPMS, Quantum Design Inc.) at temperatures 2–300 K in a magnetic field of 1 kOe. AC magnetic susceptibility down to 0.1 K was measured by a standard Hartshorn-bridge method in an AC field of 5 Oe, using a dilution refrigerator. DC magnetization measurement down to 0.46 K was done by a high-resolution capacitive Faraday force magnetometer [10] installed in the ^3He cryostat, in a field gradient of 300–500 Oe cm^{-1} . We prepared a thin plate of sintered sample to facilitate thermal equilibration in magnetization measurement at low temperature. The magnetic field was applied perpendicular to the plate surface. It should be noticed that the demagnetization effect is not negligible because the magnetization of present compounds is large. We have done the suitable correction of demagnetization effect for all data in this letter. Although the demagnetization coefficient was difficult to determine precisely, we used the demagnetization factor of 0.3 and 0.6 for the data by a SQUID and a Faraday magnetometer, respectively.

Figure 1(a) shows temperature dependence of the reciprocal DC magnetic susceptibility $\chi^{-1}(T)$ for $\text{Ho}_2\text{Sn}_2\text{O}_7$. Assuming $\chi^{-1}(T)$ obeys the Curie–Weiss law at temperatures 16–40 K, the Curie–Weiss temperature θ_{CW} becomes 1.8 K. A deviation from the Curie–Weiss law is observed below 10 K. Figure 1(b) shows temperature dependence of the reciprocal magnetic susceptibility for $\text{Ho}_2\text{Ti}_2\text{O}_7$. The behaviour is very similar to that of $\text{Ho}_2\text{Sn}_2\text{O}_7$. In the same way, θ_{CW} for $\text{Ho}_2\text{Ti}_2\text{O}_7$ is estimated to be 2.3 K which is in agreement with the previously reported value [4]. A ferromagnetic coupling of a few Kelvin exists in these compounds, which is of the order of a dipole–dipole interaction strength [5].

Temperature dependence of χ' and χ'' of $\text{Ho}_2\text{Sn}_2\text{O}_7$ are shown in figure 2. In this figure, χ' and χ'' are normalized by the value of χ' at 2.5 K. χ' at 80 Hz dramatically drops at ~ 1.3 K and becomes almost zero below 0.5 K. In addition, a single maximum appears in χ'' at ~ 1.1 K. This behaviour depends on the AC field frequency; as the frequency is lower, the position of the peak in χ' and χ'' shift toward the lower temperature side. This behaviour indicates slow relaxation of the magnetization in $\text{Ho}_2\text{Sn}_2\text{O}_7$ at low temperature.

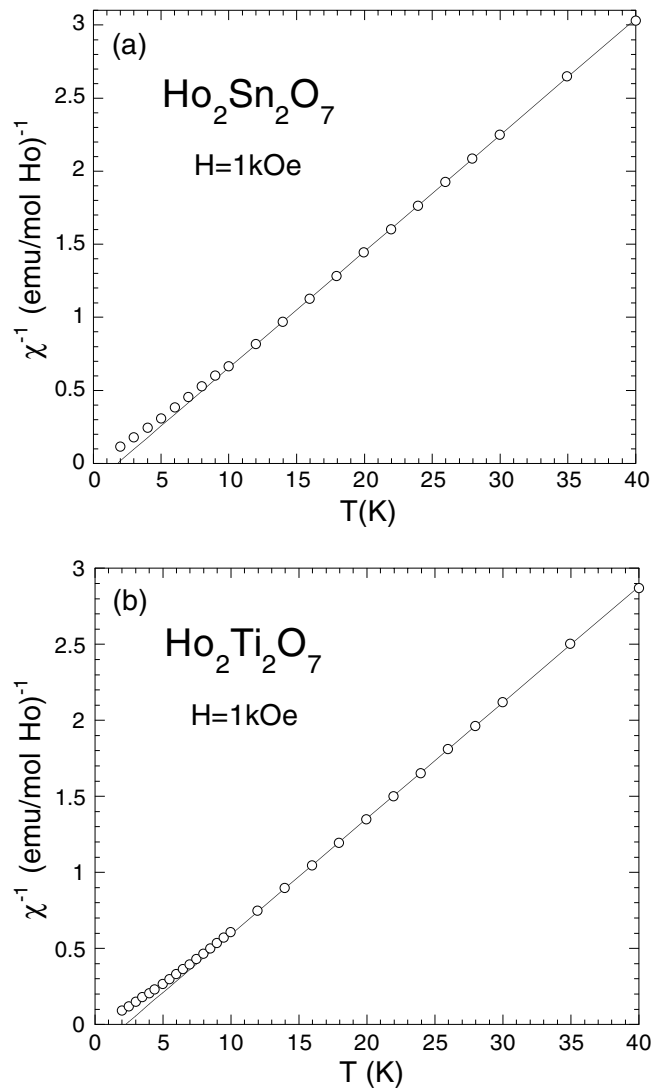


Figure 1. Temperature dependence of the reciprocal magnetic susceptibility for (a) $\text{Ho}_2\text{Sn}_2\text{O}_7$ and (b) $\text{Ho}_2\text{Ti}_2\text{O}_7$. Solid lines show a fitting to the Curie–Weiss law in the temperature range 16–40 K.

The temperature dependence of χ' and χ'' of $\text{Ho}_2\text{Ti}_2\text{O}_7$ are shown in figure 3. Again, χ' and χ'' are normalized by the value of χ' at 2.5 K. AC magnetic susceptibility of $\text{Ho}_2\text{Ti}_2\text{O}_7$ has very similar behaviour to that of $\text{Ho}_2\text{Sn}_2\text{O}_7$. χ' at 80 Hz dramatically drops at ~ 1.2 K and becomes almost zero below 0.5 K. Also, a single maximum appears in χ'' at ~ 1.0 K. Except for a slightly lower characteristic temperature in $\text{Ho}_2\text{Ti}_2\text{O}_7$, it is concluded that almost the same physical situation (magnetic anisotropy of CEF ground state and a type of dominant interaction between Ho^{3+} ions) is realized in $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$.

Frequency dependent AC susceptibility is often observed in systems such as superparamagnets [11], fine magnetic particles [12, 13], spin glasses [14, 15] and magnetic molecular clusters [16, 17] with different forms of the temperature variation of the relaxation time $\tau(T)$. In order to examine $\tau(T)$ in the present systems, we define the position of

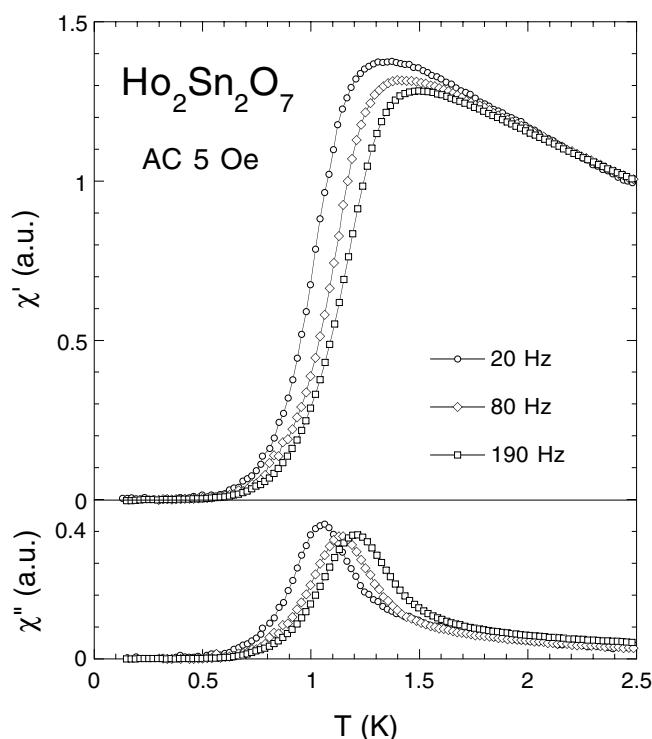


Figure 2. AC magnetic susceptibility χ' and χ'' of $\text{Ho}_2\text{Sn}_2\text{O}_7$. χ' and χ'' are normalized by the value of χ' at 2.5 K.

the maximum of χ'' as T_{\max} . From the frequency dependence of T_{\max} , we found that τ is well expressed by the Arrhenius formula $\tau = \tau_0 \exp(E_b/T)$, where E_b is the energy barrier. Figure 4 shows the frequency dependence of $1/T_{\max}$ in $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$. By using the Arrhenius formula, we obtain $E_b = 19.6$ K and 27.5 K for $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$, respectively. The characteristic relaxation time τ_0 is of the order of 10^{-10} sec. As the temperature dependence of τ is of the thermal activation type, the slow magnetic relaxation observed in $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ is attributed to a blocking of magnetization rather than a spin-glass transition.

In figure 5, we show the temperature dependence of the DC magnetization of $\text{Ho}_2\text{Sn}_2\text{O}_7$ at 1 kOe. ZFC and FC denote a zero field cooling and a field cooling, respectively. The irreversibility appears clearly below $T_p \sim 0.75$ K. The ZFC curve has a sharp peak at T_p and dramatically decreases toward zero. Below T_p , the FC curve is not flat, in contrast to what is expected in a typical spin-glass [18, 19]. Instead, the FC curve increases monotonically on cooling below the temperature where the ZFC curve indicates a maximum. This is a typical behaviour expected in a blocking phenomenon [19].

The magnetic relaxation time of $\text{Ho}_2\text{Sn}_2\text{O}_7$ will exponentially increase with decreasing temperature. Linear extrapolation of the plot in figure 4 indicates that τ exceeds 10^2 sec at around T_p , which is a characteristic time scale of our DC magnetization measurement. This increasing of τ leads to the irreversibility below T_p . From figures 2–5, we may conclude that a certain clustering occurs in the present systems at low temperature. The sharp decreasing in the ZFC curve in figure 5 implies that

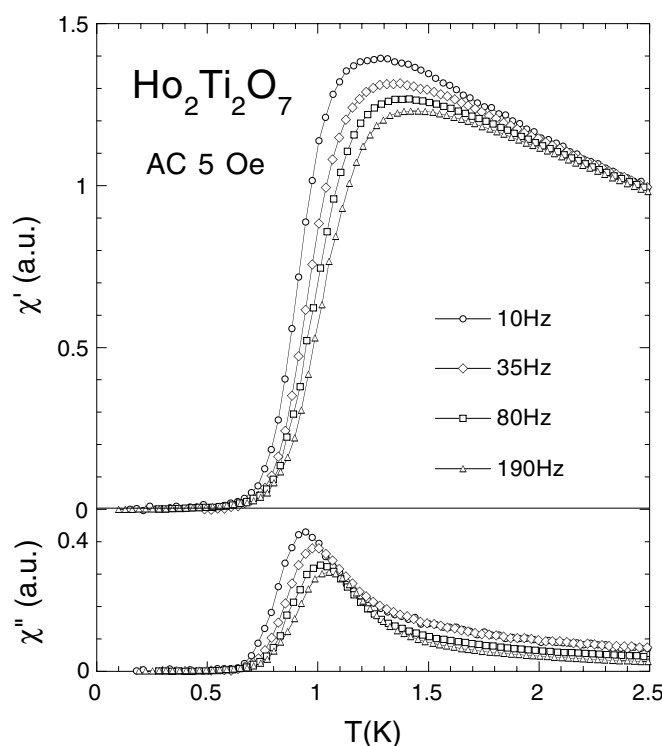


Figure 3. AC magnetic susceptibility χ' and χ'' of $\text{Ho}_2\text{Ti}_2\text{O}_7$. χ' and χ'' are normalized by the value of χ' at 2.5 K.

the distribution of the blocking temperature, and therefore the cluster size, is very narrow. This would be reasonable because the present compounds are structurally ordered systems.

In figure 6, we show the magnetization curves of $\text{Ho}_2\text{Sn}_2\text{O}_7$ for $T = 0.46$ K, 0.6 K, 0.7 K, 2 K, 4.2 K measured after ZFC from high enough temperatures. At 0.46 K, the magnetization at low fields (< 1 kOe) is almost zero in the increasing field process, consistent with the results of DC susceptibility (figure 5). A rapid increase in the moment can be seen above 2 kOe. Considering that the CEF ground state in the present compounds is $\sim |J_Z = \pm 8\rangle$, Ho^{3+} ion should have a magnetic moment of $\sim 10 \mu_B$ at every site. However, since there are $\langle 111 \rangle$ local Ising anisotropy axes the saturated moment of the single tetrahedron should reduce to about $5 \mu_B$ per ion [8]. This value is consistent with the present magnetization results in figure 6 which shows a saturation of the moment at about $4.8 \mu_B/\text{Ho}$.

In the magnetization curve measured at 0.46 K, a strong irreversibility is observed below 15 kOe; we defined this field as H^* . The irreversibility loop becomes weaker with increasing temperature. However, H^* does not depend much on the temperature. After taking the magnetization process at 0.46 K, we measured the temperature dependence of a residual magnetization with increasing temperature. The residual magnetization rapidly disappeared at around T_p . Similar irreversibility is also observed in the neutron diffraction experiment on $\text{Ho}_2\text{Ti}_2\text{O}_7$ [4]. Interestingly, a small hysteresis is still observed even at 2 K and 4.2 K. Although its origin is not very clear at present, the hysteresis may possibly be related to the clustering phenomenon.

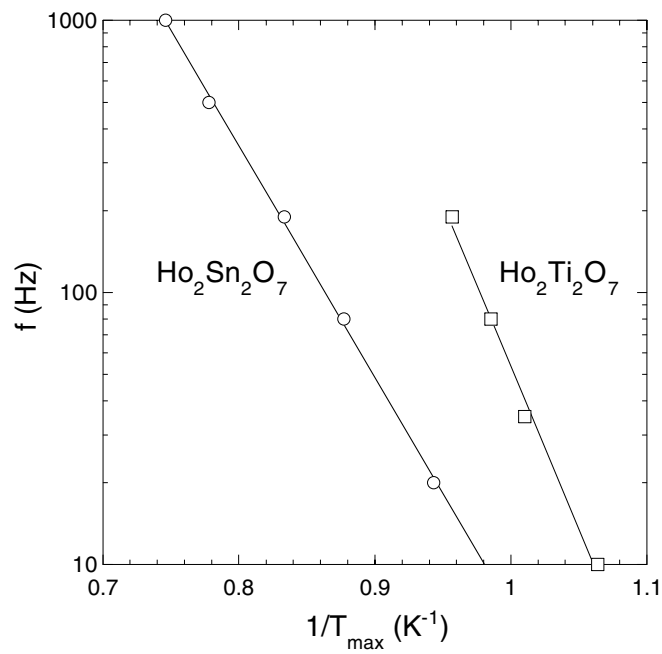


Figure 4. Frequency dependence of $1/T_{\max}$ in $\text{Ho}_2\text{Sn}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$. Solid line shows the fitting line by the Arrhenius formula.

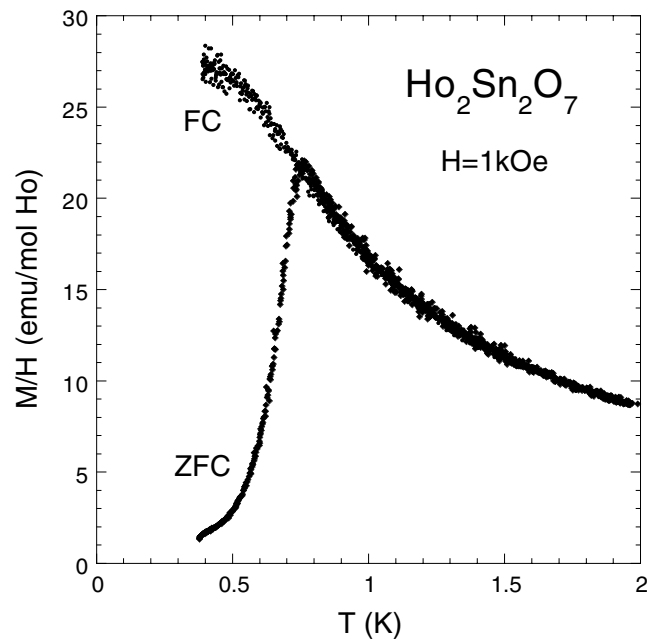


Figure 5. Temperature dependence of DC magnetization of $\text{Ho}_2\text{Sn}_2\text{O}_7$ at 1 kOe. ZFC and FC denote zero field cooling and field cooling, respectively.

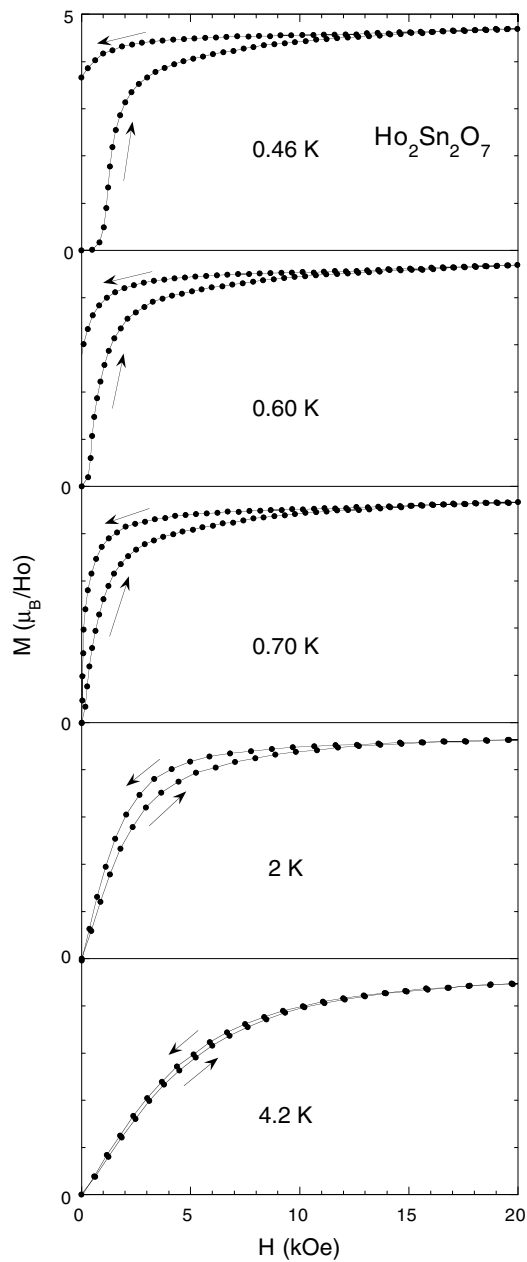


Figure 6. Magnetization curves of $\text{Ho}_2\text{Sn}_2\text{O}_7$ for $T = 0.46$ K, 0.6 K, 0.7 K, 2 K, 4.2 K measured after ZFC.

Combining the data in figure 6 with the susceptibility results, we may estimate the size of the ferromagnetic clusters. The net moment of each cluster is considered to rotate towards the field direction when the Zeeman energy exceeds E_b . Experimentally, determination of the critical field H_B for the cluster rotation is not clear-cut because the cluster size is somewhat distributed and the direction of the cluster moment coupled by the applied field is

also distributed in our orientationally averaged powder sample. From figure 6, however, it may safely be said that H_B is between 2 kOe and 15 kOe since the initial magnetization at 0.46 K mostly develops in this field range. The cluster moment is then derived to be within the range $75 \mu_B - 10\mu_B$. Considering that the magnetic moment of a single tetrahedron characterized by the simple 'two-spin-in and two-spin-out' configuration is about $20 \mu_B$, the size of the ferromagnetic cluster is estimated to be at most of the order of a few tetrahedra. This observation is in good agreement with the spin ice model in which the geometrical frustration and the strong Ising anisotropy prevent the long-range ferromagnetic ordering [4]. In the present experiment on the powder samples, however, no evidence of a phase transition is found even at finite field. Further experiment on a single crystal is planned soon.

To summarize, in the chemically ordered ferromagnetic pyrochlore compounds we have clearly observed a blocking phenomenon with the cluster size of only a few nearest neighbours. It would be interesting to confirm the short ranged ordering and the correlation length by neutron scattering. The experiment on the new compound $\text{Ho}_2\text{Sn}_2\text{O}_7$ is now in progress.

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