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Specific-heat study of the spin-structural change in pyrochlore $Nd_2Mo_2O_7$

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By measurements of specific heat, we have investigated the magnetic field (H) induced spin-structural change in $Nd_2Mo_2O_7$ that shows intriguing spin-chirality-related magnetotransport phenomena. With increasing H, a broad peak around 2 K caused by the ordering of 2-in 2-out structure of the Nd moments shifts to the lower temperature (T) up to around 3 T and then to the higher T above around 3 T irrespective of the H-direction. This is due to the crossover from antiferromagnetic to ferromagnetic arrangement between the Nd and Mo moments. While the peak T increases monotonically above 3 T for $H\|[100]$, another peak emerges around 0.9 K at 12 T for $H\|[111]$, which is ascribed to the emergence of 3-in 1-out structure. For $H\|[110]$, a spikelike peak is observed at around 3 T, which is caused perhaps by some spin flip transition.

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Interesting magnetic phenomena are frequently observed due to geometrical frustration in pyrochlore oxides where the magnetic ions reside on the vertices of linked tetrahedra. One such example is the so-called "spin ice" state in $R_2Ti_2O_7$ (R=Ho, Dy).[1] In $Dy_2Ti_2O_7$, for example, the dipolar interaction among Ising-like Dy moments induces the 2-in 2-out structure, in which the two Dy moments in a tetrahedron point inward and the other two moments point outward. However, there are macroscopically large numbers of spin structures satisfying the 2-in 2-out rule. Consequently, the macroscopically degenerate ground state is realized in this material as shown by Ramirez *et al.*[2] The spin state under magnetic field is selected from the degenerate states at zero field except in the high field region of $H\|[111]$. When a small field is applied, finite magnetization parallel to the magnetic field is induced while the 2-in 2-out structure remains intact.[3–5] For $H\|[111]$, the spin-structural transition from 2-in 2-out to 3-in 1-out structure is observed around 1 T.[3,4,6]

In $Nd_2Mo_2O_7$, the Nd moments show the 2-in 2-out structure similarly to the spin ice materials, as revealed by neutron diffraction measurements.[7,8] In this material, however, the 2-in 2-out structure is long-range ordered in such a way that the net moment of the Nd is antiparallel to that of the spin-polarized itinerant Mo 4*d* electrons. The Mo and Nd sublattices have the same structure, but are displaced from each other by half a unit cell. The antiferromagnetic *f*-*d* coupling makes the Heisenberg-like Mo moments tilted slightly (at most by several degrees[7,8]) from the direction of the net magnetization. Hence, the spin chirality in the 2-in 2-out structure of Nd moments is transmitted to the Mo spin system. Recently, an unusual behavior of anomalous Hall effect was observed in $Nd_2Mo_2O_7$ and the origin was proposed to be the spin chirality in the Mo spin system.[7] In this paper, we have investigated the spin-structural change in $Nd_2Mo_2O_7$ by means of specific heat measurements. Most of the arguments are concerning the Ising-like Nd moments, which is closely linked with the spin chirality in Mo spin system. While the ground state degeneracy has not been observed, the variation of the spin structure under magnetic field is quite similar to that in spin ice materials, including the spin state transition from 2-in 2-out to 3-in 1-out structure for $H\|[111]$. Some of these results provide a supporting evidence of the spin chirality scenario for the unusual anomalous Hall effect.

A single crystal of $Nd_2Mo_2O_7$ was grown by floating zone method. The details of the sample growth are reported elsewhere.[7,9] We reproduce the results of the magnetization and the resistivity for the $Nd_2Mo_2O_7$ crystal at H=0.5 T applied parallel to the [100] direction[7] in Fig. 1(d). The resistivity shows a metallic behavior in the whole temperature (T) region (2 K$\leqslant T\leqslant$150 K). The magnetization begins to in-

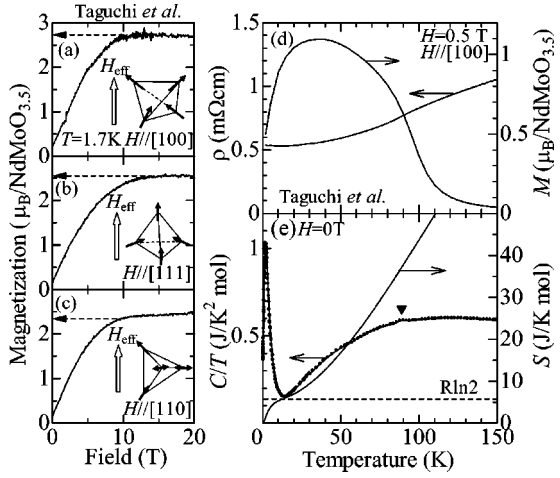

FIG. 1. (a)–(c) Magnetization curves at 1.7 K with magnetic field (H) along (a) [100], (b) [111], and (c) [110] axes. Insets in (a)–(c) show spin structures realized in the high field region of the respective configuration. (d) Temperature (T) dependence of magnetization and resistivity at 0.5 T ($H\|[100]$). (e) T-variation of specific heat and entropy at 0 T. Closed triangle indicates the ferromagnetic transition T of Mo spin. The magnetization and resistivity data in (a)–(d) are taken from Refs. 3 and 5.

crease rapidly with decreasing T below around 100 K, reflecting the ferromagnetic transition of the Mo spin ($T_C \approx 90$ K). At around 30 K, the magnetization shows the down-turn due to the ferrimagnetic ordering of Nd moments. We reproduce the magnetization curves at 1.7 K for the $H \| [100]$, [111], and [110] axes in Figs. 1(a)–1(c), respectively.[9] For all the field directions, enough high-H reverses the Nd moments, resulting in the saturated moments that are much larger than the Mo spin moment ($\approx 1.4\mu_B$/Mo). For $H \| [100]$ and [110], the saturated moments are in accord with those expected for the 2-in 2-out structure ($=1.4\mu_B + 1/\sqrt{3} g_{\mathrm{eff}}^{\mathrm{Nd}} J^{\mathrm{Nd}} \mu_B$ and $1.4\mu_B + 1/\sqrt{6} g_{\mathrm{eff}}^{\mathrm{Nd}} J^{\mathrm{Nd}} \mu_B$ for $H \| [100]$ and [110], respectively) with the magnitude being $g_{\mathrm{eff}}^{\mathrm{Nd}} J^{\mathrm{Nd}} \mu_B \approx 2.3\mu_B$. These expected values are indicated by the dashed arrows. On the other hand, in the case of $H \| [111]$, the saturated moment is larger than that expected by the 2-in 2-out structure, but coincides with that expected for the 3-in 1-out structure $\left(=1.4\mu_B + \frac{1}{2} g_{\mathrm{eff}}^{\mathrm{Nd}} J^{\mathrm{Nd}} \mu_B\right)$. This is also indicated by the dashed arrow. In the canonical case of $Dy_2Ti_2O_7$, the metamagnetic transition from the 2-in 2-out to 3-in 1-out structure is observed as a steplike increase in the magnetization curve for $H \| [111]$.[3,6] However, any trace of such a step is hardly observed in $Nd_2Mo_2O_7$ down to 70 mK.[9]

We measured the specific heat by the conventional relaxation method. The specific heat of $Nd_2Mo_2O_7$ at zero H is shown in Fig. 1(e). A small peak is discerned around 90 K as indicated by the closed triangle. This is owing to the ferromagnetic transition of the Mo spin. In the low-T region ($\leqslant 15$ K), the specific heat is dominated by an intense peak, which is caused by the ordering of the 2-in 2-out structure in the Nd sublattice. These features observed at zero H have already been reported in literature.[10] We also plot the T-dependence of the entropy S deduced from the T-integration of $C(T)/T$. For the analysis, we assumed the linear relation in C/T below the lowest T (≈ 0.4 K). The S at 15 K is almost in accord with the value of $R \ln 2$, which is expected as from the degree of freedom of Ising moments. Therefore, the entropy of Ising-like Nd moments is mostly released in the low-T ($\leqslant 15$ K) region.

In Figs. 2(a) and 2(b), we show the T- and H-variation of specific heat of the $Nd_2Mo_2O_7$ crystal below 15 K for $H \| [100]$, in which all of the four Nd moments in a tetrahedron make the same angle with the H [see the inset of Fig. 1(a)]. Whereas the peak due to the ordering of the 2-in 2-out structure becomes sharper with increasing H below 3 T, it becomes broader and the peak T increases as H is increased from 3 T. We plot the H-variation of the S at 4 K and the peak T in Figs. 2(c) and 2(d), respectively. Reflecting the crossover around 3 T in the specific heat, the S at 4 K shows down-turn and the peak T shows up-turn around *3* T. In the canonical case of $Dy_2Ti_2O_7$, the ordering T of the 2-in 2-out structure increases with increasing H along the [100] direction.[4] In the present case, the effective field for the Nd moments, that is the sum of the applied H and the *negative* molecular field from Mo spins, changes its sign from negative to positive at around 3 T. This is the reason for the nonmonotonic H-dependence of S at 4 K and peak T. Therefore, the crossover around 3 T can be ascribed to the reversal

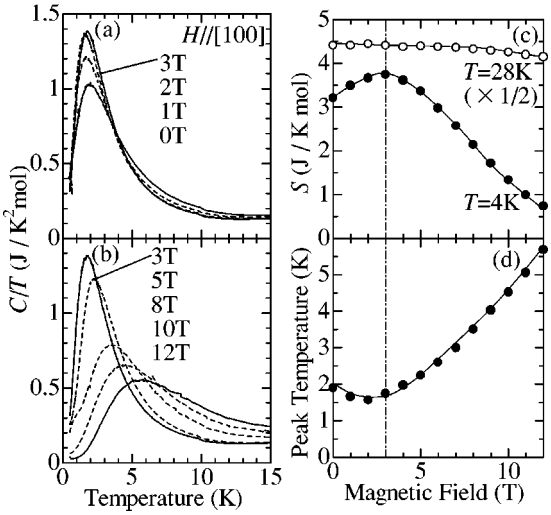

FIG. 2. (a),(b) Temperature (T) and magnetic field (H) variation of specific heat for $H \| [100]$. (c) H-dependence of entropy (S) at 4 and 28 K for $H \| [100]$. (d) H-variation of the peak T in the specific heat data shown in (a) and (b).The vertical dot-dashed line in (c) and (d) indicates the crossover H from the antiferromagnetic to ferromagnetic arrangement between Nd and Mo moments. Solid lines in (c) and (d) are merely the guide for the eyes.

of the Nd moments, which is consistent with the results of recent neutron measurements.[11,12]

We plot the S at 28 K for $H \| [100]$ in Fig. 2(c). The entropy originating from the Nd moments is almost completely released below 28 K. Nearly H-independent S at 28 K indicates the absence of zero point entropy even at zero effective field for Nd moments, namely, at around $H = 3$ T, where the decrease of S would otherwise be observed. (The slight decrease of the entropy in the high-H region corresponds to its transfer to the higher-T region above 28 K.) Thus, the ground state degeneracy seems to be lifted by the interaction with the itinerant Mo 4*d* electrons even around 3 T. The S at 28 K shows a similar behavior in the cases of $H \| [111]$ and $H \| [110]$ [see Figs. 3(d) and 4(c)], suggesting that zero point entropy has not been observed in any configuration for $Nd_2Mo_2O_7$.

We show the T- and H-variation of specific heat of the $Nd_2Mo_2O_7$ crystal for $H \| [111]$ in Figs. 3(a)–3(c). In this configuration, one out of four Nd moments in a tetrahedron is parallel to the H as shown in the inset of Fig. 1(b). Similar to the case of $H \| [100]$, the peak due to the ordering of the 2-in 2-out structure becomes sharper with increasing H up to 3 T owing to the decrease of the total effective field. The crossover around 3T is also discerned in the S at 4 K as shown in Fig. 3(d). Above 3T, the peak becomes broader with increasing H while the shift of the peak is less significant compared with the case of $H \| [100]$. Above around 9 T, the specific heat in the low-T region ($T < 1.3$ K) is gradually enhanced with increasing H. At 11 T, the specific heat shows a much broader peak, which may be viewed as composed of several peaks. Then, at 12 T, another clear peak emerges at low T (≈ 0.9 K). A kneelike structure is also observed around 4 K in the 12 T data. These low-T peak and kneelike structure can be ascribed to the emergence of the 3-in 1-out struc-

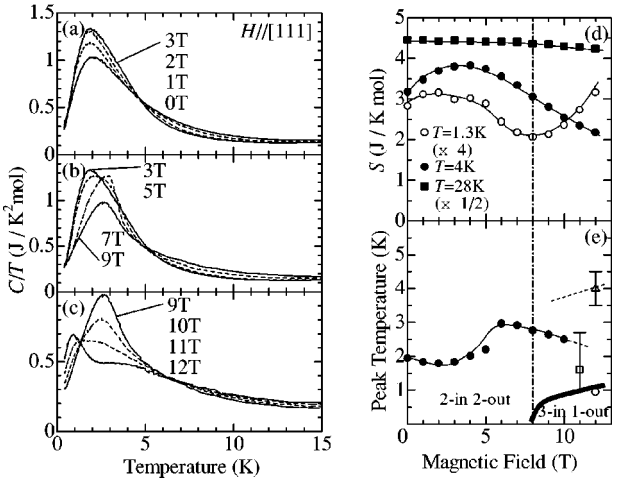

FIG. 3. (a)–(c) Temperature (T) and magnetic field (H) variation of specific heat for $H\|[111]$. (d) H-dependence of entropy (S) at 1.3, 4, and 28 K for $H\|[111]$. (e) Characteristic T obtained by the specific heat data for $H\|[111]$. Closed and open circles show the peak T due to the ordering of the 2-in 2-out and 3-in 1-out structure, respectively. An open triangle shows the T-position of the kneelike structure in the 12 T data. An open square shows the T-position of the broader peak in the 11 T data. The vertical dot-dashed line in (d) and (e) represents the crossover H at low T from the 2-in 2-out to the 3-in 1-out structure. Solid, dashed, and hatched lines in (d) and (e) are merely guides for the eyes.

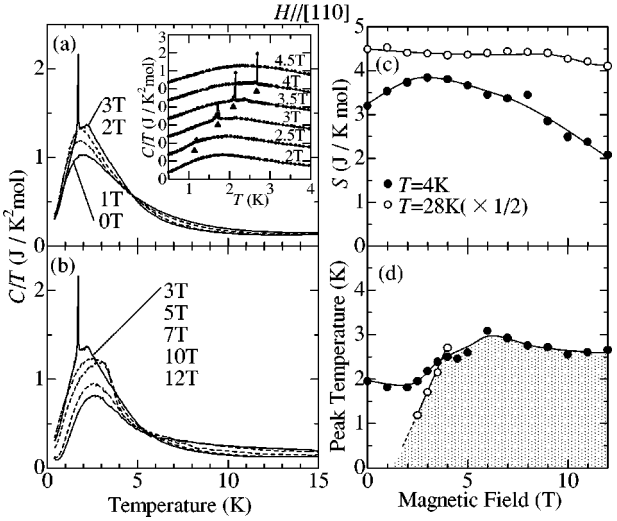

FIG. 4. (a),(b) Temperature (T) and magnetic field (H) variation of specific heat for $H\|[110]$. Inset in (a) shows the detailed specific-heat data in the T- and H-region where the spikelike peak is observed. (c) H-dependence of entropy (S) at 4 and 28 K for $H\|[110]$. (d) T-positions of the broad peak around 2 K and the spikelike peak (closed and open circles, respectively). Solid and dashed lines in (c) and (d) are merely guides for the eyes.

ture [the inset of Fig. 1(b)] and the ordering of the apical Nd moments whose Ising-axis is parallel to H, respectively,[13] in analogy to the typical spin ice material $Dy_2Ti_2O_7$, where two peaks of specific heat are discerned in the high-H region above around 1 T.[4,13] This assignment is also supported by the fact that the saturated moment for $H\|[111]$ almost coincides with that expected by the 3-in 1-out structure above 12 T.

We plot the peak T due to the ordering of the 2-in 2-out structure for $H\|[111]$ with closed circles in Fig. 3(e). An upward shift of the peak T is observed around 3 T similar to the case of $H\|[100]$. The peak T shows a kink at 6 T, above which the peak T slightly decreases with H. We also plot in Fig. 3(e) the T positions of the peak due to the ordering of the 3-in 1-out structure and the kneelike structure in the 12 T data with an open circle and triangle, respectively. The T-position of the broad peak at 11 T is also shown as an open square. The ordering T of the 3-in 1-out structure at 12 T [an open circle in Fig. 3(e)] is lower than that of the 2-in 2-out structure in the lower-H region. The broad specific-heat peak at 11 T ranging over the wide temperature region ($1.0\ \mathrm{K} \leqslant T \leqslant 2.7\ \mathrm{K}$), as indicated by the open square with a long vertical bar, can be ascribed to heavily mixed state of the 2-in 2-out and 3-in 1-out configuration in these T- and H-regions. The correlation of the 3-in 1-out structure starts to grow at lower-H than 11 T because the magnetization for $H\|[111]$ exceeds the value expected for the 2-in 2-out structure already around 8 T. The gradual enhancement of low-T ($\leqslant 1.3$ K) specific heat above around 9 T may correspond to the evolution of such correlation. We plot the H-dependence of the S at 1.3 K in Fig. 3(d). The quantity shows a minimum at around $H=8$ T, which is thought to be the onset H of the correlation of the 3-in 1-out structure. This coincides with the field where the sign change of the Hall resistivity has been observed[9] in $H\|[111]$ configuration. These observations are in accord with the spin chirality scenario for the anomalous Hall effect that predicts the sign reversal of Hall resistivity upon the sign change of the spin chirality in the course of the spin-structural change from the 2-in 2-out to 3-in 1-out structure.

We show the T- and H-variation of the specific heat of the $Nd_2Mo_2O_7$ crystal for $H\|[110]$ in Figs. 4(a) and 4(b). In this configuration, two out of four Nd moments in a tetrahedron are perpendicular to the H [see the inset of Fig. 1(c)]. Similar to the cases of $H\|[100]$ and $H\|[111]$, the peak around 2 K becomes sharper with H up to 3 T and then broader above 3 T. The H-variation of S at 4 K and the peak T are shown in Figs. 4(c) and 4(d), respectively. Corresponding to the crossover around 3 T, the S at 4 K shows the maximum. The peak T shows a local minimum around 3 T and then a kink around 6 T.[14] Because the Nd moments perpendicular to the H are hardly affected by the H, the peak T is kept almost constant in the high-H region above 8 T, which is similar to the $Dy_2Ti_2O_7$ case.[5]

An unique feature to $H\|[110]$ is a spikelike peak observed only between 2.5 and 4.0 T, as exemplified in the inset of Fig. 4(a). The peak becomes sharper and the peak T increases from 1.2 to 2.7 K with H in this H-region. In Fig. 4(d), we plot with open circles the T of the spikelike peak. The spikelike peak mainly exists below the peak T associated with the ordering of the 2-in 2-out structure. Such a spikelike peak as releasing minimal entropy is expected in the case of a spin-flip transition. Then, the question is what kind of spin-flip transition occurs. One possibility is the aforementioned transition around 3 T from the antiferromagnetic to ferro-

magnetic arrangement between Nd and Mo moments. If this were the case, the spikelike peak would be observed also for the other configurations since the transition is not specific for $H\|[110]$. Another possibility is the spin-flip transition concerning the Nd moments perpendicular to H. Even if the 2-in 2-out structure is assumed, there are two possible arrangements of the Nd moments perpendicular to H, namely, "in-out" and "out-in," in every tetrahedron for $H\|[110]$ [see the inset of Fig. 1(c)]. There might be the spin-flip transition between nearly degenerate two spin-structural phases where the arrangements of the perpendicular moments are different from each other. However, the recent neutron measurement suggests that the net perpendicular moments does not change up to 5 T.[11] At present, we cannot draw a definite conclusion about the microscopic detail of the spin-flip transition. More detailed investigations in terms of diffraction measurements would be needed.

In summary, we have investigated the specific heat in $Nd_2Mo_2O_7$ as functions of direction and magnitude of H as well as T. A broad peak is observed around 2 K at zero H, which is owing to the ordering of the 2-in 2-out structure of the Nd moments. The peak T decreases with H up to around 3 T and then increases above around 3 T irrespective of the direction of H. This is due to the crossover from antiparallel to parallel arrangement between the net magnetizations of the Nd and Mo moments. The peak T increases monotonically above 3 T for $H\|[100]$. On the other hand, in the case of $H\|[111]$, another peak emerges at around 0.9 K at 12 T, owing to the ordering of the 3-in 1-out structure of the Nd moments. This is consistent with the sign reversal of the Hall resistivity reported by a previous study.[9] For $H\|[110]$, a spikelike peak with minimal entropy release is observed at around 3 T, which is ascribed to some spin flip transition.

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[13] In the specific heat of $Dy_2Ti_2O_7$ for $H\|[111]$, the higher-T peak is discerned even below the transition H from the 2-in 2-out to 3-in 1-out structure.[4] In the present compound, on the other hand, the higher-T peak can barely be observed as the kneelike structure only in the 12 T data. The reason of this difference is that the higher-T peak possibly tends to be smeared out due to the interaction with the Mo 4*d* electrons in $Nd_2Mo_2O_7$. The kink in the peak-T associated with the ordering of the 2-in 2-out structure around 6 T [Fig. 3(e)] may indicate the onset of the separation of the parallel-moment component from the main peak.

[14] The kink can be ascribed to the bifurcation of the ordering process into lower-T, 2-in 2-out ordering, and higher-T ordering of the half of Nd moments that are not perpendicular to the H, similar to the case of $Dy_2Ti_2O_7$,[5] although the higher-T peak seems to be smeared out due to the interaction with the Mo 4*d* electrons in $Nd_2Mo_2O_7$.