

Chemical control of spin chirality in $(\text{Nd}_{1-x}\text{Dy}_x)_2\text{Mo}_2\text{O}_7$

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Magnetization and Hall resistivity have been investigated for single crystals of Dy-doped $\text{Nd}_2\text{Mo}_2\text{O}_7$. A sharp decrease of the Hall resistivity upon a metamagnetic transition, perhaps associated with magnetic-field (H) induced flop of Dy^{3+} moments, has been observed in the Dy-doped crystals only for $H\parallel[111]$ direction. In addition, the sign of the Hall resistivity at a high field, both for $H\parallel[100]$ and for $H\parallel[111]$, changes with the Dy doping. These results are explained in terms of the sign change of Mo spin chirality that is controlled by the Dy^{3+} moments with a different sign of f - d interaction from the Nd^{3+} moments.

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Transport properties in strongly correlated systems are largely affected by the configuration of spin background. Typical example is colossal magnetoresistance phenomena in manganites,¹ where magnitude of transfer interaction, and hence longitudinal conductivity, is controlled by the degree of ferromagnetic spin correlation.² Recently, it has been argued³⁻⁶ that nontrivial spin texture can give rise to quantal phase of the electron transfer interaction, and that the phase, which acts as a fictitious magnetic field, manifests itself as transverse conductivity. Experimental evidences for this mechanism of anomalous Hall effect (Berry phase mechanism) have been accumulated for various kinds of oxide materials.⁷⁻¹¹ Among them, unconventional behaviors, such as temperature variation and anisotropic magnetic field dependence, of the anomalous Hall effect in $\text{Nd}_2\text{Mo}_2\text{O}_7$ with pyrochlore structure^{9,11,12} are considered as strong evidences for the Berry phase mechanism of anomalous Hall effect, although they are not interpreted as such in some literature.¹²

The unique behaviors of the anomalous Hall effect in $\text{Nd}_2\text{Mo}_2\text{O}_7$ arise from the complex magnetic structure^{9,13} realized on that particular pyrochlore lattice. The lattice consists of two sublattices of the Nd and Mo site, both of which form corner-sharing networks of tetrahedra. One sublattice is obtained by displacing the other one by half a lattice constant along a crystallographic axis. The localized Nd moment has Ising-like anisotropy along the local $\langle 111 \rangle$ axis which differs from site to site, and the anisotropy of the Nd moment system is transmitted via f - d interaction to the Mo spin system, with which conduction electrons interact via Hund's-rule coupling. Sign reversal of the Hall resistivity at high fields applied along the $[111]$ direction is explained¹¹ in terms of field-induced flipping of Nd moments and consequent sign change of fictitious magnetic field that penetrates a Mo tetrahedron. On the other hand, a rather conventional behavior of anomalous Hall effect in $\text{Gd}_2\text{Mo}_2\text{O}_7$ is ascribed¹¹ to the isotropic nature of Gd^{3+} moment without orbital angular momentum, and to the resultant absence of spin chirality in the Mo spin system. Therefore, the anisotropy of the magnetic moment of the rare earth ion is a key ingredient in this

mechanism of anomalous Hall effect. In this communication, we fully exploit the fact that the spin chirality of the Mo system is controlled by the moment of rare earth species, and report on the variation of the Hall resistivity with the partial Dy-substitution on the Nd site. The Dy^{3+} with strong Ising anisotropy¹⁴⁻¹⁶ has a larger moment ($\approx 10\mu_B$) than the Nd^{3+} ($\approx 2.3\mu_B$), and hence, is more amenable to an applied field. Even more important is the fact that the Dy-Mo interaction is ferromagnetic as opposed to antiferromagnetic Nd-Mo interaction, as we will see. Therefore, Mo spins near the Dy moments are tilted in a different way from the undoped sample, which enables us to chemically control the spin chirality related phenomena in terms of Dy doping into $\text{Nd}_2\text{Mo}_2\text{O}_7$.

All the samples used in this study were single crystals prepared by a floating-zone method in Ar atmosphere. Powder x-ray diffraction measurements indicated that the samples were of single phase. Hall resistivity and magnetization measurements were done on the same sample for each Dy concentration and sample orientation. The Hall resistivity was measured by using the conventional four-probe method. We extracted the odd component of Hall voltage with respect to the reversal of field direction in order to eliminate the longitudinal voltage drop due to the asymmetry of Hall voltage probes.

In Figs. 1(a)–1(c), we show the magnetization process (field-decreasing run) of $(\text{Nd}_{1-x}\text{Dy}_x)_2\text{Mo}_2\text{O}_7$ with $x=0$ (at 1.6 K), $x=0.2$ and $x=0.35$ (at 2 K), whose Curie temperatures determined from alternating current susceptibility measurements are 89, 80, and 76 K, respectively. The results of the undoped ($x=0$) sample were reproduced from Ref. 11. Applied field directions are along $[100]$ (broken lines) and $[111]$ (closed lines). The magnetization due to the Mo spin system in this temperature range is about $1.4\mu_B/(\text{Nd,Dy})\text{MoO}_{3.5}$,⁹ and is indicated by a horizontal dotted line. The magnetization process of the $x=0$ crystal can be viewed¹¹ as gradual flipping process of Nd moments that are coupled antiferromagnetically with Mo spins at zero field. The partial substitution of Dy moments produces an almost parallel shift of the magnetization curves toward

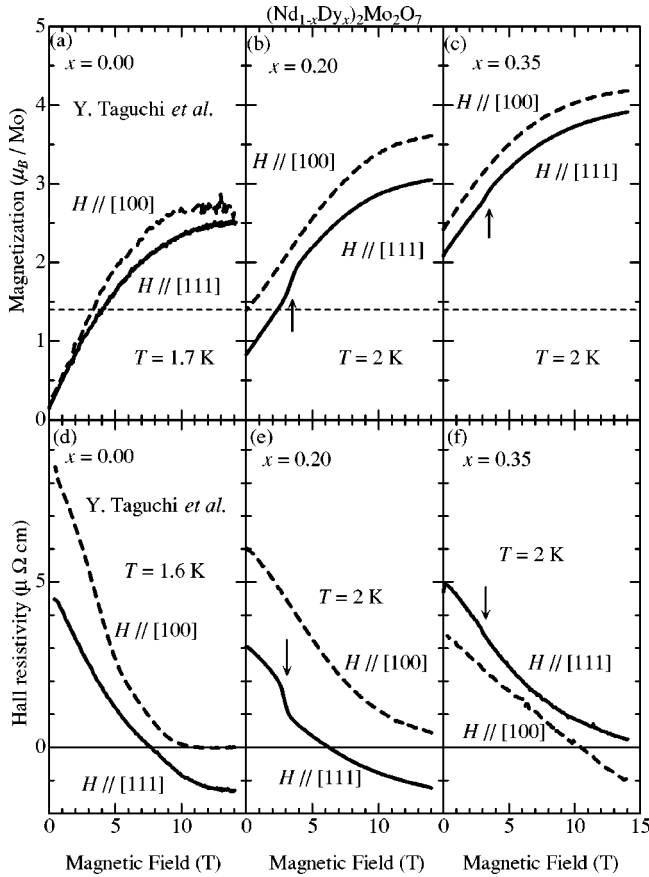


FIG. 1. Magnetic field dependence of (a)–(c) magnetization and (d)–(f) Hall resistivity of $(\text{Nd}_{1-x}\text{Dy}_x)_2\text{Mo}_2\text{O}_7$ crystals with $x=0$, 0.2, and 0.35 for the magnetic-field (H) directions, $H\parallel[100]$ and $H\parallel[111]$. Arrows in (b), (c) and (e), (f) indicate the position of the metamagnetic anomaly. A horizontal broken line in (a)–(c) represents the contribution to the total magnetization from the Mo spins alone. Magnetization and Hall resistivity data in (a) and (d) are reproduced from Ref. 11.

higher values. The Dy moments in the pyrochlore lattice are well known^{14–16} to behave like $\langle 111 \rangle$ Ising moment with larger magnitude ($\approx 10\mu_B$) than that of Nd moment ($\approx 2.3\mu_B$). The Dy-doping dependence of the magnetization values at low (0 T from the field-decreasing run) and high (14 T) field are shown in Fig. 2(a). The increased magnetization at zero field upon the partial Dy substitution indicates that the interaction between Dy moments and Mo spin system is basically ferromagnetic. As indicated by upward arrows in Figs. 1(b) and 1(c), a metamagnetic anomaly is clearly discerned at about 3 T in the Dy-doped samples when the field is applied along the $[111]$ direction. We ascribe this anomaly to the collective flipping of minority part of Dy moments that point antiparallel to the net magnetization direction, as we will later discuss in detail. There is no trace of such a metamagnetic anomaly either in the case of $H\parallel[100]$ direction for any x or in the $x=0$ crystal for any field direction.

In Figs. 1(d)–1(f), Hall resistivity (ρ_H) is plotted against magnetic field (H) for the samples with $x=0$, 0.2, and 0.35. The Hall resistivity of the undoped sample undergoes a sign

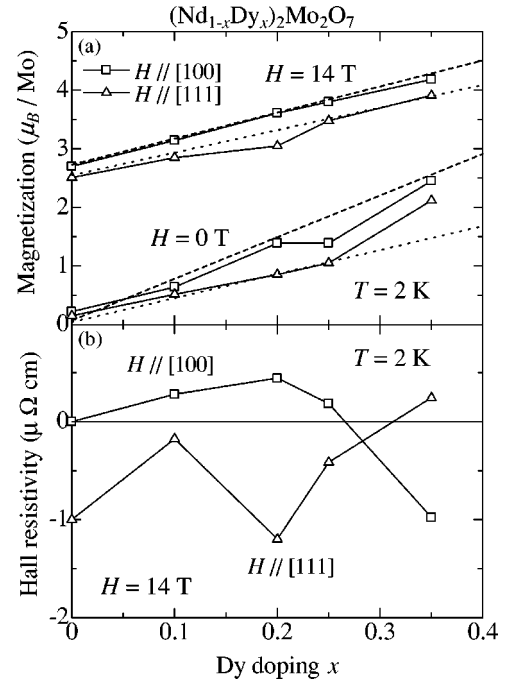


FIG. 2. Dy doping (x) dependence of (a) magnetization at 2 K and at 0 and 14 T, and (b) Hall resistivity at 2 K and 14 T for $(\text{Nd}_{1-x}\text{Dy}_x)_2\text{Mo}_2\text{O}_7$ with $H\parallel[100]$ and $H\parallel[111]$ geometries. Dotted lines are the x dependence at 0 T calculated by assuming that the moment of the doped Dy points the opposite direction to the original Nd moment on the same site, as exemplified in (b)–(e) and (n) of Fig. 4. Dashed lines are for the high-field case calculated by assuming that all the Dy and Nd moments are aligned, while keeping the Ising anisotropy, toward the H direction, as shown in the right-most column (h)–(l), (o), and (p) in Fig. 4.

change when $H\parallel[111]$, while gradually approaching zero for $H\parallel[100]$. This behavior is in accord with the prediction by the Berry phase theory, and has been interpreted¹¹ in terms of field-induced sign reversal of the Mo spin chirality. The $x=0.2$ Dy-doped crystal also exhibits a similar feature with the $x=0$ crystal. For $x=0.35$, by contrast, the Hall resistivity shows a qualitatively different behavior in the high field region: The sign of ρ_H changes from positive to negative when $H\parallel[100]$, while for $H\parallel[111]$ the sign remains positive. On the basis of chirality mechanism, this result implies that the Dy moments interacting ferromagnetically with the Mo spins may alter the sign of the Berry phase of Mo conduction electrons in an opposite way to the case of the undoped $\text{Nd}_2\text{Mo}_2\text{O}_7$ in the high field region. The sign change of the high-field (14 T) Hall resistivity as a function of Dy doping is summarized for the both field directions in the Fig. 2(b). In the low-doped region of $x \leq 0.25$, the Hall resistivity at 14 T is positive or almost zero, while it becomes negative for $x=0.35$. Conversely, the Hall resistivity for $H\parallel[111]$ direction is negative for $x \leq 0.25$, but becomes positive at $x=0.35$. (Further Dy doping beyond $x=0.35$ drives the system insulating, and makes it extremely difficult to measure the Hall resistivity.)

What is also unique for the Dy-doped crystal is a sudden decrease of Hall resistivity associated with the metamagnetic anomaly at about 3 T, as indicated by downward arrows in

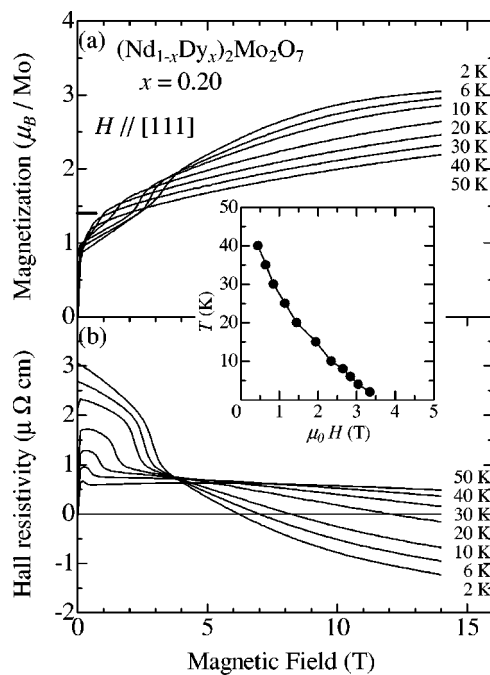


FIG. 3. (a) Magnetization and (b) Hall resistivity of $(\text{Nd}_{1-x}\text{Dy}_x)_2\text{Mo}_2\text{O}_7$ with $x=0.2$ at various temperatures are plotted against applied magnetic field (H) along [111]. The inset shows the relation between the field and the temperature (T) where the meta-magnetic transition occurs.

Figs. 1(e) and 1(f). The feature shows up most clearly in the $x=0.20$ case, but is also discerned for $x=0.35$. To show the temperature dependence of the anomaly, we show in Figs. 3(a) and 3(b) the magnetization and Hall resistivity of the $x=0.2$ sample, respectively, at various temperatures as a function of H ||[111]. As the temperature is elevated from 2 K, the magnetic field at which the anomaly occurs shifts gradually to lower field, and eventually disappears at about 50 K. In the inset to Fig. 3 is shown the relation between temperature and magnetic field where the metamagnetic transition is observed. The transition point is defined as the magnetic field where dM/dH value takes maximum at each temperature.

In the case of the undoped sample, the Nd moments form umbrella structure, or “2-in 2-out” structure,^{9,13} at a small enough field. The magnetic structure is depicted for H ||[111] configuration in Fig. 4(a), where H direction is upward. Figures 4(b)–4(e) are the cases where only one Dy is doped into the single tetrahedron. (We neglect the cases where more than one Dy ions are included in the tetrahedron, for simplicity.) The configuration of the Dy moment is determined by the combined effect of f - d and f - f interactions. The former is ferromagnetic as we have already noted, and the latter must be antiferromagnetic on the basis of the following argument. If the f - f interaction could be neglected, all the Dy moments would point to the same direction as the Mo spins or the magnetic field even at a small enough field. In this case, the expected value of the magnetization increase upon the 20% Dy doping at a small enough field would be $1.2\mu_B/(\text{Nd,Dy})\text{MoO}_{3.5}$, which is much larger than the observed value of $0.6\mu_B/(\text{Nd,Dy})\text{MoO}_{3.5}$ [see Fig. 2(a)]. Therefore, the f - f interaction cannot be neglected and has to

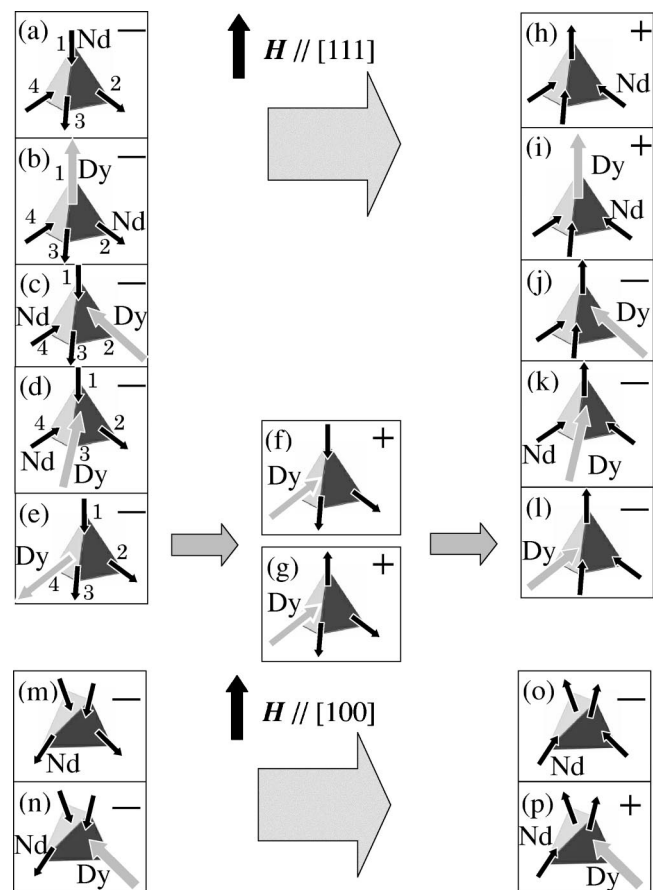


FIG. 4. The magnetic structure of rare-earth tetrahedra. In the panels (a)–(p), magnetic field (H) is applied along [111] ([100]) direction. Panels (a)–(e), (m), and (n) correspond to the cases with a small enough magnetic field while panels (h)–(l), (o), and (p) to the cases with a high magnetic field. Panels (f) and (g) represent the configuration right after the flipping of Dy moments at site 4. Nd and Dy moments are represented by smaller and larger arrows, respectively. The “+/-” symbol indicates the sign of fictitious field that penetrates Mo tetrahedra.

be taken into account. If the Dy moment substituted for site 4 points antiparallel to the net magnetization as depicted in Fig. 4(e), the magnetization increase is expected to be $0.8\mu_B/(\text{Nd,Dy})\text{MoO}_{3.5}$ at 20% Dy doping. Provided that the doped Dy moments always point antiparallel to the replaced original Nd moments in the 2-in 2-out configuration, the anticipated variation of the spontaneous ($H=0$) magnetization is shown with a dotted line in Fig. 2(a), which is very close to the observed. The configuration 4(e) is possible only when the Dy-Nd interaction is antiferromagnetic. Note that the antiferromagnetic Dy-Nd interaction is compatible with configurations 4(b)–4(d) that are made by the ferromagnetic Dy-Mo interaction. When H is increased, the Dy moments at site 4 collectively flip so as to gain the Zeeman energy, at the expense of the Dy-Nd interaction energy. The collective flipping of Dy moments corresponds to the metamagnetic anomaly observed at around 3.5 T at 2 K. The observed jump of magnetization in the 20% Dy-doped sample is about $0.3\text{--}0.4\mu_B/(\text{Nd,Dy})\text{MoO}_{3.5}$, which is in good agreement with the expected value of $0.33\mu_B/(\text{Nd,Dy})\text{MoO}_{3.5}$ for the

spin-flip process (e)→(f) in Fig. 4. The interaction energy, or equivalently the molecular field from the Nd moments, which prevents Dy moments from flipping, grows in magnitude as the ordered moment of Nd increases. This is the reason why the temperature dependence of the metamagnetic anomaly (shown in the inset to Fig. 3) is qualitatively similar to the evolution of the ordered Nd moments.

In the case of $H\parallel[100]$ as depicted in Fig. 4(n), by contrast, all the Dy moments seem to point toward the field direction. This is because this configuration is compatible with the antiferromagnetic Dy-Nd as well as the ferromagnetic Dy-Mo interactions. In fact, the observed Dy-doping dependence of magnetization for a small $H\parallel[100]$ is in reasonable agreement with the expected value [a dashed line in Fig. 2(a)], which was derived again on the assumption that the doped Dy moment always points antiparallel to the original Nd moment. Therefore, all the Dy moments are already aligned along the field direction at a small enough field, which explains why no metamagnetic anomaly is observed in the magnetization curve for $H\parallel[100]$.

Keeping these features of the (Nd,Dy) moment configuration in mind, we discuss the Hall resistivity anomaly upon the Dy-related metamagnetic transition as well as the Dy-doping induced sign reversal of Hall resistivity at a high field. As we have argued, the moments which show field-induced flipping are the Dy moments at site 4 [Fig. 4(e)]. The magnetic structures of the tetrahedron right after the Dy flipping are depicted in Figs. 4(f) and 4(g). For the purpose of simplicity, we assume that all the (Nd,Dy) tetrahedra which surround one Mo tetrahedron have the same magnetic structure. Then, the fictitious field changes the sign upon flipping of Dy moment at site 4. The sign of the fictitious magnetic field that penetrates the Mo tetrahedron is indicated by “+” or “-” in the each panel of Fig. 4. This gives rise to the sudden decrease of Hall resistivity. At a high enough field

(e.g., 14 T), all the Nd and Dy moments point to the field direction to gain the Zeeman energy, as shown in Figs. 4(h)–4(l). If we take into account the different sign of $f-d$ interaction between Nd-Mo and Dy-Mo, the sign of the fictitious magnetic field becomes positive in some of the tetrahedra that include Dy ions, as opposed to negative sign in the tetrahedra without Dy. Therefore, as the Dy concentration is increased, the number of the tetrahedra that include Dy increases, and eventually the sign of the Hall resistivity at the high field changes from negative to positive. On the other hand, when the strong magnetic field is applied along $[100]$ direction, a tetrahedron that includes Dy ion makes a negative-sign contribution to the Hall resistivity [Fig. 4(p)]. Thus, the sign of the Hall resistivity changes from positive to negative, just in the opposite way to the case of $H\parallel[111]$.

In summary, we have investigated the anisotropic magnetization and Hall resistivity for a series of $(\text{Nd}_{1-x}\text{Dy}_x)_2\text{Mo}_2\text{O}_7$ single crystals. A metamagnetic anomaly is observed in the magnetization curve for $H\parallel[111]$. The Hall resistivity shows a sudden decrease upon the metamagnetic transition. We attribute this anomaly to collective flipping of minority part of Dy moments, and the decrease of Hall resistivity to the sign change of fictitious field that penetrates Mo tetrahedra near the flipped Dy moments. As the Dy concentration is increased, the sign of the Hall resistivity at a high enough field has changed from negative to positive for $H\parallel[111]$, and vice versa for $H\parallel[100]$. This is caused by the change of Mo spin tilting that is controlled by the Dy moments with different sign of $f-d$ interaction from that of Nd.

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