Successive Phase Transitions and Magnetic Fluctuation in a Double-Perovskite NdBaMn$_2$O$_6$ Single Crystal

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Abstract. We have succeeded in growing large high-quality single crystals of double-perovskite NdBaMn$_2$O$_6$ with c-axis aligned. Curie-Weiss paramagnetism and metallic conduction are observed above 290 K ($T_{MI}$). The magnetic susceptibility suddenly drops at $T_{MI}$ accompanied by a metal-insulator transition. Previous studies using polycrystalline samples proposed that this material undergoes a ferromagnetic phase transition near 300K, and that the magnetic anomaly at $T_{MI}$ should be ascribed to layered antiferromagnetic phase transition. However, single-crystalline samples do not show any anomaly that indicates the ferromagnetic phase transition above $T_{MI}$. We assign the onset of magnetic anisotropy at 235 K as antiferromagnetic transition temperature $T_N$. Though the magnetization just above $T_{MI}$ shows the ferromagnetic-like magnetic-field dependence, the magnetization does not saturate under 70kOe at 300K. The magnetization behavior implies ferromagnetic fluctuation in the paramagnetic phase. The ferromagnetic fluctuation are also observed just below $T_{MI}$. Because a metamagnetic transition is observed at a higher magnetic field, the ferromagnetic fluctuation competes with antiferromagnetic fluctuation in this temperature range.

1. Introduction
The physical properties of a family of double-perovskite manganites REBaMn$_2$O$_6$ (where RE is divalent rare earth) were attracting much attention in terms of A-site randomness-free perovskite manganites.[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] Because magnetic and electric ordering phases are stabilized by the A-site ordering, the phase diagram of REBaMn$_2$O$_6$ is completely different from that of A-site disordered perovskite manganites RE$_{0.5}$Ba$_{0.5}$MnO$_3$, where the magnetic ground state is paramagnetic or spin glass phase. When the ionic radius of RE is equal to or smaller than Sm, charge ordering phase is observed even above 380 K. The highest charge order is observed at 550 K in YBaMn$_2$O$_6$. This material has the potential for room temperature magnetoresistance device due to the melting of the charge ordering. Actually, fairly large magnetoresistance at
room temperature was observed in A-site ordered Sm$_{1-x}$La$_{x+y}$Ba$_1-y$Mn$_2$O$_6$.[12] On the other hand, when the ionic radius of RE is equal to or larger than Nd, the charge ordering phase is not observed. The previous studies using the NdBaMn$_2$O$_6$ polycrystal suggested that a ferromagnetic phase transition was observed near 310 K, and A-type antiferromagnetic phase was stabilized below 290 K.[7, 11]

Recently, we succeeded in the single crystal growth of a double-perovskite manganite SmBaMn$_2$O$_6$, and revealed that the magnetic property was different from polycrystals.[13] Moreover, we found that the spatial inversion symmetry was broken in low-temperature charge ordering phase by means of the single crystal structure analysis using synchrotron x-ray diffraction.[14, 15] These results suggest the importance of the studies using single crystal for double perovskite manganites. We also succeeded in the single crystal growth of NdBaMn$_2$O$_6$.[16] The studies on the magnetic, electric and crystal structure using the single crystal provided new information about the phase transitions. In particular, the study on the magnetic anisotropy showed that a steep change of magnetic susceptibility near 290 K ($T_{MI}$) was not caused by the antiferromagnetic phase transition and the Néel temperature was near 235 K ($T_N$) which was more 50 K lower than $T_{MI}$. Additionally, we did not clearly observe the ferromagnetic transition near 300 K, which were proposed by previous papers. In general, two dimensional metallic conduction is observed in A-type antiferromagnetic phase[17]. Nevertheless, an insulating behavior was observed not only along the $c$-axis but also in the $ab$-plane below $T_{MI}$. The magnetic phases around $T_{MI}$ might be more complicated than reported by pervious studies. In this paper, we revise the magnetic phase diagram of NdBaMn$_2$O$_6$ through magnetization measurements using single crystals.

2. Experimental

Single crystals of NdBaMn$_2$O$_6$ were grown by floating zone (FZ) method. Powders of Nd$_2$O$_3$, BaCO$_3$, and Mn$_3$O$_4$ were mixed, ground, and calcined at 1290 °C for 48 hours in Ar (6N) atmosphere, and then pulverized. The resultant powder was shaped into a cylinder under a hydrostatic pressure of 30 MPa and sintered at 1290 °C for 12 hours in Ar (6N) atmosphere to form feeding and seeding rods. An FZ furnace equipped with two halogen incandescent lamps and hemielliptic focusing mirrors was used for the crystal growth. The molten zone was vertically scanned at a rate of 2 mm/h in Ar gas mixed with a tiny portion (≤ 0.1 %) of H$_2$. The melt grown bar was annealed in O$_2$ atmosphere at 500 °C for 48 hours. In order to measure anisotropic properties, we cut the crystal boules into some pieces, and the orientation of the $c$-axis was determined by x-ray diffraction. Laue photographs confirmed that every sample was a single crystal. Magnetization was measured using a commercial superconducting quantum interface device magnetometer (Quantum Design MPML-XL). The electrical resistivity was measured by a conventional four-probe method.

Figure 1. Temperature dependence of (a) magnetic susceptibility, (b) magnetic anisotropy, and (c) electrical resistivity.[16] The solid and open squares in (a) and (b) denote the cooling and warming processes, respectively.
3. Results and Discussions

Figure 1 shows that the magnetic susceptibility steeply changes around 290 K ($T_{MI}$). This magnetic anomaly is accompanied by a metal-insulator transition. Though previous studies using poly-crystal samples suggested that $T_{MI}$ should correspond to A-type antiferromagnetic phase transition temperature, no clear magnetic anisotropy is observed down to 235 K. Therefore, we conclude that Néel temperature $T_N$ of NdBaMn$_2$O$_6$ is not identical to $T_{MI}$ but 235 K. When an applied magnetic field is 100 Oe, magnetic susceptibility steeply increases with a decrease of temperature around 310 K, as denoted by a large arrow in Fig. 1(a). On the other hand, when an applied magnetic field is 10 kOe. No anomaly is observed above $T_{MI}$. To reveal the magnetic phase just above $T_{MI}$, magnetic field dependence of magnetization was investigated in this temperature range. At 350 K which is sufficiently higher than $T_{MI}$, the magnetization linearly increases with an applied magnetic field, like a typical paramagnet. The magnetization curves become convex when approaching $T_{MI}$. Below 10 kOe, the magnetization steeply increases with the applied magnetic field. The increase becomes gradual above 20 kOe. The magnetization is smaller than the magnitude of full magnetic moments of Mn$^{3.5+}$ even when the applied magnetic field is 70 kOe. It suggests that ferromagnetic fluctuation in the paramagnetic phase is steeply enhanced down to $T_{MI}$. We conclude that the temperature at which the ferromagnetic fluctuation arises is 310 K ($T_F$) from Weiss temperature in our previous report.[16]

Next, we discuss the magnetic phase just below $T_{MI}$. Fig. 3 (a) shows that no magnetic anisotropy is observed below 70 kOe in this temperature range. The magnetization jumps near 20 kOe. The isotropic magnetic susceptibility below metamagnetic phase transition and the metamagnetic behavior imply that the long-range antiferromagnetic ordering is not present but the antiferromagnetically fluctuating domains exist in the magnetic ground state in this temperature range. The metamagnetic phase transition field depends on the measurement process. Because the phase transition at $T_{MI}$ is of the first-order, the higher magnetic field phase is essentially identical to that above $T_{MI}$. In low magnetic field range, the magnetization curve of sequence 3 is ferromagnetic-like and different from that of sequence 1. Fig. 3 (b) shows that, below 1 kOe, the magnetization curve after zero field cooling is different from the others. This magnetic field dependence of magnetization in a low magnetic field suggests that the application of a magnetic field induces a phase transition, and the initial state never revives by further field sweeping. At 270 K, which is a little lower than 286 K but still higher than $T_N$, the metamagnetic transition field shifts to higher one. Additionally, the ferromagnetic-like behavior in low magnetic field decreases. Hence the ferromagnetic fluctuation is suppressed with a decrease of temperature. As shown in Fig. 4, at 150 K which is below $T_N$, the magnetization linearly increases to an applied magnetic field, and the magnetic anisotropy is clearly observed. The ferromagnetic fluctuation is disappeared at $T_N$ and this phase below $T_N$ is antiferromagnetic single phase in which the magnetic moments of Mn ions lie in $ab$ plane. In general, $ab$ plane of nearly half doped perovskite manganite shows metallic conductivity in A-type antiferromagnetic phase.[17] However, as shown in Fig.1 (c), NdBaMn$_2$O$_6$ shows a metal-insulator transition at $T_{MI}$ not only along $c$-axis but also within $ab$ plane. The complicated magnetic phase could be one of the origin of the three dimensional insulating conductivity below $T_{MI}$.
Finally, we show magnetic phase diagram of NdBaMn$_2$O$_6$ which are concluded from the study. Though ferromagnetic fluctuation in paramagnetic phase steeply increase just below 310 K ($T_P$), long-range ferromagnetic ordering is not realized above 290 K ($T_{MI}$). At $T_{MI}$, magnetic susceptibility suddenly drops due to antiferromagnetic fluctuation. However, just below $T_{MI}$, long-range antiferromagnetic ordering is not realized due in part to the remaining ferromagnetic fluctuation. The ferromagnetic fluctuation decreases with a decrease of temperature, and disappears at 235 K ($T_N$). Below $T_N$, A-type antiferromagnetic single phase is realized.

4. Conclusion

Through the measurements of the magnetic field dependence of magnetization around $T_{MI}$ in detail, the magnetic phases of NdBaMn$_2$O$_6$ are identified. Below 310 K, ferromagnetic fluctuation in paramagnetic phase grows as it gets closer to $T_{MI}$. On the other hand, the
A-type antiferromagnetic \((S ^{-} c)\)

Paramagnetic

Ferromagnetic fluctuation in paramagnetic phase

Ferromagnetic fluctuation in antiferromagnetically fluctuating domains

\[ T_N = 235 \text{ K} \]

\[ T_{MI} \approx 290 \text{ K} \]

\[ T_p \approx 310 \text{ K} \]

**Figure 5.** Magnetic phase diagram of \(\text{NdBaMn}_2\text{O}_6\). \(S\) is Mn spin moments vector.

Ferromagnetic fluctuation is observed in the temperature range between \(T_{MI}\) and \(T_N\). The metamagnetic phase transition which is caused by melting the antiferromagnetic domains is observed by relatively low magnetic field. Because these magnetic phases are strongly coupled with electric conduction properties, a large magnetoresistance effect is expected in this temperature range.

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