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# Magnetic properties of $Mn_2V_2O_7$ single crystals

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**Abstract**

Magnetic properties of $Mn_2V_2O_7$ single crystals are investigated by means of magnetic susceptibility, magnetization, and heat capacity measurements. A structural phase transition of the $\alpha$–$\beta$ forms is clearly observed at the temperature range of 200–250 K and an antiferromagnetic ordering with magnetic anisotropy is observed below 20 K. A spin-flop transition is observed with magnetic field applied along the [110] axis of $\beta$-$Mn_2V_2O_7$, of which corresponds to the [001] axis of $\alpha$-$Mn_2V_2O_7$, suggesting that the spins of $Mn^{2+}$ ions locate within honeycomb layers which point likely in the [110] direction of $\beta$-$Mn_2V_2O_7$ or the [001] axis of $\alpha$-$Mn_2V_2O_7$. However, a rather small jump of magnetization at spin-flop transition suggests a possible partition of crystal to some domains through $\beta$-to-$\alpha$ transition on cooling or much complex spin structure in honeycomb lattice with some frustration.


*Keywords:* $Mn_2V_2O_7$; Vanadates; Antiferromagnet; Spin-flop transition

## 1. Introduction

Search for low-dimensional magnetic materials has been one of the most active fields in solid state chemistry and physics, which has brought various fascinating magnetic phenomena. For example, novel spin-Peierls transition and Haldane spin-liquid ground state are observed in one-dimensional (1D) spin-$\frac{1}{2}$ and spin-1 systems [1,2], respectively, while spin-glass behavior [3], spin-flop transition [4], Kosterlitz–Thouless behavior [5], and even superconductivity [6] are found in two-dimensional (2D) spin systems. From a structural viewpoint, compounds with a linear chain structure usually display a characteristic 1D magnetism and compounds with a layer structure display a prototype of 2D magnetism. Such correlation between magnetic properties and their structures is well understood by our recent investigation on the compounds with a general formula $AM_2V_2O_8$ ($A$ = Ba, Sr; $M$ = Cu, Ni, Co, Mn), in which $BaCu_2V_2O_8$ [7], $BaCo_2V_2O_8$ [8], and $BaMn_2V_2O_8$ [9] show a typical 1D magnetism due to their chain structure along the $c$-axis, while $BaNi_2V_2O_8$, however, is a good example for 2D spin systems due to its honeycomb structure [10].

$Mn_2V_2O_7$ is found to have a peculiar distorted honeycomb structure, which exhibits two phases of a high-temperature form ($\beta$-form) and a low-temperature form ($\alpha$-form) [11]. The $\beta$-form crystallizes in monoclinic system of space group $C2/m$ with $a = 6.7129(6)$ Å, $b = 8.7245(5)$ Å, $c = 4.9693(4)$ Å, and $\beta = 103.591(8)^\circ$, while the $\alpha$-form crystallizes in a triclinic system of space group $P\bar{1}$ with $a' = 6.868(2)$ Å, $b' = 7.976(2)$ Å, $c' = 10.927(2)$ Å, $\alpha = 87.81(1)^\circ$, $\beta = 72.14(1)^\circ$, and $\gamma = 83.08(1)^\circ$. As shown in Fig. 1, one of the most significant differences in their structural features between $\alpha$ and $\beta$ forms is that the honeycomb layers in the $\beta$-form are parallel to the (001) plane and those in the $\alpha$-form are parallel to the $(1\bar{1}0)$ plane. A comparison of structural features in the $\alpha$- and $\beta$-forms of $Mn_2V_2O_7$ shows that the relation of the primitive vectors of the $\alpha$-form (triclinic) to the $\beta$-form (monoclinic) can be expressed as follows: $a' = \frac{1}{2}(a-b+2c)$, $b' = \frac{1}{2}(a-b-2c)$, and $c' = a+b$, where the primed characters refer to the primitive vectors of the $\alpha$-form (triclinic). The directions of [001], [110] and $[1\bar{1}0]$ in the monoclinic $\beta$-form are found to correspond to those of $[1\bar{1}0]$, [001] and [110] in the triclinic $\alpha$-form of $Mn_2V_2O_7$, respectively. Such structural phase transition of the $\alpha$–$\beta$ forms was reported

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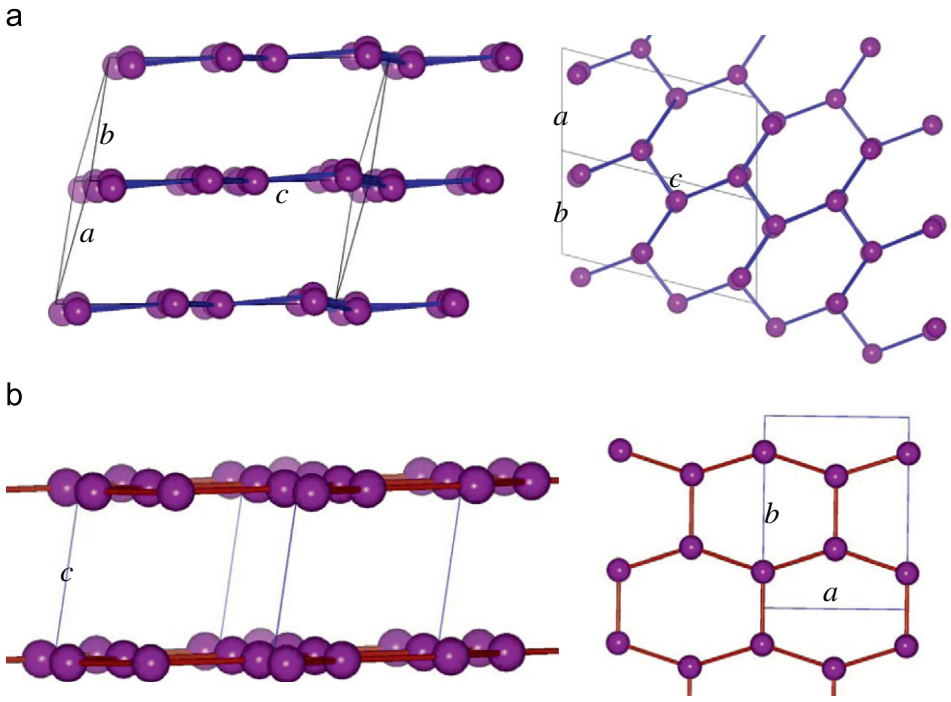


Fig. 1. A distorted honeycomb layer structure of $Mn_2V_2O_7$ built by $Mn^{2+}$ ions: (a) the $\alpha$-form and (b) the $\beta$-form.

to occur at ~296 K in polycrystalline sample and magnetic behaviors were investigated using polycrystalline sample, due to lack of a large sized single crystal [11].

In this study, we report magnetic behaviors of $Mn_2V_2O_7$ using a single crystal sample by means of magnetic susceptibility, magnetization and heat capacity measurements. Our experimental results show that a structural phase transition of the $\alpha$–$\beta$ forms with large hysteresis occurs (at ~250 K on heating and at ~200 K on cooling) and $Mn_2V_2O_7$ crystals exhibit an antiferromagnetic ordering with magnetic anisotropy below ~20 K, in which the spins of $Mn^{2+}$ ions locate within honeycomb layers, pointing likely in the [110] direction of $\beta$-$Mn_2V_2O_7$ or the [001] axis of $\alpha$-$Mn_2V_2O_7$.

## 2. Experimental section

$\beta$-$Mn_2V_2O_7$ single crystals were successfully obtained by a flux method using $SrV_2O_6$ as flux [12]. The mixture of high purity reagents of $MnC_2O_4 \cdot 2H_2O$ (3 N, 25 g), $V_2O_5$ (4 N, 20 g), and $SrCO_3$ (4 N, 5 g), corresponding to the ratio of $Mn_2V_2O_7$:$SrV_2O_6 = 2$:1, was ground carefully, homogenized thoroughly, and then packed into an alumina crucible capped with a cover using $Al_2O_3$ cement (C-989, Cotronics Corp.). Such closed crucible was put into a homemade electric furnace with an adjustable temperature gradient and then the furnace was heated up to 1080 °C and kept at 1080 °C for 10 h to ensure that the solution melts completely and homogeneously. The furnace was cooled slowly down to 800 °C at a rate of 0.5 °C/h while keeping at a constant temperature several times, and then cooled down to room temperature at a rate of about 100 °C/h. Based on this procedure, single crystals with a pillar-like morphology were obtained by mechanical separation from the crucible and the cleaved planes are found to be the natural facets (110) and (350) of the $\beta$-form [12].

Magnetic susceptibility and magnetization were measured along the directions parallel and perpendicular to the $c$-axis and the (110) plane of the $\beta$-form in a grown crystal using a superconducting quantum interference device (MPMS-5S, Quantum Design) magnetometer and the heat capacity was measured at zero applied field by a relaxation method using a commercial Physical Property Measurement System (PPMS, Quantum Design).

## 3. Results and discussion

Fig. 2(a) shows the temperature dependence of magnetic susceptibilities from 5 to 350 K on heating, which are measured in an applied field 1 T along the directions parallel and perpendicular to the $c$-axis and the (110) plane of $\beta$-$Mn_2V_2O_7$, $H\parallel[001]$, $H\parallel[110]$ and $H\perp[110]$, respectively. Different histories are clearly seen below 20 K, dependent on the magnetic field applied along different directions. This indicates magnetic anisotropy in the system, suggesting an antiferromagnetic (AF) ordered ground state. On the other hand, a jump in the susceptibility is seen at ~250 K, showing the appearance of a phase transition. This phase transition at ~250 K is suggested to be a structural phase transition of the $\alpha$–$\beta$ forms, in which a large hysteresis is observed at 200–250 K on the cooling and heating regimes with a rate of 2 K/min as seen in the inset of Fig. 2(a). The phase transition is very sharp compared with the previous report on polycrystalline

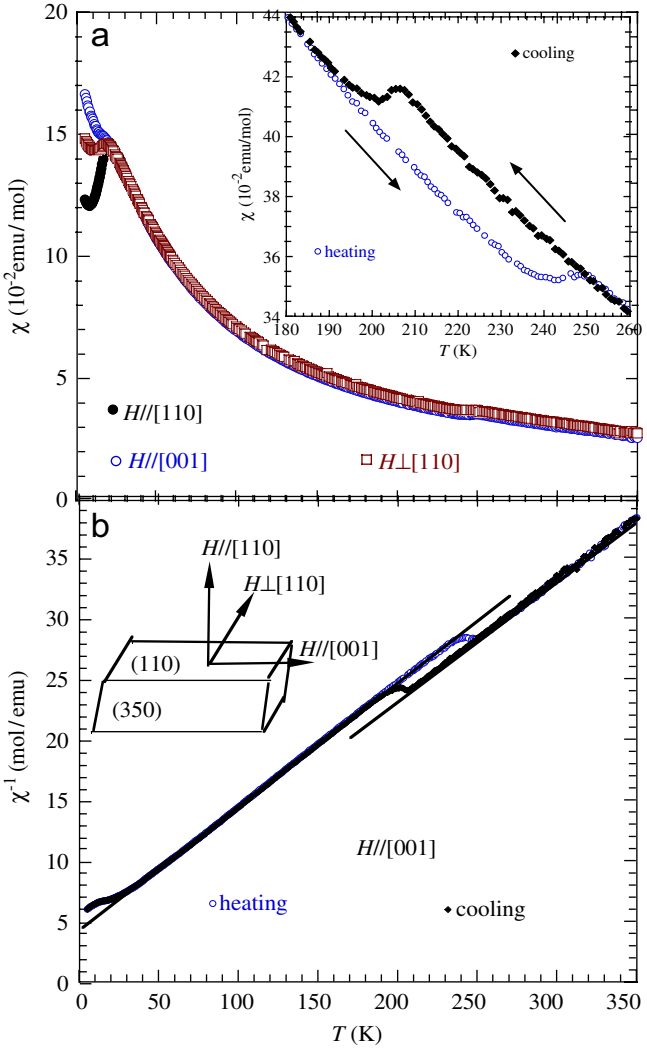


Fig. 2. (a) Magnetic susceptibilities measured from 5 to 350 K on heating regime in a magnetic field of 1 T along the directions parallel and perpendicular to [001] and [110] in a $\beta$-$Mn_2V_2O_7$ single crystal. The inset shows a large hysteresis at 200–250 K on the cooling and heating regimes with a rate of 2 K/min. (b) The reciprocal susceptibility measured along the [001] direction of $\beta$-$Mn_2V_2O_7$ on the cooling and heating regimes. The image of sample and the directions of magnetic field are seen.

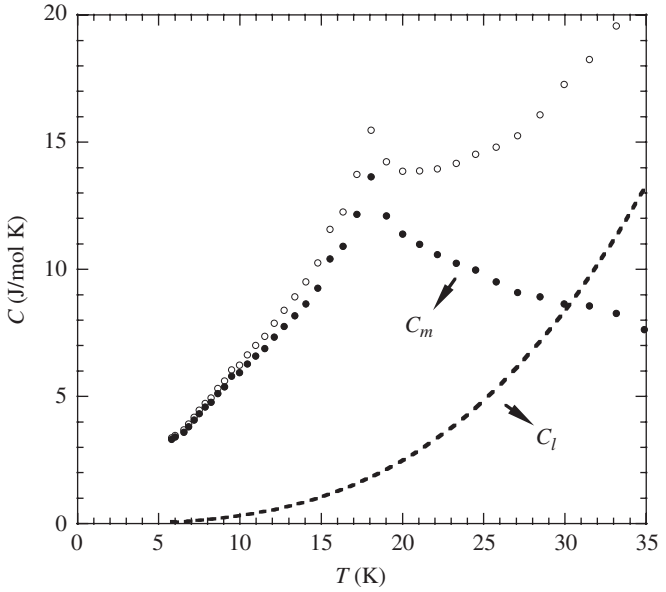


Fig. 3. Heat capacity ($C_p$) measured in zero magnetic field. The dashed line represents the lattice contribution ($C_l$) and the closed circles the magnetic one ($C_m$) calculated from $C_m = C_p - C_l$.

sample [11]. However, we found that the temperature of $\alpha$–$\beta$ form phase transition on a single crystal is clearly lower than that at ~296 K suggested previously on polycrystalline sample [11]. We also measured magnetic susceptibilities by using pulverized sample of crystals and found the same transition temperature and hysteresis as in crystal. The origin of this difference on the temperature of structural transition between the present and previous reports is not clear. This may be due to different structural relaxations, which are likely affected by sample quality or cooling/heating rate.

Fig. 2(b) shows the reciprocal susceptibility measured along the [001] direction of $\beta$-$Mn_2V_2O_7$ on the cooling and heating regimes. Above 20 K, a typical Curie–Weiss behavior is observed in the $\alpha$- and $\beta$-forms of $Mn_2V_2O_7$, giving the Curie constant $C = 9.829(8)$ emu K/mol and Weiss constant $\theta = -42.66(7)$ for the $\alpha$-form and $C = 9.895(9)$ emu K/mol and $\theta = -26.66(7)$ for the $\beta$-form, respectively. The effective magnetic moment ($\mu_{eff}$) is calculated to be 6.27(1) $\mu_B$ in the $\alpha$-form and 6.29(1) $\mu_B$ in the $\beta$-form, both of which are larger than the value of 5.91(6) $\mu_B$ for $S = \frac{5}{2}$ with a $g$ factor of 2, showing that $Mn^{2+}$ ions have a high spin state and the system exhibits magnetic anisotropy due to admixture of the orbital moment. Also, the negative Weiss constant suggests that the interactions between $Mn^{2+}$ ions are AF. We note that the value of $\theta$ in the $\alpha$-form is larger than that in the $\beta$-form, clearly showing an increase in AF interaction due to structural transition from the $\beta$-form to the $\alpha$-form of $Mn_2V_2O_7$. This is in good agreement with a decrease of the volume from the $\beta$-form (565.76 Å, $Z = 4$) to the $\alpha$-form (564.5 Å, $Z = 4$) [11], indicating an enhancement of interactions between $Mn^{2+}$-bonds.

Fig. 3 shows heat capacity data in applied field of $H = 0$. A $\lambda$-like feature is clearly seen around 18 K, giving clear evidence for a long-range AF ordering. Since $Mn_2V_2O_7$ is an insulator, the total heat capacity $C$ can be considered as the sum of the lattice term ($C_l$) and the magnetic term ($C_m$), $C_p = \gamma T + \beta T^3$, where $\gamma T$ corresponds to the magnetic contribution $C_m$ from spin systems and $\beta T^3$ to the lattice one $C_l$ from phonons. Heat capacity data at low temperature (below 15 K) can be fitted well with $\gamma = 0.60(5)$ J mol$^{-1}$ K$^{-1}$ and $\beta = 3.1(4) \times 10^{-4}$ J mol$^{-1}$ K$^{-4}$. Therefore, the magnetic contribution can be calculated as $C_m = C_p - C_l$ and the magnetic entropy integrated over $\lambda$-like anomaly is estimated to be $\Delta S = \sim 3.87(5)$ J mol$^{-1}$ K$^{-1}$, which corresponds to approximately 27.3% of $R\ln(2S+1)$ expected for spin-$\frac{5}{2}$ systems. Such underestimation of spin entropy might be due to an overestimation of lattice contribution or a development of short range ordering

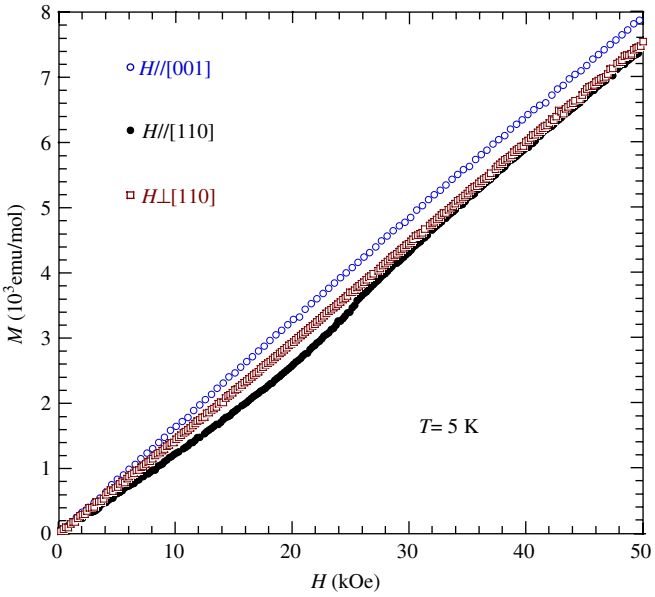


Fig. 4. Magnetization ($M$) as a function of applied field ($H$) along the directions parallel and perpendicular to [001] and [110] in a $\beta$-$Mn_2V_2O_7$ single crystal at $T = 5$ K.

above $T_N$. Actually $T_N$ of ~20 K is rather low compared with Weiss constant $\theta$ of ~43 K and some geometrical frustration in honeycomb lattice might suppress 3D magnetic ordering.

Fig. 4 shows magnetization ($M$) as a function of applied field ($H$) at $T = 5$ K. A linear increase in magnetization is observed in $H\|[001]$ and $H\perp[110]$ for $\beta$-$Mn_2V_2O_7$, agreeing with an AF ordering below 20 K, while a rapid increase is observed at $H = \sim 2.5$ T along the [110] direction of $\beta$-$Mn_2V_2O_7$, showing a spin-flop transition. These results provide clear evidence for magnetic anisotropy in the system.

The structural phase transition of the $\alpha$–$\beta$ forms of $Mn_2V_2O_7$ is found to occur at the temperature range of 200–250 K, giving a clear evidence that only $\beta$-$Mn_2V_2O_7$ single crystals can be grown at room temperature and magnetic behaviors investigated at low temperature are related to $\alpha$-$Mn_2V_2O_7$. Therefore, spin-flop transition observed with the applied field along the [110] direction of $\beta$-$Mn_2V_2O_7$ at $T = 5$ K (Fig. 4) means a field-induced spin-flop transition in the [001] direction of $\alpha$-$Mn_2V_2O_7$, due to the fact that the [110] direction in the monoclinic $\beta$-form corresponds to the [001] direction in the triclinic $\alpha$-form of $Mn_2V_2O_7$. This shows that the spins of $Mn^{2+}$ ions may locate within honeycomb planes, pointing likely in the directions of [001] of $\alpha$-$Mn_2V_2O_7$ or the directions of [110] of $\beta$-$Mn_2V_2O_7$. However, the jump of magnetization at spin-flop transition is rather small, compared with expected one in simple collinear type antiferromagnet. This suggests a possible partition of crystal to some domains through $\beta$-to-$\alpha$ transition on cooling or much complex spin structure in honeycomb lattice with some frustration. In addition, $Mn_2V_2O_7$ has a distorted honeycomb layer structure, 2D magnetism, indicative of a broad peak in susceptibility as shown in $BaNi_2V_2O_8$ [10] is not observed in our investigation on crystal sample, agreeing with the results of polycrystalline sample [11]. Such absence of 2D magnetic feature may indicate a large interaction between honeycomb layers of $Mn_2V_2O_7$, due to its distorted structural feature. We suggest that further studies such as neutron scattering, ESR, and NMR on single crystals are needed to identify the magnetic nature of $Mn_2V_2O_7$.

## 4. Conclusions

Magnetic properties of $\beta$-$Mn_2V_2O_7$ single crystals have been investigated by magnetic susceptibility, magnetization, and heat capacity measurements. The results show that a structural phase transition of $\alpha$–$\beta$ forms occurs at the temperature range of 200–250 K, of which is lower than that observed previously in polycrystalline sample. An antiferromagnetic ordering occurs below 20 K and a spin-flop transition is observed with magnetic field applied only along the [110] axis of $\beta$-$Mn_2V_2O_7$, indicating that $Mn_2V_2O_7$ has magnetic anisotropy. The spins of $Mn^{2+}$ ions are suggested to locate within honeycomb planes, which point likely in the directions of [110] of $\beta$-$Mn_2V_2O_7$, corresponding to the [001] axis of $\alpha$-$Mn_2V_2O_7$. Although $Mn_2V_2O_7$ has a honeycomb layer structure, 2D magnetic feature was not observed.

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