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Magnetic properties of $Mn_2V_2O_7$ single crystals

Zhangzhen He*, Yutaka Ueda

Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan

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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 α–β 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 β-$Mn_2V_2O_7$, of which corresponds to the [001] axis of α-$Mn_2V_2O_7$, suggesting that the spins of Mn^{2+} ions locate within honeycomb layers which point likely in the [110] direction of β-$Mn_2V_2O_7$ or the [001] axis of α-$Mn_2V_2O_7$. However, a rather small jump of magnetization at spin-flop transition suggests a possible partition of crystal to some domains through β-to-α 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 (β-form) and a low-temperature form (α-form) [11]. The β-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 α-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 α and β forms is that the honeycomb layers in the β-form are parallel to the (001) plane and those in the α-form are parallel to the $(1\bar{1}0)$ plane. A comparison of structural features in the α- and β-forms of $Mn_2V_2O_7$ shows that the relation of the primitive vectors of the α-form (triclinic) to the β-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 α-form (triclinic). The directions of [001], [110] and $[1\bar{1}0]$ in the monoclinic β-form are found to correspond to those of $[1\bar{1}0]$, [001] and [110] in the triclinic α-form of $Mn_2V_2O_7$, respectively. Such structural phase transition of the α–β forms was reported

*Corresponding author. Fax: +81 4 7136 3436.
E-mail address: he@issp.u-tokyo.ac.jp (Z. He).

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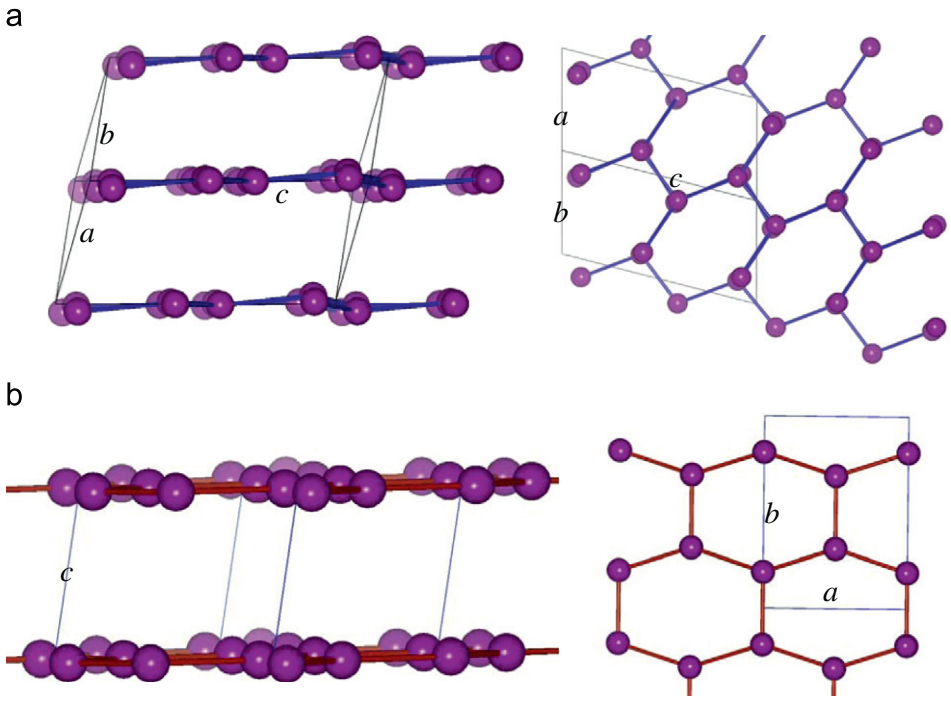

Fig. 1. A distorted honeycomb layer structure of $Mn_2V_2O_7$ built by Mn^{2+} ions: (a) the α-form and (b) the β-form.

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 α–β 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 β-$Mn_2V_2O_7$ or the [001] axis of α-$Mn_2V_2O_7$.

2. Experimental section

β-$Mn_2V_2O_7$ 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 β-form [12].

Magnetic susceptibility and magnetization were measured along the directions parallel and perpendicular to the c-axis and the (110) plane of the β-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 β-$Mn_2V_2O_7$, $H\parallel[001]$, $H\parallel[110]$ 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 α–β 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