Electron Spin Resonance in a New Triangular-Lattice Mn Layered Oxide

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Abstract. We have performed electron spin resonance (ESR) measurements on single crystals of a new Mn layered oxide Rb₄Mn(MoO₄)₃. The Mn²⁺ ions with S = 5/2 form an equilateral triangular-lattice. The magnetization process of this compound is well reproduced by a theoretical calculation in terms of an Ising-like Heisenberg antiferromagnet on a triangular-lattice. The frequency dependence of the ESR resonance fields along the easy-axis in the low-temperature phase is well explained by the calculations expected from the Ising-like Heisenberg model. We have evaluated the anisotropy and exchange interaction constants, and confirmed that this compound is a good example of the Ising-like Heisenberg antiferromagnet on the regular triangular-lattice.

1. Introduction

Two-dimensional triangular-lattice antiferromagnet (TAFM) has been studied extensively as a typical example of geometrically frustrated magnets. Recently, with the development of sample preparation techniques, many new TAFMs have been successfully synthesized. Some of them show no long-range order (LRO) down to extremely low temperatures suggesting novel types of ground state [1, 2]. Furthermore, some TAFMs are discovered to be multiferroics, which show ferroelectric polarization related to their spin structure [3, 4]. There are, however, few examples of the nearest-neighbor Ising-like Heisenberg (IH) TAFM [5]. The magnetic field versus temperature phase diagram and magnetization process of IH TAFM are theoretically calculated by a classical Monte Carlo method in Ref. [6]. The theory shows an existence of four types of phases and appearance of a 1/3 magnetization plateau in magnetic field parallel to the easy-axis. Very recently, Ishii et al. have successfully synthesized high-quality single crystals of Mn Layered oxide Rb₄Mn(MoO₄)₃, which is expected to be a model substance of insulating TAFM [7]. Magnetic properties of this compound have been investigated by magnetization, magnetic susceptibility, and specific heat measurements. The obtained phase diagram showing two successive phase transitions at T_N₁=2.4 K and T_N₂=2.8 K at zero field and magnetization process including 1/3 magnetization plateau between about 4.1 T and 8.8 T at 0.97 K reproduce those expected for the IH TAFM [7]. Thus, Rb₄Mn(MoO₄)₃ is expected to be a good candidate for insulating IH TAFM.

In this paper, we performed multi-frequency electron spin resonance (ESR) measurements on single crystals of Rb₄Mn(MoO₄)₃. We show that the experimental results can be explained by
Figure 1. (Color online) (a) Frequency dependence of ESR absorption spectra of Rb$_4$Mn(MoO$_4$)$_3$ at 1.4 K for $H//c$. The signals, indicated by arrows, appear below $T_{N1}$, and those indicated by open circles appear independently of temperature across $T_{N1}$ and $T_{N2}$. (b) The enlarged figure of the spectrum around 7 T at 34.4 GHz. The dotted lines are Lorenz functions, and the broken line is a summation of them.

the simple IH TAFM model, and evaluate precisely the anisotropy and the exchange interaction constants.

2. Material and Methods
Single crystals of Rb$_4$Mn(MoO$_4$)$_3$ were grown by a flux method [7]. The Mn$^{2+}$ ions (3$d^5$, $S = 5/2$) form an exact triangular lattice in the $c$-plane. It has a hexagonal structure with $P6_3/mmc$ symmetry and the lattice parameters $a = 6.099$Å and $c = 23.711$Å (interplane Mn separation is $c/2$), indicating high two dimensionality. The details of the crystal structure will be published elsewhere [7].

ESR measurements were performed by utilizing a 16 T superconductive magnet (Oxford Instruments, UK) and a vector network analyzer MVNA with some extensions (ABmm, France) for the frequencies between 20 GHz and 500 GHz at 1.4 K in magnetic field up to 14 T. At 20.0 GHz and 34.4 GHz, we used home made cylindrical ESR cavity resonators.

3. Experimental results
Figure 1(a) shows the frequency dependence of the ESR absorption spectra at 1.4 K for $H//c$. The arrows indicate resonance signals which appear only below $T_{N1}$. These signals are considered to come from the transitions from the ground state. Since the resonance signals, indicated by the circles, are temperature independent across $T_{N1}$ and $T_{N2}$, it is considered to arise from paramagnetic resonances caused probably by impurity due to deliquescence on the surface of the samples. The ESR spectrum at 34.4 GHz in Fig. 1(b) is composed of three superposed resonance signals which are shown by dotted Lorentzian lines, and the broken line is a summation of three dotted lines. All the resonance fields are plotted in the frequency-field diagram as seen in Fig. 2. The resonance modes from the intrinsic signals, indicated by the closed circles, have two zero-field gaps. The paramagnetic resonances, indicated by the open circles, are well fitted by a paramagnetic resonance line with the $g$-factor $g=2.0$. 
### 4. Analyses and Discussion

We analyze the experimental results in terms of a mean-field approximation assuming the IH model. Thus, the spin Hamiltonian is written as,

\[ \mathcal{H} = J \sum_{<ij>} \mathbf{S}_i \cdot \mathbf{S}_j + D \sum_i (S^z_i)^2 - g \mu_B \sum_i \mathbf{S}_i \cdot \mathbf{H} \]  

where \( D \) is the anisotropy of the easy-axis type (\( D < 0 \)), \( \mu_B \) the Bohr magneton, \( \mathbf{H} \) the external magnetic field, the \( z \)-axis parallel to the \( c \)-axis, \( <ij> \) all the nearest neighbor pairs. In the present case, the spin structure can be described by three sublattice model. Then, the free energy \( F \) is expressed by the following form using the mean-field approximation,

\[ F = A \sum_{<ij>} \mathbf{M}_i \cdot \mathbf{M}_j + K \sum_{i=1}^3 (M^z_i)^2 - \sum_{i=1}^3 \mathbf{M}_i \cdot \mathbf{H}, \]  

where \( A = 3J/(N(g\mu_B)^2) \), \( K = 3D/(N(g\mu_B)^2) \), and \( M_i = N g \mu_B S_i/3 \). \( N \) is the number of magnetic ions, and \( \mathbf{S}_i \) is the spin on the \( i \)-th sublattice. We derive the resonance conditions by solving the equation of motion \( \partial \mathbf{M}_i / \partial t = \gamma [\mathbf{M}_i \times \mathbf{H}_i] \), where \( \gamma \) is the gyromagnetic ratio and \( \mathbf{H}_i \) a mean-field acting on the \( i \)-th sublattice moment given by \( \mathbf{H}_i = -\partial F / \partial \mathbf{M}_i \).

To solve the equation of motion, we use a method applied for ABX_3-type triangular lattice antiferromagnets [8].

For \( H//c \), we find numerically two phase transitions at 5.0 T and 7.2 T as shown in the schematic pictures in Fig. 2 and obtain good agreement between the experiment and the calculation with the parameters \( J/k_B = 1.01 \) K, \( D/k_B = -0.17 \) K. In the case (i) \( 0 \) T < \( H < 5.0 \) T, the ground state is 120° spiral spin configuration, and the directions of the spins on two sublattices come close to the applied field direction with increasing field, keeping the spins on the other one point oppositely to the field. We obtain two gapped modes, \( \hbar \omega_1 \) and \( \hbar \omega_2 \), and a gapless mode, \( \hbar \omega_3 = 0 \). In the case (ii) \( 5.0 \) T < \( H < 7.2 \) T, the collinear spin configuration becomes stable, in which the spins on the two sublattices are parallel and those on one sublattice are antiparallel to the external field, which corresponds to a 1/3 magnetization plateau. While the \( \hbar \omega_1 \) shows gradual changes except at 7.2 T, \( \hbar \omega_2 \) and \( \hbar \omega_3 \) show two bendings at 5.0 T and

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**Figure 2.** (Color online) Frequency-field diagram of the ESR resonance fields of Rb_4Mn(MoO_4)_3 at 1.4 K for \( H//c \). The closed and open circles correspond to the resonance fields of the signals indicated by arrows and open circles in Fig. 1, respectively. The solid and broken lines represent calculated resonance modes and a paramagnetic-resonance line, respectively. The broken lines at 5.0 T and 7.2 T indicate the calculated phase transition fields. The illustrations show schematic views of spin configuration in the external field.
7.2 T. In the case (iii) \(7.2 T < H < 16.3 T\), the spins on the two sublattices are parallel to each other and make a canted state with the other spin. All the spins are aligned with the applied field direction at 16.3 T, which corresponds to a saturation field.

5. Conclusion

We performed multi-frequency ESR measurements on single crystals of the newly synthesized triangular-lattice antiferromagnet \(\text{Rb}_4\text{Mn(MoO}_4\text{)}_3\). Below \(T_{N1}\), the frequency dependence of the ESR resonance fields for \(H//c\) are well explained by our analysis, indicating that \(\text{Rb}_4\text{Mn(MoO}_4\text{)}_3\) is a good example of insulating Ising-like Heisenberg triangular-lattice antiferromagnet. The details including experimental and analytical results for another directions will be presented elsewhere.

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