Frustrated magnetism in a Mott insulator based on a transition metal chalcogenide

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Abstract. A three dimensional geometrically frustrated Mott insulator of tetrahedral cluster compound GaTa₄Se₈ has been studied by X-ray diffraction, susceptibility and specific heat measurements. Temperature dependence of the magnetic susceptibility shows an anomaly peak at 53 K, which is supposed to be the structural transition from cubic to tetragonal structure on the analogy of GaNb₄S₈. Moreover, small g factor compared with GaNb₄S₈ compound revealed strong spin orbit coupling (SOC) which is inherent in this 5d compound.

1. Introduction

Recently, geometrically frustrated Mott insulators have attracted intensive attentions. The geometrical frustration can suppress the formation of long range magnetic order state like antiferromagnetic order due to the symmetry of the lattice and allow for the fascinating phenomena, such as quantum spin liquid state and spin quadrupole moment [1-2]. For examples, the organic Mott insulator -(BEDT-TTF)₂Cu₂(CN)₃ [3-5], which has a dimer spin s = 1/2 located on a geometrically frustrated triangular lattice, exhibits spin liquid state. Exotic two dimensional (2D) magnetism is found to be the triangular lattice antiferromagnet NiGa₅S₄ [2,6-7], where long range interaction plays a role due to the proximity to the Mott transition.

GaTa₄Se₈ belongs to lacunar spinel compounds GaM₄X₈ with M = V, Nb or Ta and X = S, Se or Te [8,9]. The crystal structure can be divided into two unit on geometrically frustrated face centered cubic (fcc) lattice : GaM₄ and M₄X₄ including M₄ cluster. Considering that valence of this compound is Ga³⁺(M³⁺.²⁵⁺)₄(X²⁻)₈, the M₄ cluster has seven valence electrons. M ions are located on the center of the octahedron formed by X ions, so that the 3d band splits into e₉g and t₂g bands. According to molecular orbital theory, by making cluster, six electrons fill the lower energy state and one electron occupies three-fold degenerate t₂g states [10]. Due to strong SOC inherent in 4d and 5d transition metals, s = 1/2 is entangled with effective orbital angular moment l_eff = 1. Thus, total angular moment j_eff = 3/2 states are proposed to be induced [11]. Then the ground state of this system can be considered as quarter filled j_eff = 3/2 Mott state, which is similar with iridiate compounds [12].

Lacunar spinel compounds GaM₄X₈ can exhibit a variety of unusual transport and magnetic behavior. For examples, the insulating states were observed at ambient pressure for GaNb₄S₈, GaNb₄Se₈, and GaTa₄Se₈ [9,13]. Under high pressure, the insulating states can transfer into a metallic or superconductor state in Ga(Nb,Ta)₄Se₈ system [13]. But this insulating state theoretically is not suggested at room temperature according to LDA + U calculation result [9].
By considering SOC additionally, this insulating state could be theoretically explained. Thus these compounds can be considered as unconventional Mott insulator [11] where the electronic conduction originates from the electrons hopping among the widely separated $M_4$ clusters. A sudden drop of the susceptibility is observed around 31 K and effective moment is 0.86 $\mu_B$ [14] for GaNb$_4$S$_8$. However $\mu$SR and NMR measurements show there is no long range magnetic order down to 4.5 K [15,16]. Moreover, these measurements reveal that spin singlet state is formed and Nb$_8$ octamer consisting of two Nb$_4$ clusters is proposed. Above 53 K, from the NMR measurement dynamical Jahn-Teller effect is suggested.

In this work, we report geometrically frustrated Mott insulator GaTa$_4$Se$_8$ which would realize strong SOC since 5$d$ transition metal Ta ($s = 1/2$) cluster is included. Here we performed the susceptibility and heat capacity measurements to investigate the physical properties.

2. Experimental
Polycrystalline samples of GaTa$_4$Se$_8$ were synthesized by a solid state reaction method sealed in a quartz tube. Then it is heated at 900$^\circ$C. The structural properties were checked by X-ray diffraction (RINT2100, RIGAKU). Temperature dependences of magnetic susceptibility were measured by a commercial SQUID magnetometer (MPMS, Quantum Design) from 2 K to 300 K. Heat capacity was checked by a commercial system (PPMS, Quantum Design) from 2 to 70 K under 0 and 9 T.

3. Results and Discussion
3.1. X-ray diffraction
Room temperature XRD shows the sample is single phase with no impurities. All diffraction peaks can be indexed by the cubic GaTa$_4$Se$_8$ structure type ($Fm3m$) with an fcc unit cell, and the lattice constant $a = 10.385(2)$ Å.

![Figure 1. Temperature dependence of the magnetic susceptibility measured with magnetic field $B = 1$ T. The inset shows the inverse susceptibility $1/\chi$. The green lines are linear fit from 70 K to 300 K.](image)
3.2. Susceptibility
The magnetic susceptibility $\chi = M/B$ shows a peak at 53 K shown in Fig 1, which is presumably related to the structural distortion as observed on the analogy of GaNb$_4$S$_8$ [14]. A more sharp peak is observed for our sample around 53 K indicating that high quality polycrystals were synthesized. By fitting high temperature $1/\chi$ using Curie-Weiss Law, Weiss temperature and effective moment of GaTa$_4$Se$_8$ is $\theta_W = -86.2$ K and 0.86\(\mu_B\)/Ta cluster, respectively.

The large negative Weiss temperature suggested the strong antiferromagnetic interaction between inter Ta cluster with $s = 1/2$. Considering that this compound has geometrically frustrated fcc lattice, strong magnetic frustration might be realized. The effective moment is much smaller than the theoretical value 1.73 \(\mu_B\) calculated by $g = 2$ and $s = 1/2$. On the other hand, $g$ factor of GaTa$_4$Se$_8$ is around 0.99 calculated with $s = 1/2$ and $p_{eff} = 0.86 \mu_B$. This value is much smaller compared with $g$ factor of GaNb$_4$S$_8$, which is $g = 2.03$ by using the value of previous report [14,17]. Thus, GaTa$_4$Se$_8$ is thought to be one of best candidates to demonstrate large SOC and $j_{eff}$ physics.

In the intermediate temperature between 53 K and 70 K, the inverse magnetic susceptibility deviates from linear fit. This is similar to a prediction made by theoretical calculations for double perovskite compounds which also have $j_{eff} = 3/2$ and magnetic ions are located on the fcc lattice and in this compounds spin nematic state is discussed [18]. Actually, the origin of this behavior is unclear, but the unconventional behavior in this temperature region is possibly related to quadropole state [18].

3.3. Heat capacity
The temperature dependence of specific heat is shown in Fig 2 (a). We estimated the amount of entropy change $\Delta S$ which is obtained by peak integration between 42 K and 56 K. $\Delta S$ is about 5 J/K close to Rln2. But, when both orbital and magnetic moment degrees of freedom are released, Rln4 should be obtained. If only orbital or magnetic degrees of freedom were released, $\Delta S$ would give Rln2. Considering the case of GaNb$_4$S$_8$, there is possibility that the $\Delta S$ comes from the formation of spin singlet state proximity to 53 K. Then, it is speculated that the orbital degrees of freedom might be already released above 53 K and magnetic degrees of freedom remain. In this case, dynamic Jahn-Teller effect, which doesn’t involve structural distortions, is expected to occur at high temperature to release the orbital degree.

Figure 2 (b) is fitted by $C/T = \gamma + \beta T^2$ and $\gamma$ value means residual entropy at the low
temperature. By applying magnetic field, $\gamma$ value decreased. We can interpret this decreasing on two ways. One is the spin singlet breaking and the other interpretation is residual spins. But in the high magnetic field measurement, there are no sign of singlet breaking like magnetic moment jump. In this case, the decreasing of $\gamma$ value is not from spin singlet breaking but residual moment.

4. Summary

We succeeded in synthesizing single phase polycrystalline samples of GaTa$_4$Se$_8$. Magnetic susceptibility shows an anomaly at 53 K and deviation from Currie Weiss fit in the range of 53–70 K. Our magnetism investigation revealed that this compound exhibits strong SOC. Moreover from both magnetic and specific heat measurement results spin singlet state might realize in the compound. To confirm spin singlet state, further measurements such as $\mu$SR should be carried out to detect a long range ordering.

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