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量子スピン軌道相関系の実験的研究

Experimental Study of Quantum Spin-Orbital Entangled Systems

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Quantum liquid state has been one of the major research interests in condensed matter physics. The ground state, which is characterized by the long-range quantum entanglement, is said to host new interesting physics, like fractional quasiparticle and low-energy excitation above the ground state. Although such ground state has yet to be confirmed experimentally, it is suggested that the key elements to realize it is to have frustration between electronic degrees of freedom (e.g. spin, orbital, or charge), and quantum fluctuation at low temperature. In magnetic system, a quantum spin liquid state may be realized by having geometrical frustration and small magnetic moment (S = 1/2).

To find candidate materials for quantum spin liquid, one can search the materials which possess special structure known as geometrically frustrated lattice. In geometrically frustrated lattice, spins cannot minimize the spin interaction energy due to incompatibility between spin interaction and lattice geometry. This would leads to macroscopic degeneracy. Moreover, magnetic ordering temperature of frustrated system is often found to be suppressed far below its Curie-Weiss temperature. The small magnetic moment is important as well, because it enhance quantum fluctuation at low temperature. Several candidates for quantum spin liquid have been proposed, ranging from organic salts to copper based oxides.

In this thesis, I focused on the 6H-perovskite-compound $Ba_3CuSb_2O_9$ (space group: $P6_3/mmc$). In this copper based oxide, we found a magnetically frustrated ground state, indicated by the absence of magnetic order down to 20 mK (θ_{CW} ~ 50 K)[1]. A recent study has suggested that the orbital state are remain fluctuating down to low temperature, as well as the possible correlation with magnetic spin fluctuations [2, 3]. This would be a rare example of new ground state, characterized by spin-orbital correlation that is usually difficult to be realized due to the large energy scale difference between those associated with spin and orbital degrees of freedom.

Recently, we were able to synthesize single crystalline sample of $Ba_3CuSb_2O_9$ by flux method, using $BaCl_2$ as the flux. Depending on the growth condition, we could obtain two types of single crystalline sample. The single crystalline sample that is grown with only $BaCl_2$ as the flux has cooperative Jahn-Teller transition from hexagonal to orthorhombic symmetry (space group: *Cmcm*) at temperature below 200 K. Such sample is then labeled as *orthorhombic* sample. On the other hand, when we add a small amount of $Ba(OH)_2$ to the flux, we obtain single crystalline samples which retain hexagonal symmetry down to low temperature. This sample is then labeled as *hexagonal* sample. From previous study, it is suggested that hexagonal sample has better stoichiometry compared to orthorhombic sample [1].

$Ba_3CuSb_2O_9$ is initially reported in 1978 as a perovskite compound with layered triangular structure (space group: $P6_3mc$)[4]. A perovskite-type compound generally has a chemical formula of ABX_3 and it has BX_6 octahedra which can be linked by either face-sharing or corner-sharing joint, depends on A site ion's size. If we are to rewrite $Ba_3CuSb_2O_9$ formula as $Ba(Cu_{1/3}Sb_{2/3})O_3$, the A-site will be occupied by barium and B-site will be shared by copper and antimony. This means there are both face-sharing $CuSbO_9$ bi-octahedra ("dumbbell") and corner-sharing SbO_6 octahedra. In this structure Cu ions form two-dimensional triangular lattice with its neighboring Cu, so one may expect a frustrated ground state if the nearest-neighbor coupling is antiferromagnetic. As mentioned before, this system also supposed to be Jahn-Teller active, due to the orbital degeneracy of Cu^{2+}. In this system, orbital degeneracy is provided by the three-fold rotation symmetry of dumbbell.

Our study is motivated by the possibility of finding quantum spin liquid in $Ba_3CuSb_2O_9$. A similar study has proposed a quantum spin liquid ground state based on two dimensional triangular lattice[5]. However, from our X-ray experiments on single crystalline sample, we found that the suitable space group might be different. The previous $P6_3mc$ space group is *non-centrosymmetric*, meaning that copper and antimony sites are not equivalent. In our proposed space group $P6_3/mmc$, copper and antimony sites *are* equivalent so that they are allowed to exchange position to each other. This choice comes from comparing experimental data to the calculation of structure factor. Moreover, pyroelectric current measurement and Second-Harmonic Generation scanning microscopy indicate a cancellation of electric dipole moment that originates from copper and antimony ions' charge difference. These results suggest a staggered dumbbell order and can be used to derive a structure, in which one-third of dumbbells are flipped, forming hexagonal (honeycomb) structure of copper ions (Figure 1). Here, the site of copper ions on the flipped dumbbell are labeled as Cu'.

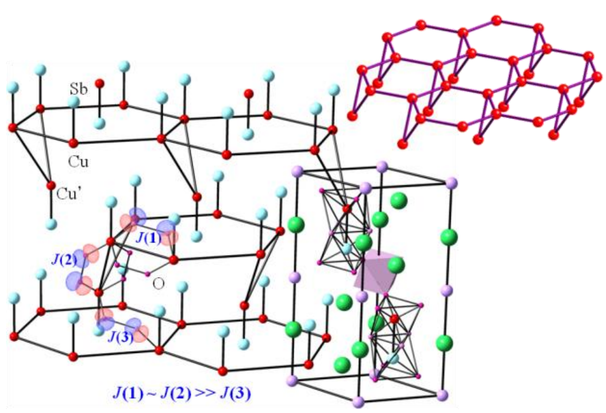

Figure 1. $Ba_3CuSb_2O_9$ crystal structure[1]. (Upper right) Hexagonal structure composed of Cu ions.

In this thesis, we have further studied the low temperature properties of $Ba_3CuSb_2O_9$ by magnetization and specific heat measurements[6]. The AC and DC magnetization are performed by using Superconducting Quantum Interference Device (SQUID) installed in dilution refrigerator at ISSP, University of Tokyo. The specific heat is measured by using He3 system in commercial Physical Properties Measurement System (PPMS) made by *Quantum Design*.

The DC and AC susceptibility measurement (Figure 2a, 2b) both show a peak at 120 mK, which is associated with spin freezing. This spin freezing is slightly glassy, as indicated by the hysteresis between zero-field cooled and field cooled in DC susceptibility, as well as the slight frequency dependence of the freezing temperature in the AC susceptibility. Moreover, below freezing temperature, the susceptibility does not drop rapidly to zero, suggesting only small amount of spin is frozen[7].

The temperature dependence of the low temperature magnetic specific heat (Figure 2c) is dominated by Schottky-type anomaly which can be observed below 10 K. The bump that associated with Schottky anomaly is gradually suppressed as applied magnetic field increases, but remains visible under magnetic field up to 9 T. This anomaly might comes from orphan spins contribution, which are the free-ion like copper on Cu' sites. The subtraction of this Schottky heat capacity give linear temperature dependence, similar to what have been found in low temperature specific heat of gapless spin liquid candidates[8].

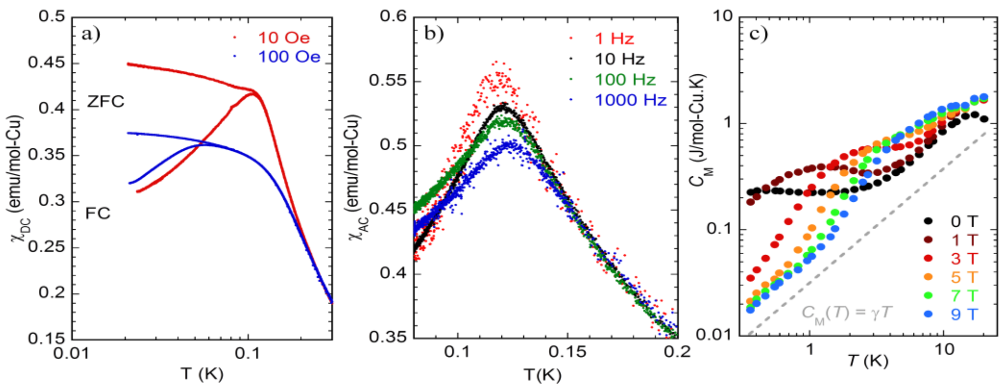

Figure 2. a) DC susceptibility, b) AC susceptibility, and c) Magnetic specific heat of $Ba_3CuSb_2O_9$ at low temperature

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