Abstract of Doctoral Dissertation

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p-electron Magnetism in Alkali-metal Superoxides probed by μSR
(μSR で探るアルカリ金属超酸化物の p 電子磁性)

There are less examples of inorganic molecular systems which show the *p*-orbital magnetism. One typical example is the oxygen molecule (O_2). The crystal structure of O_2 shows some transitions with decreasing temperature followed by the formation of an antiferromagnetic (AF) long-range ordered state of the magnetic spins on O_2 molecules below 24 K. Nowadays, a wide variety of oxygen-containing materials are essential for technology due to their tremendous applicability and robustness. This is largely due to the special nature of oxygen, which is able to form both ionic and covalent bonds with a wide range of other elements, which makes oxides tremendously interesting materials in many senses.

Alkali-metal superoxides AO_2 (A= Na, K, Rb, and Cs) represent the other rare example of inorganic compounds with unpaired electrons on it *p*-orbitals. Superoxides, O_2^-, is an anionic state of molecule oxygen, which commonly have a dumbbell-type bonding state of two O atoms with only one unpaired electron on it. This O_2^- leads the high reactivity with the alkali-metal resulting in the ionic state of $A^+O_2^-$. This series of superoxides have been synthesized in the 1960's. Although nearly a half century have passed after the first discovery of those systems, there are less studies on those magnetic properties due to difficulties of the synthesis and their high reactivities with surroundings.

One attractive feature of those alkali-metal superoxides is that the magnetic properties are well affected by changes in the lattice symmetry. It has been argued that magnetic structures significantly affected by the relative orientation of O_2^- species within the crystal lattice. In addition to this, those changes in the structure and magnetic properties depend on the alkali-metal ion. For that reason, systematic investigation on magnetically ordered states of AO_2 is very important to reveal the overall magnetic scheme of the superoxide. Furthermore, from a NMR study on CsO_2, Tomonaga-Luttinger Liquid (TLL) behavior was suggested to appear below about 30 K where antiferromagnetic (AF) spin chains were formed as a result of the *p*-orbital ordering. A magnetically ordered state is predicted to appear below about 10 K from both of the NMR and susceptibility measurements. In addition to this, the TLL model suggested a field-induced magnetic order appeared in CsO_2. In order to confirm those expectations, detailed investigations on the magnetic properties in the zero-field (ZF) condition are strongly required in the magnetically ordered state of CsO_2 and of other alkali-metal superoxides.

Spontaneous magnetic ordering was observed in RbO_2 and CsO_2. Even though RbO_2 and CsO_2 are isostructural compound at room temperature, the magnetic properties is different. The current study revealed that differences in the magnetic properties between RbO_2 and CsO_2 are caused by changes in lattice symmetries. Our XRD result predicted that the lattice symmetry of RbO_2 below 100 K is lower compared to that of CsO_2. The temperature dependence of χ in RbO_2 showing no appearance of a broad peak which was observed in CsO_2. This is a large difference from the case of CsO_2 in which the clear peak characterized by the low-dimensional magnetic interaction is observed around 30 K. We found that CsO_2 has a mixed state between the long-range ordered and dynamic fluctuating spin states while RbO_2 shows almost static state whole though the sample.

The susceptibility measurement confirmed that the clear anomaly was observed at the temperature between 200 K and 230 K, defined as T_1 and T_2, respectively in NaO_2. These anomalies are consistent with the earlier reported expected structural phase transition. The magnetic susceptibility, χ, drops sharply at below 40 K, defined as T_3. The absence of muon spin precession down to 0.3 K excludes the presence of long-range magnetic order in NaO_2. The formation of one dimensional spin system can be considered in NaO_2.

Finally, the study on p-electron magnetism in alkali-metal superoxides probed by μSR indicates the possibility of controlling the intermolecular interactions by changing the cation.