Spin dynamics for p electrons in CsO_2 and NaO_2

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Alkali metal superoxides (AO_2) such as NaO_2, KO_2, RbO_2, and CsO_2 forming ionic crystals that adopt crystal structures related to rocksalt structures are ideal model system for the study of the p-electron magnetism. The magnetic properties of KO_2 and RbO_2 systems have already been well investigated, unlike those of NaO_2 and CsO_2, because of the ease of fabricating the sample. In a superoxide anion $(O_2)^-$, there is one unpaired spin (S = ½) because three electrons occupy a pair of degenerate antibonding π^* molecular orbitals. AO_2 compounds undergo structural distortion splitting the π^* energy levels and lifting the orbital degeneracy similar to the Jahn-Teller effect for degenerate orbitals. Orbital ordering similar to that found in transition metal systems may be expected, but has scarcely been studied experimentally.

The neutron diffraction, EPR, and AFMR measurements revealed the crystal structure of KO_2, RbO_2, and CsO_2 to be FM in the crystallographic *ab* plane and AFM along the crystallographic *c* axis.

From the NMR study on CsO_2 by Klanjsek et al., a huge, nonmonotonic temperature dependence of the exchange coupling originating from thermal liberations of O_2^- molecules above ~70 K was observed. Tomonaga-Lutingger liquid behavior (~15K – 40K) was observed, in which antiferromagnetic (AFM) spin chains are formed as a result of p-orbital ordering, and then magnetic phase transition occurs again jumping to the ordered Neel state at around ~10 K [1]. The latter supports the prediction of susceptibility measurement in which an anomaly in the magnetic susceptibility was observed around 10 K, indicating a possible crossover from 1D chain character which was fit with the original Boner-Fisher formulation (15 K – 70 K) to 3D AFM ordering [2].

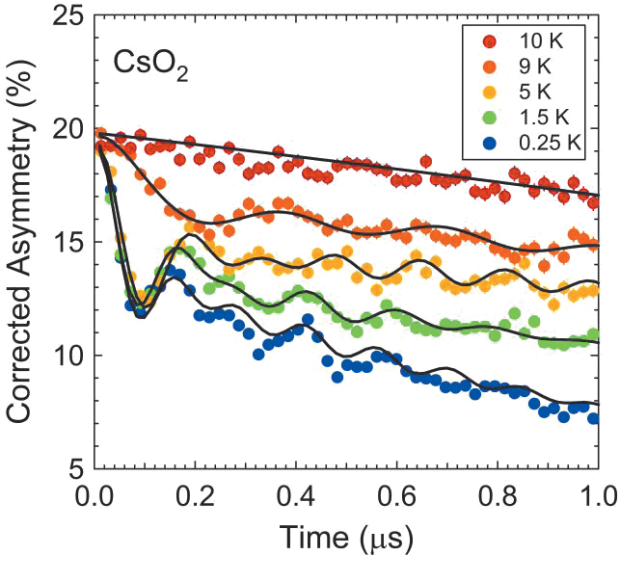

Fig. 1. ZF-μSR time spectrum for CsO_2 for the first microsecond from 10 K down to base temperature.

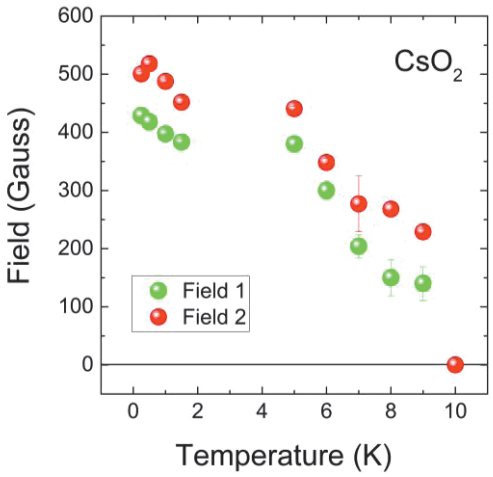

Fig. 2. Internal Field from at least 2 muon sites in CsO_2.

We performed μSR measurement at the Continuous Muon Facility PSI, Switzerland. We obtained time spectra show a non-ordered state still until 10 K and then the internal field appeared at around 8 K from at least 2 muon sites in CsO_2 and tends to increase with decreasing temperature [Figs. 1 and 2]. There is no clear enhancement in the depolarization rate due to the spin dynamics observed around the transition temperature. We confirm that this sample is of good quality based on our susceptibility measurement with a small contribution of the paramagnetic state in the low temperature regime.

The sample quality of NaO_2 revealed by our susceptibility measurement was not very good. We only observed a paramagnetic state from the M-H curve. Unfortunately, we could not obtain μSR data from the PSI for NaO_2 owing to a cryostat problem. We only have ZF-μSR data obtained using the Pulsed Muon at the RIKEN-RAL Muon Facility in the UK. The initial asymmetry from room temperature to 6 K shows a gradually decreasing trend, indicating fast depolarization behavior with a small volume fraction. Furthermore, in the next measurement at the RIKEN-RAL, we plan to determine whether NaO_2 is magnetically ordered in the ground state, like CsO_2.

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References

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