Magnetic neutron diffraction study on alkali-metal superoxides CsO_2 and RbO_2

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In alkali-metal superoxide AO_2 (A = Na, K, Rb, Cs), the doubly degenerate π^* orbital of the O_2^- moleculer ion accommodates three electrons and is in a spin-1/2 state. For CsO_2, the magnetic susceptibility shows a broad maxima at low temperatures and fits well with the Bonner-Fisher model of one-dimensional Heisenberg antiferromagnetism (AFM) [1,2]. The high-field magnetization also shows a typical low dimensionality [2]. AFM order occurs below the Néel temperature of T_N = 9.6 K. A density functional theory (DFT) calculations showed that the crystal symmetry lowering is due to the tilting of O_2^- molecules, and the π^* orbital ordering due to the cooperative Jahn-Teller effect is predicted to give rise to the one dimensional magnetism [1]. On the other hand, for RbO_2, the magnetic susceptibility does not show any low dimensionality and shows only a three-dimensional AFM order below 15 K. The dimensionality of the magnetism and its changes are expected to depend on the orbital ordering, but this has not been clarified experimentally. The magnetic structures also have not been resolved yet. In this study, we aim to clarify the ground state magnetic structure of CsO_2 and RbO_2 by neutron diffraction, and to elucidate the mechanism of the peculiar magnetism in these systems.

CsO_2 and RbO_2 powder samples were synthesized at Okayama Univ. and neutron diffraction measurements were performed at JRR-3 T1-1.

For CsO_2, we used a larger quantity of samples than in the previous experiment (No. 21558) to obtain higher statistical data of the magnetic Bragg peaks at low temperatures. As a result, we propose the most plausible AFM structure as follows [3]. The propagation vector of the AFM is (0, 1/2, 0), *i.e.*, antiferromagnetic with double period in the b-axis direction and ferromagnetic in the a-axis direction as shown in Fig. 1. The ordered magnetic moment is oriented along the a-axis. The ordered moment is found to be about 0.2 μ_B, which is much smaller than 1 μ_B expected from the spin-1/2 state. The strong suppression of the ordered moment can be understood to originate from the one-dimensional nature of the magnetism in this system. We also propose a possible π^*-orbital ordering model, which can explain both the magnetic structure and the one dimensionality of the magnetism in CsO_2 [3].

For RbO_2, we measured the temperature dependence of neutron diffraction below and above the Néel temperature of ~ 15 K. However, we could not find clear magnetic diffraction peaks. It is necessary to synthesize a larger quantity of good quality samples and re-measure them in the near future.

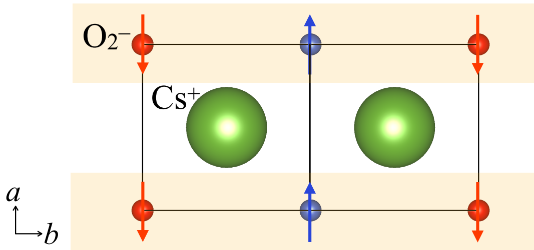

Fig. 1. Schematic illustration of the magnetic structure of CsO_2 viewed in the ab plane. The red and blue arrows indicate the ordered moment of the O_2^- ions. Antiferromagnetic spin chain exists along the b axis.

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[2] M. Miyajima *et al.*, J. Phys. Soc. Jpn. **87**, 063704 (2018).
[3] T. Nakano *et al.*, J. Phys.: Condens. Matter. **35**, 435801 (2023).