Anionogenic Magnetism Combined with Lattice Symmetry in Alkali-metal Superoxide RbO₂

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X-ray powder diffraction (XRPD), magnetic susceptibility and muon-spin relaxation (μSR) measurements were carried out to investigate lattice symmetries and magnetic properties of one of alkali-metal superoxides, RbO₂. Two structural transitions were observed around 170 and 100 K in conjunction with the appearance of anomalies in the magnetic susceptibility. A static antiferromagnetic long-range ordered state of unpaired spins on O₂⁻ dumbbells with the full magnetic volume fraction was confirmed from μSR below about 15 K. In comparison with CsO₂, it is suggested that small changes in the lattice symmetry driven by changes in the O₂⁻ dumbbell orientation causes different magnetic properties in alkali-metal superoxides.

Unpaired electrons in p-orbitals can show novel magnetic properties. They are different from those observed in other systems which contain local magnetic moments at ionic positions. Typical examples of those p-orbital magnets are organic molecular systems which consist of light elements like carbon and hydrogen. The first discovered organic magnet, p-NPNN, shows a ferromagnetic transition at 0.65 K and opens the research field of the p-orbital magnetism.1) Until now, many types of organic magnets with different basic molecules are synthesized.2-6)

Compared to those organic molecular magnets, there are less inorganic molecular systems which possess the p-orbital magnetism. One typical example is the oxygen molecule, O₂.7) The O₂ molecule has a magnetic moment with S = 1. This magnetic moment originates from two unpaired electrons on the π* orbital of each oxygen atom.8) O₂ molecules are crystallized at low temperatures. The crystal structure shows some transitions with lowering temperatures and an antiferromagnetic (AF) long-range ordered state of O₂ spins appears below 24 K.9,10)

Another example is a superoxide. This system commonly has a dumbbell-type bonding state of two oxygen atoms, O₂⁻, with only one unpaired electron on it. The O₂⁻ has the high reactivity with the alkali-metal forming the alkali-metal superoxides, AO₂⁻ (A = Na, K, Rb, and Cs). The series of AO₂ is a rare example inorganic compound which have unpaired electrons on the p-orbital. The alkali-metal 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 their magnetic properties due to difficulties of the synthesis and the high reactivity with surroundings.11-16)

The orientation of the O₂⁻ dumbbell in KO₂, RbO₂, and CsO₂ is along the c-axis of the unit cell at the room temperature.17) One attractive feature of alkali-metal superoxides is that the magnetic properties are well affected by changes in the lattice symmetry. The change in the lattice symmetry has been proposed to be caused by changes in the orientation angle of the O₂⁻ dumbbell against the c-axis.18) In addition, those changes in the structure and magnetic properties depend on the alkali-metal ion.

In the case of CsO₂, a zig-zag like one-dimensional (1D) magnetic chain along the b-axis was expected to appear after experiencing some structural transitions.19,20) This low-dimensional magnetic property was confirmed from the susceptibility measurement by observing a broad peak around 30 K. This broad peak can be explained by the Bonner–Fisher model. Besides, the Tomonaga–Luttinger liquid (TLL) state was suggested to appear below about 30 K followed by a magnetic ordering below 10 K.20,21)

The high-field magnetization measurement on CsO₂ at 1.3 K revealed remarkable up-turn behavior in the magnetization curve around the saturation field of about 60 T.22) The magnetization behavior was reproduced by the exact calculation assuming the 1D Heisenberg spin system at low fields but showed some unavoidable inconsistency with the calculation at high fields. This fact suggested that inter-chain magnetic interactions could not be neglected.

In the case of RbO₂, magnetic properties are still less explored compared to CsO₂. RbO₂ and CsO₂ have the same tetragonal symmetry at room temperature and show structural transitions with lowering temperatures.14,19) Ambiguous factors, like the smearing of diffraction lines and/or less temperature points, made discussions on the crystal symmetries and structural transitions unclear in past studies.14) Those ambiguous factors could be due to the sample quality. Detail investigations to achieve the deeper insight for structural and magnetic properties of RbO₂ are the main objective of this study.

In this letter, we report the results of the X-ray powder diffraction (XRPD), magnetic susceptibility and muon-spin relaxation (μSR) measurements on RbO₂. Two structural transitions were observed from the XRPD measurement in conjunction with changes in the magnetic susceptibility. The appearance of a static long-range ordered state of magnetic moments on O₂⁻ dumbbells was confirmed from μSR below the magnetic transition temperature T_N ~ 15 K with the full magnetic volume fraction. The current study suggests that small changes in the lattice symmetry causes different magnetic properties in alkali-metal superoxides.

The polycrystalline sample of RbO₂ was synthesized in Okayama University by the oxidation of the Rb metal in the...
liquid ammonia. The sample was kept in an Ar-filled glove box. For the XRPD measurement, the sample was sealed in a glass capillary with the diameter of 0.3 mm. The XRPD measurement was performed to obtain lattice parameters and symmetries. 23) Obtained lattice constants were reported to appear around 150 K in CsO2. 22) The lattice structural transition from tetragonal to orthorhombic is indicated as has been already reported. 19) Weak incommensurate peaks appeared below T\textsubscript{S1} in the orthorhombic phase as has been reported in Ref. 14. Below T\textsubscript{S1}, these peaks tended to shift to the higher angle side with decreasing temperature and became independent of the temperature below T\textsubscript{S2}. Assuming the monoclinic structure, lattice parameters at 30 K were estimated to be a = 4.1486(1) Å, b = 7.0102(1) Å, c = 4.1070(1) Å, and β = 90.623(2)° by using the Le Bail method, although incommensurate peaks were ignored from the fitting.

Figure 2 displays the temperature dependence of the magnetic susceptibility times temperature, μ\textsubscript{eff}T, measured under 1 kOe after the field-cooling procedure. The inset in Fig. 2(a) is the temperature dependence of χ, showing no appearance of a broad peak at high temperatures. This is a large difference from the case of CsO2 in which the clear peak characterized by the Bonner–Fisher model is observed around 30 K. 20,22) The sharp peak around 15 K is a signature of the appearance of a magnetic transition indicated as T\textsubscript{S1}.

Insets in Figs. 2(b) and 2(c) are temperature dependences of 110 and 200 peak positions observed by the XRPD measurement in RbO2. Those peak positions were estimated by the fitting using the Gaussian function. Crystal structural transition temperatures from tetragonal to orthorhombic and from orthorhombic to the lower symmetry are indicated as T\textsubscript{S1} ~ 170 K and T\textsubscript{S2} ~ 100 K, respectively.

There were two anomalies observed in the temperature dependence of μ\textsubscript{eff}T as seen in Figs. 2(b) and 2(c). One was around 100 K and the other was around 170 K. Those anomalies were well coincident with T\textsubscript{S1} and T\textsubscript{S2}. Accordingly, we analyzed the temperature dependence of the magnetic susceptibility by using the Curie–Weiss law within temperature regimes between 250 K and T\textsubscript{S1}, T\textsubscript{S3}, and T\textsubscript{S2}, and then between T\textsubscript{S2} and 50 K. Those temperature regimes are high enough from T\textsubscript{N}. Broken lines in Figs. 2(b) and 2(c) are the best fit results. For each temperature regime, effective magnetic moments (μ\textsubscript{eff}) were extracted from the Curie constant to be 1.93 μ\textsubscript{B}, 1.94 μ\textsubscript{B}, and 1.92 μ\textsubscript{B}, respectively. Those values of μ\textsubscript{eff} were somewhat larger than the spin-only value of 1.73 μ\textsubscript{B}. This result suggests the importance of orbital contributions to μ\textsubscript{eff}. The Curie–Weiss temperature, Θ, was also estimated in each temperature regime to be ~26.49(27), ~30.86(18), and ~27.56(6) K, respectively. Negative values of Θ indicate the AF magnetic interaction between O\textsubscript{2} dumbbells as well as the case of CsO2. 20,21)

Figure 3 exhibits ZF-μSR time spectra of RbO2 within the short-time region up to 1 μs measured at several temperatures above and below T\textsubscript{N}. The time spectrum measured at 16 K showed the slow relaxing behavior. This indicates that the muon spin depolarizes by random and static nuclear dipole
fields distributed at the muon site and that the system is in the paramagnetic state. As the temperature decreased, the time spectrum suddenly changed and the spontaneous muon-spin precession behavior appeared below about 15 K. This observation of the muon-spin precession proved the appearance of the AF long-range magnetic ordered state of spins on O\textsubscript{2}/\textsuperscript{12} dumbbells.

In order to deduce more detailed information from the results of the ZF-\(\mu\)SR measurement, the following function was used to analyze time spectra measured below \(T_N\):

\[
A(t) = A_1 e^{-\lambda_1 t} \cos(\omega_1 t + \phi_1) + A_2 e^{-\lambda_2 t} \cos(\omega_2 t + \phi_2) + A_3 e^{-\lambda_3 t}
\]

In order to analyze time spectra, we simply assumed that there were two muon-spin precession frequencies. The first and second terms express two muon-spin precession components with frequencies of \(\omega_1\) and \(\omega_2\). \(A_1\) and \(A_2\), and \(\lambda_1\) and \(\lambda_2\) are initial asymmetries and relaxation rates of the first and second components, respectively. The third component is to describe slowly relaxing behavior even after 1 \(\mu\)s.

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Solid lines in Fig. 3 are the best-fit results of ZF-\(\mu\)SR time spectra by using Eq. (1). The magnetic volume fraction of the long-range ordered state determined from the ratio of asymmetry parameters is estimated to be \(\sim 100\%\textsuperscript{24)}\). This result indicates that almost all spins on O\textsubscript{2}/\textsuperscript{12} dumbbells undergo the AF long-range ordered state.

Internal fields at muon sites, \(H_{\text{int}}(T)\), were calculated from muon-spin precession frequencies \(\omega_i\) by using the equation, 

\[
\omega_i = \gamma_i H_{\text{int}}(T), \quad \text{where} \quad \gamma_i \text{ is the gyromagnetic ratio of the muon spin (2}\pi \times 13.55 \text{kHz/G).}
\]

Figure 4 shows the temperature dependence of \(H_{\text{int}}(T)\). In order to achieve the information of the dimensionality of the magnetic interaction, following Eq. (2) was applied to the temperature dependence of \(H_{\text{int}}(T)\):

\[
H_{\text{int}}(T) = H_0 [1 - (T/T_N)^\beta]^{-\sigma}.
\]
where $\beta$ is the critical parameter to describe the dimensionality of the magnetic interaction and $\alpha$ is to express the spin excitation at low temperatures. Solid lines in Fig. 4 show the fitting results by Eq. (2). The results obtained from the fitting to $H_{\text{int}}$ and $H_{\text{int}}^2$ were slightly different, so that we took average values. Those were $T_N = 15.1(2)$ K, $\beta = 0.36(6)$, and $\alpha = 2.88(43)$. Although it was not so clear to judge the dimensionality of the magnetic interaction from these results due to fairly big fitting errors, those results supported the appearance of the static long-range ordered state on the basis of the three-dimensional (3D) Heisenberg magnetic interaction.\footnote{References in lattice symmetry between RbO$_2$ and CsO$_2$, \cite{21} In addition, we suggested the existence of the low dimensional magnetic interaction which is expected in CsO$_2$. This is a large difference in the magnetic properties between RbO$_2$ and CsO$_2$ found in the current study.

LF’s were applied at 1.78 K to investigate whether spins on O$_2^-$ dumbbells were frozen or not in the AF ordered state. Figure 5 indicates the LF dependence of the $\mu$SR time spectrum. Measured time spectra were almost flat in the long-time region and shifted upward in parallel with increasing LF. This result indicates that no fluctuating spin was left in RbO$_2$ on O$_2^-$ dumbbells from the view of the characteristic time window of $\mu$SR which is from $10^8$ to $10^{11}$ Hz. This is another large difference in the magnetic properties from those of CsO$_2$. In the case of CsO$_2$, the TLL state with the existence of the low dimensional magnetic interaction which is expected in CsO$_2$. This is a large difference in the magnetic properties between RbO$_2$ and CsO$_2$ found in the current study.

Even though RbO$_2$ and CsO$_2$ are isstructural compounds each other at room temperature, we found through the current study that there were some differences in their low temperature structure, magnetic properties and the spin dynamics of the O$_2^-$ dumbbell. The orthorhombic structure remains down to ~20 K in CsO$_2$,\footnote{References} while RbO$_2$ shows possible another change into the lower lattice symmetry than orthorhombic at $T_{S2} \sim 100$ K. Taking into account possible changes in the lattice symmetry below $T_{S2}$ in RbO$_2$, it is strongly expected that differences in magnetic properties are caused by differences in lattice symmetry between RbO$_2$ and CsO$_2$, especially below $T_{S2}$.

A possible mechanism to understand changes in the lattice symmetry is on the basis of differences in the ionic radius between Rb and Cs. The shorter ionic radius of Rb than that of Cs makes the inter-atomic distances in the ab plane shorter. This causes the rigid structure in RbO$_2$ which could result in the deformation of the orthorhombic structure around 170 K smaller than that of CsO$_2$. In order to release the free energy from the lattice, RbO$_2$ changes the lattice symmetry again below $T_{S2}$. In the case of KO$_2$, which is another isostructural compound, the crystal structure was predicted to change to be triclinic at temperature below $T_N \sim 7$ K.\footnote{References} This triclinic structure lifts up the degeneracy of $\pi^*$ orbital as well as the Jahn–Teller effect and generates the interlayer AF coupling leading the formation of the 3D AF ordered state.\footnote{References}

In the case of KO$_2$, Kim et al. proposed from the electronic structural calculation that the appearance of the 2$p$ ferro- (FO) ordering on O$_2^-$ dumbbells within the ab plane was essential to realize the AF magnetic structure determined from the neutron scattering experiment.\footnote{References} This theoretical study also suggested that this FO ordering was triggered by the tilting of O$_2^-$ dumbbell orientation opening the band gap simultaneously. This scenario can also explain the AF interaction in RbO$_2$ with the appearance of the orbital ordering as suggested by other studies.\footnote{References} It was predicted that the emergence of in-plane antiferro-orbital ordering with the untitled O$_2^-$ dumbbell in the c-direction was the most favored state in RbO$_2$.\footnote{References}

It was suggested that the O$_2^-$ dumbbell in CsO$_2$ tilted about 5° from the c-axis in the orthorhombic phase.\footnote{References} The alternative tilting on the basis of the space group Immm was proposed in order to explain the orthorhombic structure.\footnote{References} However, it is impossible to uniquely determine the tilting state of the O$_2^-$ dumbbell from this space group. What is allowed by this space group is that the average angle of the O$_2^-$ dumbbell against the c-axis should be zero. This means that we cannot exclude a possibility that the O$_2^-$ dumbbell does not tilt even in the orthorhombic phase and/or a possibility of the mixture of those states making the average of tilting angle to be zero.

Because the ionic shape of alkali-metal is quite spherical and symmetric, it is highly expected that the driving force of the appearance of the lower lattice symmetry is due to changes in the orientation of O$_2^-$ dumbbell axis. Accordingly, further investigations on the detail lattice symmetry of RbO$_2$ at low temperatures including the O$_2^-$ dumbbell tilting behavior are highly required to reveal the whole view of the anionogenic magnetism of superoxides.

In summary, we investigated lattice symmetries and magnetic properties of one of the series of alkali-metal superoxides, RbO$_2$ by XRPD, magnetic susceptibility and $\mu$SR measurements.\footnote{References} ZF- and LF-$\mu$SR revealed the presence of the 3D long-range AF ordered state below $T_N \sim 15$ K and that all spins on O$_2^-$ dumbbells were frozen. XRPD measurements showed possible changes in the lattice symmetry around $T_{S1} \sim 170$ K and $T_{S2} \sim 100$ K. It is suggested that the lattice symmetry of RbO$_2$ below $T_{S2}$ is to be lower compared to that of CsO$_2$. The current study revealed that differences in the magnetic properties between RbO$_2$ and CsO$_2$ are caused by changes in lattice symmetries. We also suggest that it is important to clarify changes in the
orientation of the $O_2^-$ dumbbell from the $c$-axis down to low temperatures which is of important to understand the relationship between the anionogenic magnetism of super-lattice symmetries.

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