Antiferromagnetic and structural transitions in the superoxide KO$_2$ from first principles: A 2$p$-electron system with spin-orbital-lattice coupling

Minjae Kim, Beom Hyun Kim, Hong Chul Choi, and B. I. Min
Department of Physics, PCTP, Pohang University of Science and Technology, Pohang, 790-784, Korea
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KO$_2$ exhibits concomitant antiferromagnetic (AFM) and structural transitions, both of which originate from the open-shell 2$p$ electrons of O$_2$ molecules. The structural transition is accompanied by the coherent tilting of O$_2$ molecular axes. The interplay among the spin-orbital-lattice degrees of freedom in KO$_2$ is investigated by employing the first-principles electronic structure theory and the kinetic-exchange interaction scheme. We have shown that the insulating nature of the high symmetry phase of KO$_2$ at high temperature (T) arises from the combined effect of the spin-orbit coupling and the strong Coulomb correlation of O 2$p$ electrons. In contrast, for the low symmetry phase of KO$_2$ at low T with the tilted O$_2$ molecular axes, the band gap and the orbital ordering are driven by the combined effects of the crystal-field and the strong Coulomb correlation. We have verified that the emergence of the O 2$p$ ferro-orbital ordering is essential to achieve the observed AFM structure for KO$_2$.

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Magnetism due to the correlated 2$p$ electrons has attracted revived attention for the possibility of the new kinds of the magnetic informative materials. Some 2$p$ magnetic oxides exhibit the structural phase transition concomitantly with the magnetic phase transition. Solid oxygen is a typical example, which has both antiferromagnetic (AFM) and structural phase transitions below 24 K. Alkali superoxides, AO$_2$ (A=Na, K, Rb), which are of our present interest, belong to another example. In AO$_2$, one alkali-metal atom provides one electron to an oxygen molecule, and thereby each O$_2$ anion has nine electrons at the 2$p$ molecular levels with the electronic configuration of $2\pi^2\pi_u\pi_g^3$ (see the inset of Fig. 1). The partially occupied antibonding $\pi_g$ molecular states play the most important role in determining the electronic and magnetic properties of alkali superoxides.

One hole in $\pi_g$ generates the magnetic moment of 1 $\mu_B$ for each O$_2$. The degeneracy of the $\pi_g$ level is expected to be lifted by lowering the crystal symmetry, as occurs due to the Jahn-Teller effect. In fact, it was suggested that, for KO$_2$, the symmetry lowering would occur via coherent tilting of the O$_2$ molecular axes, the so-called magnetogyration, which invokes the accompanying AFM ordering.

At room temperature, KO$_2$ crystallizes in the tetragonal structure of CaC$_2$ type, in which the O$_2$ molecular bond axes are parallel to the $z$-axis (Fig. 1(a)). KO$_2$ retains this structure down to 197 K and exhibits the paramagnetic behavior. Upon cooling, O$_2$ molecular bond axes seem to tilt uniformly by $\sim 20^\circ$ to have a lower crystal (monoclinic) symmetry. The magnetic phase is still paramagnetic down to 7 K. Below 7 K, the AFM ordering emerges in the triclinic crystal structure with the uniform tilting of O$_2$ molecular bond axes by $\sim 30^\circ$. According to neutron experiment, the AFM phase has the magnetic structure having opposite spin arrangements along the $z$-direction between two oxygen layers of O1 and O2. This feature in KO$_2$ reflects the strong interplay among spin, orbital, and lattice degrees of freedom, as in rare-earth manganites.

There have been several theoretical reports to study the coupled structural and magnetic transitions in KO$_2$, but those studies were mostly qualitative and lacked the quantitative description of the electronic structures for the low symmetry phase of KO$_2$. Even the direction of the tilted molecular bond axis is still uncertain between two possibilities. The first one is [R1] in Fig. 1(b), in which the molecular bonds are rotated around the [100] axis. The second one is [R2] in Fig. 1(c), in which the molecular bonds are rotated around the [110] axis. Moreover, the recent band structure study for the high symmetry phase of KO$_2$ (Fig. 1(a)) in the local density approximation (LDA) reveals that the degenerate $\pi_g$ states do not split, resulting in the metallic nature, which is contradictory to the insulating nature of KO$_2$.

In this Rapid Communication, we have investigated comprehensively the electronic structures of both high and low symmetry phases of KO$_2$, and explored the

FIG. 1: (Color online) (a) The tetragonal [T] structure of KO$_2$ with unrotated O$_2$ molecular bond axes. The molecular axes are along the $z$-direction. K atoms are in blue and O atoms in red. (b) [R1] with molecular bonds rotated by $\sim 30^\circ$ around the [100] ($x'$) axis with bond axes along the $z'$-direction. (c) [R2] with molecular bonds rotated by $\sim 30^\circ$ around the [110] ($x''$) axis with bond axes along the $z''$-direction. There are two independent types of oxygen O1 and O2 for each structure.
We have employed the full-potential augmented plane wave (FLAPW) band method (GGA+U) to study the electronic structure of AFM KO$_2$ with [T] structure. The SO effect is included in the GGA+U framework. Charge densities of occupied and unoccupied molecular levels of O$_2$ and K$_2$O$_2$ are plotted on the (001) and (010) planes. These results demonstrate that the splitting of $\pi_g$ states originates from the SO effect. In fact, the large SO effect results from the Coulomb correlation. The electronic structure of AFM KO$_2$ with [T] structure is close to that of FM KO$_2$, and so the band gap at $E_F$ opens in the same way.

For KO$_2$ with [R1] and [R2] structures, the crystal field effect will be activated due to tilting of O$_2$ molecular axes toward K$^+$. Figure 3(a) shows the local PDOSs and the spin densities in the GGA+U+SO for the FM phase of KO$_2$ with [R1] structure. Notable feature in...
the DOS is the opening of band gap at $E_F$. The GGA band calculation does not produce the band gap, whereas both the GGA+$U$ and the GGA+$U$+SO yield almost the same insulating band structure. This implies that, in producing the band gap, (i) the symmetry lowering just by tilting of molecular axes is not sufficient, (ii) the Coulomb correlation effect is essential, and (iii) the SO effect for [R1] is not as important as that for [T]. The orbital magnetic moment is almost quenched having only $0.002 \mu_B$ per O$_2^-$ molecule. Therefore, it is the combined effect of the Coulomb $U$ and the crystal field from K$^+$ cations that splits the degenerate $\pi_g$ states into the directional orbitals, $\pi_{g'}$ and $\pi_{g''}$ states. Interestingly, due to the complex interplay of the Coulomb $U$ and the crystal field effect in the molecular states, the splitting of $\pi_g$

TABLE I: Magnetic exchange constants [meV] between O$_2^-$ molecules for direct and indirect (via K$^+$) hopping channels in the [R1] and [R2] structures of KO$_2$. J$_1$ and J$_2$ are the in-plane exchange constants along the $x$ and the $y$-direction, and J$_3$ is the inter-plane exchange constant. Positive $J$ represents the AFM interaction.

|          | J$_1$  | J$_2$  | J$_3$  |
|----------|--------|--------|--------|
| R1 (direct) | $0.353$ | $1.486$ | $0.209$ |
| R1 (via K$^+$) | $0.023$ | $0.023$ | $0.027$ |
| R2 (direct) | $0.419$ | $0.419$ | $0.680$ |
| R2 (via K$^+$) | $-0.215$ | $-0.215$ | $0.005$ |

FIG. 4: (Color online) (a) The local PDOS of the O 2$p$ states in the GGA+$U$+SO ($U=6.53$ eV) for the AFM phase of KO$_2$ with [R1] structure. The spin densities of unoccupied $\pi_{g'}$ states are plotted on the (100) and (200) planes. Blue and red colors in the spin densities represent opposite spins. (b) The local PDOS of the O 2$p$ states in the GGA+$U$+SO ($U=6.53$ eV) for the AFM phase of KO$_2$ with [R2] structure. The spin density of occupied minority spin $\pi_{g''}$ states is plotted on the (110) plane. Black solid lines in the DOS plots represent the PDOS of K 4$p$ states.

FIG. 5: (Color online) (a) The in-plane exchange constants, J$_1$ and J$_2$, on the xy-plane for KO$_2$ with [R2], where the unoccupied $\pi_{g'}$ and occupied $\pi_{g''}$ states are represented by red and green, respectively. (b) The inter-plane exchange constant J$_3$ on the (110) plane. The paths A and B correspond to the direct and indirect (via K$^+$) hopping channels, respectively.
as revealed in Fig. 1, there exists the nonnegligible hybridization between the O 2p and K 4p states.

Table I presents the estimated exchange constants based on the microscopic calculation of the kinetic exchange interaction for KO2 with the [R1] and [R2] structures.20 The 2p electrons in each O2 are assumed to have the atomic orbital states as in our band results for [R1] and [R2]. The kinetic exchange interactions both from the direct and indirect hoppings were considered independently to calculate the exchange constant for each channel. For [R1], the exchange constants are obtained to be all AFM, and the dominant channel is the direct hopping between O2 anion along the y-direction, which is AFM ($J_2=1.486$ meV). The large $J_2$ results from the tilting of O2$^-$ molecular axis along the [010]. The inter-plane interactions from both direct and indirect channels yield smaller exchange constants ($J_3=0.209$ and 0.027 meV). Then the resulting magnetic structure for [R1] will not be consistent with the experimental AFM structure which has alternating AFM spins along [001].

On the other hand, the kinetic exchange interactions for [R2] turn out to be consistent with the experimental AFM structure. The dominant one is the interplane AFM interaction coming from the direct hopping ($J_3=0.680$ meV). The in-plane exchange constants are 0.419 and $-0.215$ meV for direct and indirect channels, respectively. Hence the total exchange constants between two nearest neighbor (NN) O2 along x and y-directions are 0.204 meV. For each O2$^-$ in [R2], there are eight interplane NN O2$^-$ and four in-plane NN O2$^-$.

In contrast, for the inter-plane kinetic exchange in Fig. 5(b), the lobes of $\pi^*$ orbitals of both O2 molecules are away from K+, and so the indirect kinetic exchange results in the weak AFM interaction ($J_3=0.005$ meV).

In conclusion, we have investigated electronic and magnetic structures of KO2 superoxide, the strongly correlated 2p electron system. We have found that, for the correct description of the insulating electronic structure of KO2, the SO coupling as well as the large Coulomb correlation is important for the high symmetry phase, while, for the low symmetry phase, the crystal field from K+, as well as the large Coulomb correlation, is important. The concurrent AFM spin and FO orderings with the band-gap opening clearly demonstrate the strong coupling among the spin-orbital-lattice degrees of freedom in KO2. In the low symmetry phase of KO2 with [R2] structure, the emergent FO ordering yields the kinetic exchange interactions that are consistent with the experimental AFM structure.

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